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CHEMICAL PRECURSORS TO THE 1998-1999 ERUPTION OF COLIMA VOLCANO, MEXICO

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ABSTRACT

Colima volcano is the most active in Mexico, including a significant eruption in 1991. Geochemical monitoring of the volcano started in January 1996 with: 1) airborne measurements of the SO_2 flux by COSPEC; 2) collection of fumarolic gases from the summit crater every three months, and 3) collection of water samples from three springs on the S-SW slopes of the volcano every two months. Chemical compositions of volcanic gases did not show systematic trends, except for the isotopic composition of the volcanic vapor. Starting from the summer of 1997, the volcanic water became gradually enriched in deuterium, which indicates a contribution from deep, less degassed magma. Three other possible precursor signals were identified for the 1998-99 eruption: 1) a two to three-fold "peak" in the boron concentration approximately 3 months before the eruption, 2) a step-wise increase in HCO_3 and the calculated partial pressure of dissolved CO_2, approximately 1.5 years before the eruption , 3) until September 1998, the SO_2 flux from the volcano was at a low level of less than 100 t/d, often below the detection limit of the instrument. A sharp increase in the SO_2 flux was recorded a month before the eruption started, from 400±50 t/d up to 1,600 t/d two days before the new lava, emerged on 20 November, 1998. The SO_2 flux was in a good correlation with seismicity.

Keywords: Volcanic eruption, volcanic gases, hydrogeochemistry, SO_2-flux

RESUMEN

El volcán de Colima es el más activo de México. Esta actividad ha incluido una erupción efusiva significativa en 1991. En enero de 1996 se inició un monitoreo geoquímico con: 1) mediciones de los flujos de SO_2 en la atmósfera mediante COSPEC; 2) recolección de gases fumarólicos del cráter cada tres meses; 3) recolección de muestras de agua de tres manantiales ubicados en los flancos S-SO del volcán, cada dos meses. La composición química de los gases volcánicos no mostró tendencias sistemáticas, a excepción de la composición isotópica del vapor volcánico. A partir del verano de 1997, el agua del volcán se enriqueció gradualmente en deuterio, lo que indica una contribución de magma profundo, menos desgasificado. Se identificaron otras tres posibles señales precursoras para la erupción de 1998-99: 1) un pico de dos a tres veces en la concentración de boro aproximadamente 3 meses antes de la erupción, 2) un incremento gradual de HCO_3 y de la presión parcial calculada de CO_2 disuelto, aproximadamente 1.5 años antes de la erupción, y 3) hasta septiembre de 1998, el flujo de SO_2 del volcán se mantuvo a niveles bajos de menos de 100 t/d, a menudo bajo el límite de detección del instrumento. Un mes antes del inicio de la erupción se registró un incremento agudo en el flujo de SO_2 , de 400 ± 50 t/d hasta 1600 t/d dos días antes del surgimiento de nueva lava el 20 de noviembre de 1998. El flujo de SO_2 presentó una buena correlación con la sismicidad.

Palabras clave: Erupción volcánica, gases volcánicos, hidrogeoquímica, flujo de SO_2

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INTRODUCTION

Chemical surveillance of active volcanoes is a necessary part of applied volcanlogy and usually includes both remote-sensing and direct-sampling methods. Changes in the gas flux from a volcano along with the temperature and composition of the gas and water discharges from a volcano-hydrothermal system, can be attributed to changes in magmatic activity. Anomalies and trends in fluxes, temperatures, and compositions sometimes can be observed earlier than increases in seismicity or ground deformation. There is no "general theory" for chemical precursors to a volcanic eruption, but some obvious rules can be applied to explain noticeable physical and chemical variations in the behavior of volcanic fluids and ground waters discharging on the slopes of a volcano prior to an eruption.

In this paper chemical and isotopic compositions of fumarolic gases and ground waters are reported with data on the SO_2 flux from the crater. Results were obtained during a period of almost 3 years before onset of the eruption on November 20th, 1998, through the two first months of the eruption. Samples of fumarolic gases were taken from two fumarolic fields in the crater with maximum temperatures of 840°C and 410°C, respectively, approximately every three months. Three springs at an elevation of 1,500 to 1,800 m above sea level on the S-SW slopes of Colima volcano, with temperatures from 14°C to 32°C, were sampled on average every two months. The COSPEC measurements of SO_2 flux from the crater were not so systematic due to a low gas flux that was often below the detection limit of the instrument (~50 t/d). Only one month before the eruption, the vapor plume from the crater appeared to be more intense, and the measurements were conducted on a regular basis.

The hydrogen and oxygen isotopic composition of fumarolic vapor and the chemical composition of ground waters showed relatively early pre-eruption anomalies, which we believe to be related to the ensuing eruption. The total gas output from the volcano drastically increased a few weeks before the eruption and thus definitely represents a good short-time precursor for the activity of Colima volcano. This interpretation is supported by correlation of the SO_2-flux with seismisity.

COMMENTS ON THE CHEMICAL MONITORING OF ACTIVE VOLCANOES

Studies on the relationship between chemical and isotopic variations of volcanic fluids and volcanic activity are currently at an empirical and experimental level. After about 30 years of comprehensive geochemical surveillance of volcanoes around the world, volcanologists have learned that each volcano has its own response to an upcoming eruption as manifested in the chemistry and temperature of volcanic gases and waters.

One year before the catastrophic eruption of El Chichón volcano in 1982, its fumarolic activity consisted of weak, boiling-point-temperature (96°C) fumaroles at the base of the old dome, discharging Cl-free and H_2S-rich vapor (Templos, 1981, unpublished data). Fumaroles of Momotombo volcano in Nicaragua (last eruption in 1907) showed a sudden increase in temperatures from 200°C to 915°C in 1980-1985 and retained these temperatures high for several years, although no eruption occurred (Menyailov *et al.*, 1986a). A similar increase in fumarolic temperature, up to 710°C, and drastic changes in the chemical and isotopic compositions of gases occurred at Vulcano, Italy, in 1991, again, without eruption (Tedesco, 1995; Chiodini *et al.*, 1995; Capasso *et al.*, 1997). Satsuma-Iwojima volcano, Japan, has maintained very high gas temperatures over a period of more than 800 years (Shinohara *et al.*, 1993). At Kudryavy volcano, Kuriles, which has been quiet for at least 100 years, fumarole temperatures have been recorded at up to 940°C, the highest measured for a passively degassing volcano (Taran *et al.*, 1995). Fumaroles at the crater rim of Avacha volcano, Kamchatka, measured between 1959 and the last eruption in 1991, were at boiling point temperatures of 92 to 101°C, Cl-free, SO_2-poor, with almost no changes in the flow rate and chemical composition during this interval. Moreover, this eruption started without any seismic activity. After the eruption the temperature of the fumaroles rose to 500°C, and clear magmatic signatures were observed in the gas compositions (Taran *et al.*, 1997). The mentioned volcanoes include many different types: the trachyandesitic extrusive dome of El Chichón; the rhyolitic dome of Satsuma Iwojima; the basaltic lava composed cone of Kudryavy; the trachydacitic cinder cone of Vulcano; the basaltic-andesitic strato-volcano edifices of Avacha and Momotombo.

An increase in fumarolic activity and gas flux before an eruption has been observed at Galeras volcano, Colombia (Fischer *et al.*, 1996), Ebeko volcano, Kurile Islands (Menyailov *et al.*, 1986b); Shiveluch volcano, Kamchatka (Kirsanova *et al.*, 1983); during repeated eruptive activity at Mount St. Helens following the May 18th, 1980 event (Symonds *et al.*, 1994); Mt Ruapehu, New Zealand (Christenson, 1997), and Kuju, Japan (Ohba *et al.*, 1997). The statistics of chemical precursors is not well understood because of the lack of long-term and systematic time-series observations ended by an eruption (Hirabayashi and Ohba, 1997).

Results, in general, are controversial and appear to depend on the specific structure of each volcano and volcano-hydrothermal system. For example, the Cl/S ratio in fumaroles of Izu-Oshima volcano significantly increased three months before the 1957 eruption (Noguchi and Kamia, 1963). A similar effect and 3-month precursor interval were observed by Naughton and collaborators (1975) prior to the 1971 eruption at Kilauea. However, at Asama volcano the same authors reported that in 1958 the Cl/S ratio drastically dropped, again 3 months before an eruption. Kirsanova and collaborators (1983) reported an increase of temperature and Cl/S ratio in fumaroles of Shiveluch volcano, Kamchatka, 4-5 months before a dome started to grow, but only in fumaroles located directly above the future dome. Other fumaroles, at the base of the crater walls, did not change their composition. During the 2 years before a phreato-magmatic eruption of Ebeko volcano, Menyailov and collaborators (1986b) recorded a gradual decrease of the Cl/S ratio with no change in fumarole temperatures.

To make progress with this approach it is clearly necessary to know in detail about the volcano-hydrothermal system under consideration. Usually, an increase of the Cl/S ratio before an eruption is observed in low-temperature fumaroles connected with a Cl-rich boiling aquifer inside a volcanic edifice. If a new portion of magmatic fluid enters into this "buffering" aquifer, the "brine" becomes more acidic and the transfer of Cl from solution to fumarolic vapor increases (Taran *et al.*, 1997). If a part of the aquifer is drying out due to an increase of the heat flow (*e.g.*, above a conduit), the Cl/S ratio in fumaroles connected with this part of the aquifer should also increase, like in the case of Kilauea or Shiveluch volcano (Naughton *et al.*, 1975; Kirsanova *et al.*, 1983). An increase of the Cl/S ratio, as a rule, is associated with increasing temperature because of the dry-out effect.

The chemical consequences of the input of new magma and the arrival of a new portion of "fresh" magmatic volatiles are different for low-temperature fumarolic vapors released from a boiling aquifer compared to high-temperature vapors released directly from a magma body. The approaching new magma should liberate relatively more SO_2 than HCl, compared to the "old", already partially degassed magma feeding high-temperature fumarolic fields, and in this case the Cl/S ratio probably should decrease. Long-lived high-temperature fumaroles or fumarolic fields, like at Satsuma-Iwojima or Kudryavy volcanoes and, as we guess, at Colima, are almost directly connected to convecting magma in a conduit and gas usually does not significantly change its composition and temperature over long time periods (Shinohara *et al.*,1993; Taran *et al*., 1995; Kazahaya *et al.*, 1994; Taran *et al.*, 2000). The gas composition depends strongly on the free gas phase/melt ratio in a conduit. If the gas/melt ratio close to an open conduit is high, variations in gas composition should be low and vice versa (Giggenbach, 1996). Fluctuations of the gas/melt ratio will cause corresponding fluctuations in the gas composition and may "mask" any systematic chemical trends.

Little is known about pre-eruption variations of the chemical compositions of thermal and mineral waters derived from a volcano-hydrothermal system or shallow ground waters discharging on the slopes of a volcano (Hirabayashi and Ohba, 1997). It seems that acidic Cl-SO_4 waters with a short recharge time are more "sensitive", because they are formed as the result of mixing between magmatic vapor and shallow ground water beneath the volcano edifice (Kiyosu and Kurahashi, 1983; Taran *et al.*, 1996). Chemical variations in such waters, as observed by Sturchio and Williams and collaborators (1990) at Nevado del Ruiz after an eruption, appear to have a delay (~ 400 days), whose magnitude probably depends on recharge time.

COSPEC and other gas-flux remote-sensing methods are now used at many active volcanoes. The main problem in the interpretation of total gas flux data is that for many volcanoes the apparent gas flux is much higher than it is possible to store in the erupting magma. The best example of this, so-called "excess of volatiles", is the Popocatépetl volcano (Gerlach *et al.*, 1997, Love *et al.*, 1999). During 1995-1999, Popocatépetl released on average 10,000 t/day of SO_2-gas, which is hundreds of time more than corresponds to the solid products erupted at the same time. One believes that for other, "normal" volcanoes, with no "excess of volatiles", the amount of gases released before and during an eruption should correspond to the associated erupted magma, like for Unzen volcano, Japan, during the 1990-1995 eruption (Hirabayashi and Ohba, 1997). In such cases, on the basis of systematic SO_2-flux measurements and the volume of lava extruded, the duration of an eruption can be predicted. It seems that the most powerful tool will be obtained when a combination of remote-sensing spectral methods will be applied for routine measurements of fluxes of the different individual gas species like SO_2, CO_2, and HCl (a universal spectrometer unifying COSPEC, GASPEC, and FTIR (Mori *et al.*, 1993; Williams, 1997). This would allow for the determination of gas ratios, similar to what is obtained by direct gas sampling, and improve the interpretation of the results in light of eruption forecasting.

GENERAL SETTINGS

Colima volcano (19.51°N, 103.61°W, 3,855 m above sea level) is the youngest and the only active andesitic cone of the large Quaternary Colima volcanic complex located in the western portion of the Trans-Mexican Volcanic Belt (TMVB), a continental arc related to the NE-SW (?) convergence of the North American plate and the Cocos and Rivera plates (Figure 1a). The present active cone of the Colima volcano began to grow about 4,000 years ago (Luhr and Carmichael, 1990a; Komorowski *et al.*, 1997). Historically, Colima has been the most active volcano in Mexico and one of the most active in the Americas. According to Luhr and Carmichael (1990b), since 1560 the volcano has evolved through three very similar eruptive cycles, the last one ending in 1913. The modern eruptive history and erupted products have been described in detail by Luhr and Carmichael (1990a). Several lava domes have risen in the crater since 1930 and now a steaming lava plug exists on the top of the volcano with small flat explosive craters after eruptions of 1987, 1991, and 1994. The surface of the summit before the1998 eruption consisted of unsorted lava blocks. No well-expressed fumarolic fields or fumarolic jets existed in the crater, but a diffuse, "unsaturated", gas flow occurred everywhere within an area of approximately 200x200 m with an average SO_2 flux during the last three years of no more than 100 t/d . The crater could be divided into several zones, each with a different temperature of gas discharge (Connor *et al.*, 1993). The highest temperature zone

Z3 was located in the northern part of the crater. Red-glowing holes with temperatures of 700-800°C could be seen here between lava blocks covered by green-blue incrustations. Yellow and white-yellow, sulfur-like incrustations, often forming small stalactites in cracks and niches, covered a middle-temperature (~ 400°C) zone Z2 in the NE part of the crater. The morphology of the crater area varied with time due to new fracturing, small avalanches and land-slides, but the main fracture network has been changed drastically only in July 1998, and before then had remained generally unchanged since 1990 (Connor *et al.*, 1993), in spite of the 1991 and 1994 eruptions (Cortés *et al.*, 1998).

There is almost no surface hydrothermal activity within the Colima volcanic complex. A few low-salinity and low-outflow rate springs discharge ground water at elevations from 1,500 to 1,800 m (Figure 1b) on the S-SW slopes of the Colima volcano, with a recharge area on the slopes of Colima and Nevado de Colima volcanoes as deduced from the water isotope composition (Taran *et al.*, 2000). The presence of a low-temperature hydrothermal system beneath the volcanic edifices is suggested by the existence of the San Antonio and Santa Cruz warm springs (32°C and 24°C) with 130 and 80 mg/kg of Cl, respectively.

METHODS

SAMPLING AND ANALYSIS

Fumarolic gas. All vents in the Colima crater with temperatures from the boiling point up to 800°C discharge gases with a very high content of air. Therefore, it was impossible to use pre-evacuated Giggenbach flasks for gas sampling. We instead used a 1.2 m -long silica sampling tube and pumped gas through two or three consecutive traps, each one with 30 ml of 4-6N NaOH solution, cooled by ice. Condensates for elemental and isotopic analyses were pumped into two consecutive glass traps cooled by ice. The collection of 20 to 30 ml of a pure condensate usually took more than two hours.

Absorbed gases were analyzed by standard techniques (Giggenbach, 1975). A portion of pure condensate was analyzed for H and O isotopes by mass spectrometry. Isotopic results for H_2O are expressed in the δ-notation relative to V-SMOW. The reproducibility of δ-values for D/H is ±2‰ and for $^{18}O/^{16}O$ is ± 0.2‰.

Spring waters. Temperature and pH were measured in the field. pH was measured potentiometrically, and the pH-calibration was made with buffer solutions submerged in the spring outflow and allowed to equilibrate at the water temperature. Water was collected in plastic bottles. One liter was used for the determination of alkalinity, conductivity, Cl^-, F^-, SiO_2, B and SO_4^{2-}. Another 500 ml aliquot of water was added to 1 ml of concentrated HNO_3 and used for the analysis of metals.

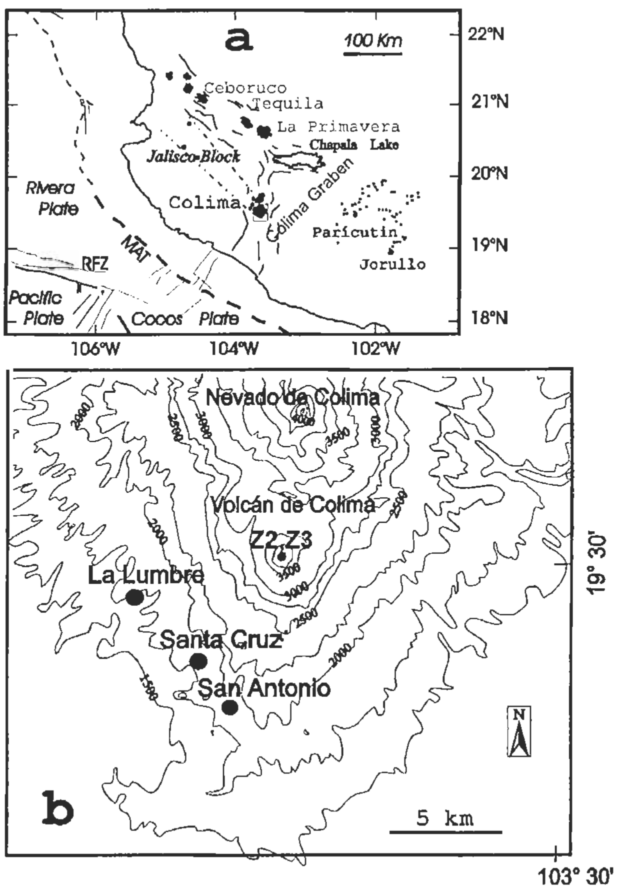

Figure 1. a. Location map showing main structures and the position of Colima volcano. Volcanic complexes of the western part of the Mexican Volcanic Belt are shown in heavy stipple pattern. MAT - the Mid-America Trench; RFZ -Rivera fracture zone.
b. Topographic map (>1,500 m) of the southern part of the Colima volcanic complex with the locations of three mineral springs: La Lumbre, San Antonio and Santa Cruz.

Chemical analyses were performed by wet methods, basically following the procedures described in APHA (1995). Bicarbonates were measured by acid titration using a mixed indicator of methyl red and bromcresol green. Na, K, and Fe were determined by atomic absorption on a Perkin Elmer 23 instrument. SO_4 was measured by turbidimetry. Mg and Ca concentrations were obtained by complexometric titration with EDTA. Boron was colorimetrically measured through its reaction with carminin acid. Chloride and fluoride were potentiometrically determined with ion selective electrodes. SiO_2 was determined by the molibdosilicate colorimetric method. Precision was <5% for all the major ion determinations. Other species had the following precisions: ±5% for B, ± 2% for SiO_2. Results were verified by duplicate sample analyses and ionic balance.

Dissolved gas in a few samples of spring waters was extracted by a method of equilibration with Ar and/or He as described in Capasso and collaborators (1998) and analyzed by gas chromatography with average analytical errors ± 5%.

COSPEC measurements

The overall emission rate of SO_2 from the summit crater was measured with a correlation spectrometer (COSPEC). The COSPEC measures the path-length concentration (ppm/m) of SO_2 in a cross section of the plume by analyzing incident ultraviolet radiation for absorption by SO_2. Traverses were made by flying beneath and perpendicular to the plume. The plume width was calculated from the width of the part of the chart recorder trace indicating the presence of SO_2 and the aircraft speed. The aircraft speed and the plume velocity were determined by using the on-board internal navigation system (GPS) with an accuracy of ± 10%. The method and an analysis of the errors are described in Hoff and Millan (1981). The reported values of the SO_2 emission rate are the mean value of at least two traverses.

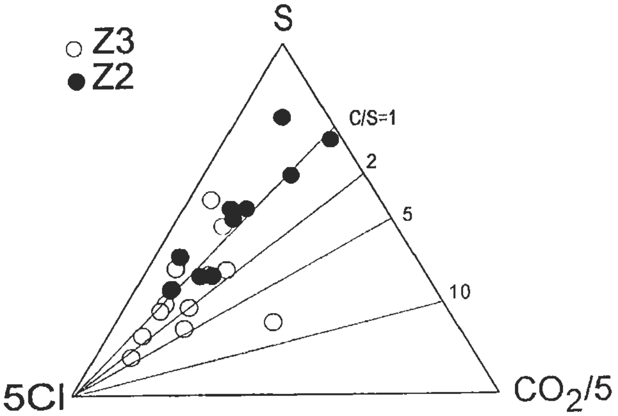

Figure 2. Relative molar concentrations of sulfur, chlorine, and carbon in fumarolic gases of the Colima volcano. Z3 and Z2 refer to the 800°C and 400°C monitoring sites, respectively.

GENERAL CHARACTERISTICS OF VOLCANIC GASES AND MINERAL WATERS

VOLCANIC GASES

Chemical and isotopic compositions of fumarolic gases are shown on Figures 2 and 3, and given in Tables 1 and 2. Gases are water-rich, with variable Cl contents up to 5 mmol/mol. Their chemical and water isotopic compositions, on average, are typical for subduction-type "andesitic" gases (Taran *et al.*, 1989; Giggenbach, 1992). Due to mixing with air inside the volcanic edifice at high temperature it is difficult to estimate the initial oxidation state of the volcanic gases. At the surface, as it has been shown by the composition of mineral precipitates (Taran *et al.*, 2000), the redox conditions are higher than those for the hematite-magnetite oxygen buffer. The most significant feature in the isotopic compositions of volcanic vapors is the difference between high- and low-temperature fumaroles (Figure 3a). High-temperature vapors from the Z3 site have $\delta^{18}O$ in the range of +5.7 to +8.0 ‰, which corresponds to "magmatic" values, and variable δD values from -57 to -26 ‰. The latter can be attributed to magma degassing which is supported by a negative correlation δD-Cl (Figure 3b). Isotopic compositions of vapors from low-temperature fumarole Z2 show trends of mixing between "magmatic" vapor and local meteoric water.

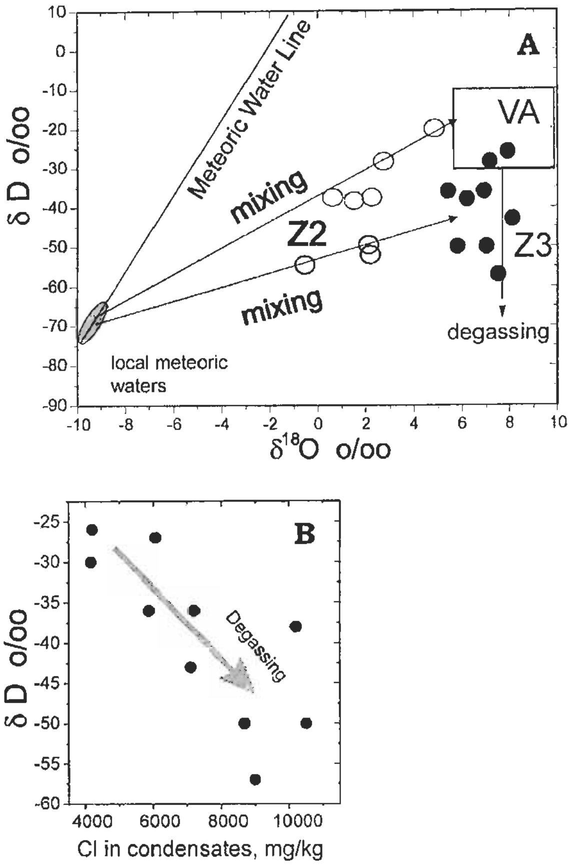

Figure 3. Isotopic systematics of the Colima volcanic gases.
a. Craig plot for isotopic composition of the volcanic vapor. VA area corresponds to the isotopic composition of "Volcanic Arc Waters" (Taran *et al.*, 1989; Giggenbach, 1992). The points for the Z3 high-temperature fumarole show a trend of degassing, whereas a mixing trend with local meteoric water can be seen for the Z2 400°C fumarole.
b. Correlation between Cl and δD for Z3 fumarolic vapor. A negative trend can be explained by magma degassing (see text).

SPRING WATERS AND DISSOLVED GASES

Three springs: La Lumbre (LU), San Antonio (SA), and Santa Cruz (SC) discharge diluted slightly acidic (pH from 5 to 6) water. The ranges in chemical composition of spring waters are shown in Table 3. The most mineralized SA water contains on average only 130 mg/kg of Cl, with Na/K ratios and SiO_2 concentrations corresponding to a temperature of approximately 140°C for the last equilibrium at depth. A mixing line can be drawn in coordinates Cl versus

Table 1. Major species (mmol/mol) for Z3 and Z2 fumaroles of Colima volcano (alkaline traps)

Date	T°C	H_2O	CO_2	S	HCl	HF
			Z3 site			
01.96	740	966.6	26.2	11.1	4.0	0.24
05.96	752	972.6	18.5	5.3	3.1	0.51
08.96	820	977.3	13.6	5.6	3.4	0.15
09.96	801	973.9	15.4	6.2	4.2	0.29
10.96	802	891.8	92.3	10.8	4.6	0.41
12.96	742	972.0	20.4	4.1	3.3	0.22
03.97	791	986.0	9.4	3.6	5.1	0.46
06.97	747	955.1	22.4	18.1	3.7	0.19
08.97	n.d.	982.3	11.8	2.0	3.6	0.27
11.97	782	986.5	8.2	2.4	2.5	0.22
03.98	763	950.8	15.4	27.9	4.9	0.19
05.98	789	979.2	9.7	8.0	3.0	0.15
			Z2 site			
01.96	382	953.0	26.2	18.9	1.5	0.40
05.96	401	973.3	14.0	11.1	1.7	0.16
08.96	370	973.1	12.0	11.2	3.7	0.16
09.96	375	961.3	24.7	10.0	3.6	0.39
12.96	407	962.6	14.7	10.9	1.7	0.11
03.97	382	972.0	16.2	7.7	3.7	0.22
06.97	378	959.6	10.3	19.4	0.8	0.05
08.97	n.d.	986.1	10.3	9.5	1.6	0.13
11.97	386	984.2	8.6	4.6	2.2	0.19

Table 2. Chemical composition (major components, mg/kg) and isotopic composition (δD and $\delta^{18}O$, permil, VSMOW) of condensates.

Date	T°C	SO_4	Cl	F	B	δD	$\delta^{18}O$
			Z3 site				
01.96	740	2038	8690	251	12.5	-50	+7.0
05.96	750	965	7113	407	6.7	-43	+8.1
09.96	801	2458	8993	234	n.d.	-57	+7.5
10.96	800	595	9670	490	18.9	n.d.	n.d.
12.96	742	5870	5870	193	27.3	-36	+5.4
03.97	791	1568	10500	310	27.5	-50	+5.8
06.97	747	3992	7200	198	17.3	-36	+7.9
08.97	n.d.	1280	4200	268	30.8	-26	+6.9
11.97	782	10620	4160	253	18.4	-30	n.d
03.98	763	4900	10200	245	20.0	-38	+8.9
05.98	789	9430	6063	30	6.5	-27	+6.8
			Z2 site				
01.96	382	7888	3220	500	43.3	-38	+0.7
05.96	401	4010	3720	206	23.8	-29	+2.3
08.96	370	9875	6510	n.d.	n.d.	-38	+1.7
09.96	375	2402	4590	362	n.d.	-55	+1.6
12.96	407	921	3104	97	13.6	-55	-1.0
03.97	382	12110	8250	290	15.7	-20	+4.8
06.97	378	26400	1550	96	7.8	n.d.	n.d.
08.97	n.d.	11160	1353	84	9.2	-54	+1.4
11.97	386	784	6320	286	12.4	-38	+2.3

SO_4 for all three waters (Figure 4). It indicates that at least chlorine and sulfur have a common, most probably, deep source. SA and SC waters contain a relatively high amount of bicarbonate, but the more Cl-rich SA water is less abundant in HCO_3. Water from both these springs is over-saturated in calcite and precipitates slightly colored Ca-Mg carbonates near the vents.

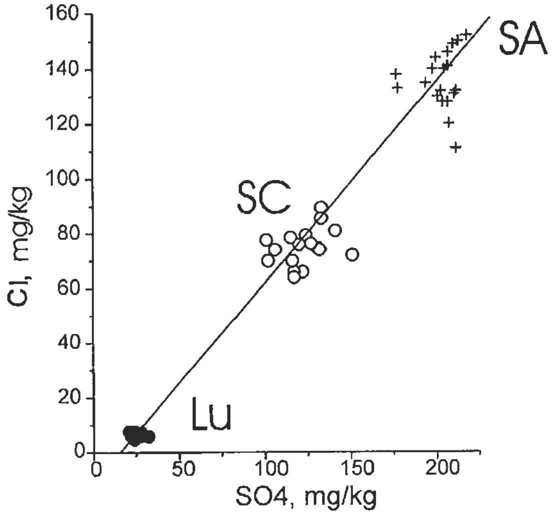

Figure 4. A mixing plot showing a single source for Cl and SO_4 in Colima mineral springs.

There is no free (bubbling) gas in the springs. A few available analyses of the dissolved gas (Table 4) show that the spring water is saturated with N_2 and Ar from air and considerably undersaturated with O_2. The SC water contains up to 350 mlSTP/kg of dissolved CO_2 gas, and low, but measurable amounts of He, H_2, H_2S, and CH_4. Dissolved gases from SA and LU waters are CO_2-poor, with H_2 and He close to or below the detection limit. The most diluted LU-water is enriched in CH_4, with about 1 cm^3STP/kg.

RESULTS AND DISCUSSION

TIME SERIES FOR CHEMICAL AND ISOTOPIC COMPOSITIONS OF VOLCANIC GASES

Tables 1 and 2, and Figure 5 (a-c), show temporal variations in the chemical composition of gases from sites Z2 and Z3. There are no systematic trends in the behavior of the gas compositions, with the possible exception of some decreases in the CO_2 and HF contents with time. Ratios of the concentrations show considerable fluctuations. Colima gases from the Z3 area are very hot, close to the subsolidus temperature, which may indicate that the partially molten magma body was very close to the surface. According to recent theoretical models of shallow convective magma degassing (Kazahaya *et al.*,1994; Stevenson and Blake, 1998), degassing drives convective overturn of the denser, degassed

Table 3. Chemical compositions of mineral springs at Colima volcano (maximum and minimum values), mg/kg

Spring	*La Lumbre*	*San Antonio*	*Santa Cruz*
t°C	13.0-15.5	30-33	21-24
pH_f	5.72-6.52	6.24-6.92	5.47-6.29
pH_{lab}	6.31-6.73	6.42-7.15	6.27-7.00
Na	13.2-16.9	147-195	112-158
K	3.5-4.0	4.8-5.7	5.0-6.0
Ca	15.9-20.4	25-38	57-81
Mg	6.3-14.1	81-97	51-71
Fe	0.0-0.80	0.0-3.1	0.0-3.5
Cl	4.8-7.6	120-152	64-90
HCO_3	105-126	452-486	519-590
SO_4	20.9-31.8	177-218	101-151
F	0.39-0.51	0.69-1.01	0.77-1.1
B	0.0-1.4	0.0-2.3	0.0-2.2

Table 4. Gas content and composition (mmol/mol in dry gas) of dissolved gases in waters of the Colima springs.

spring	Xg cm^3 STP/kg	He	H_2	N_2	Ar	O_2	CO_2	CH_4
La Lumbre	37.5	<0.01	0.006	621	5.3	124	244	5.6
San Antonio	64.6	<0.01	0.032	386	2.9	86	525	0.5
Santa Cruz	346	0.015	0.014	84	1.7	3.9	904	2.1

magma in the conduit back to depth, while less-dense gas-rich magma rises to replenish the shallow degassing zone. For volcanoes with a low total gas flux, like Colima before the 1998 eruption, gas composition should be sensitive to fluctuations in the gas/melt volume ratio (Giggenbach, 1996). If free gas and the melt are close to phase equilibrium, the total gas should be more enriched in the less soluble CO_2 and SO_2 at low gas/melt ratio, and enriched in water and Cl at high gas/melt ratio. Therefore, variations in the gas composition during the pre-eruption stage of Colima volcano, when the total gas flux was low, were most probably caused by fluctuations in the gas/melt volume ratio.

The temporal behavior of the isotopic composition of volcanic vapor (δD) is shown in Figure 5c. There is an obvious evolution from the values around -50‰ to values close to -30‰. Last value is close to the accepted range for the "andesitic" waters - volcanic vapor from subduction-type volcanoes (-30 to -10‰, Sakai and Matsubaya, 1977; Taran *et al.*, 1989; Giggenbach, 1992). If the negative correlation between δD and HCl for the high-temperature Z3 fumarole (Figure 3) is considered, this trend can be explained as a transition from gas depleted in D and enriched in Cl from more degassed magma, toward gas enriched in D and relatively depleted in HCl from less degassed magma. This suggestion is in agreement with both isotopic fractionation of hydrogen between a silicate melt and a fluid phase and the relatively high solubility of Cl in silicate melts (Taylor *et al.*, 1983; Dobson *et al.*, 1989; Carroll and Webster, 1994; Webster *et al.*,1999). The observed trend in δD-values may be, therefore, the result of the degassing of batches of progressively less degassed magma. The closer to the eruption date, the more of the less degassed magma supplied the shallow degassing zone.

In summary, only the trend in δD-values for the high-temperature Z3 fumarole can be considered as a long-term precursor for the 1998 eruption, but not the chemical composition of the fumarolic gas. A general decrease in the HF content with time (Figure 5a) may also be attributed to the magma degassing phenomena due to very high fluorine solubility, but this only is a speculation.

VARIATIONS IN THE CHEMICAL COMPOSITION OF GROUND WATERS

Plots for the temporal variation of each component and ratios of them are shown in Figures 7-12 and discussed below.

Temperature. Temperature of springs varied within 3°C and did not show seasonal or other regular trends.

TOTAL DISSOLVED SOLIDS (TDS) AND MAJOR COMPONENTS

Correlations between TDS and concentrations of major species are shown in Figure 6. A positive correlation between

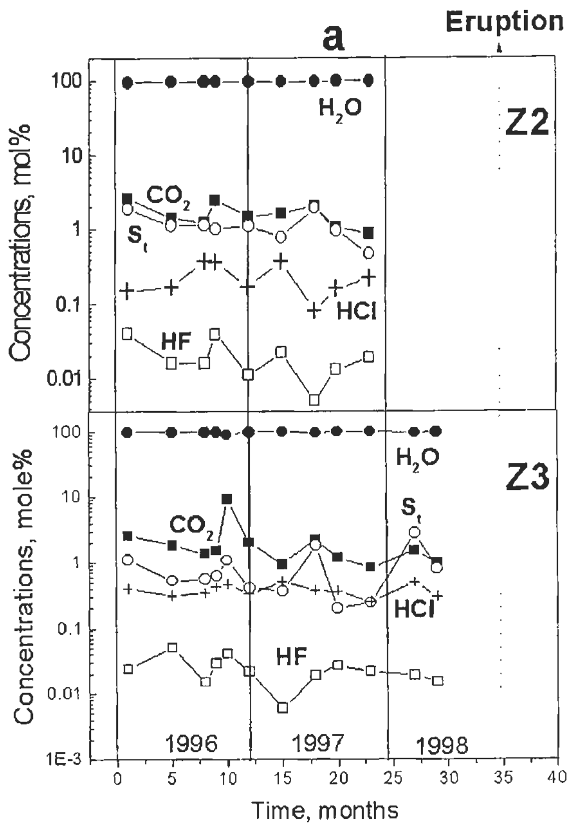

Figure 5.Variations over time in the chemical and isotopic compositions of volcanic gases from Z3 and Z2 fumaroles from January 1996 until July 1998. a. Variatons of concentrations of major species in Z2 and Z3 fumaroles.

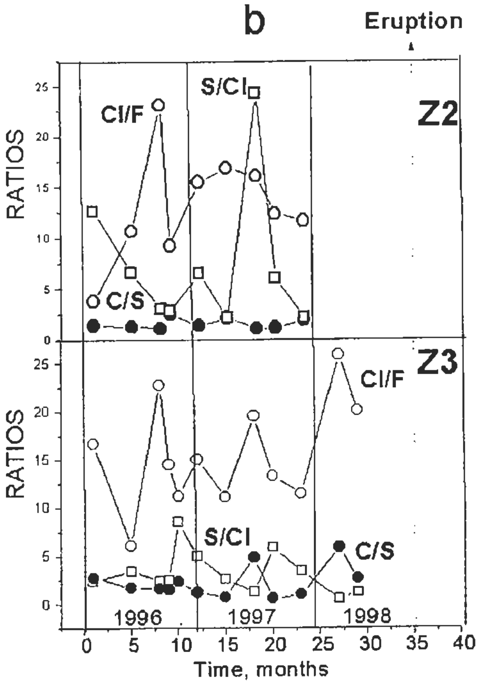

Figure 5b. Variations of C/S, Cl/F and Cl/S ratios over time in Z2 and Z3 fumaroles.

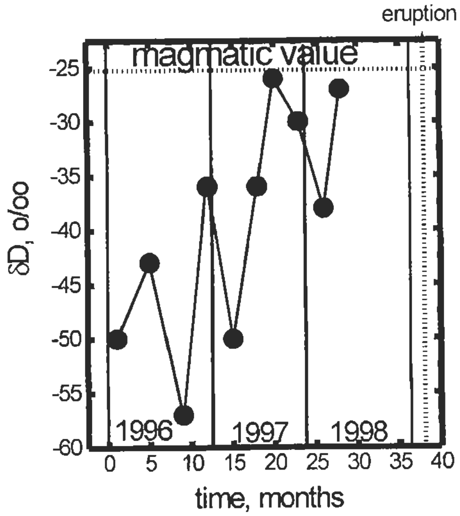

Figure 5c. Variations in δD of volcanic vapor for the Z3 fumarole. "Magmatic" values correspond to "Volcanic Arc water" (Figure 3a).

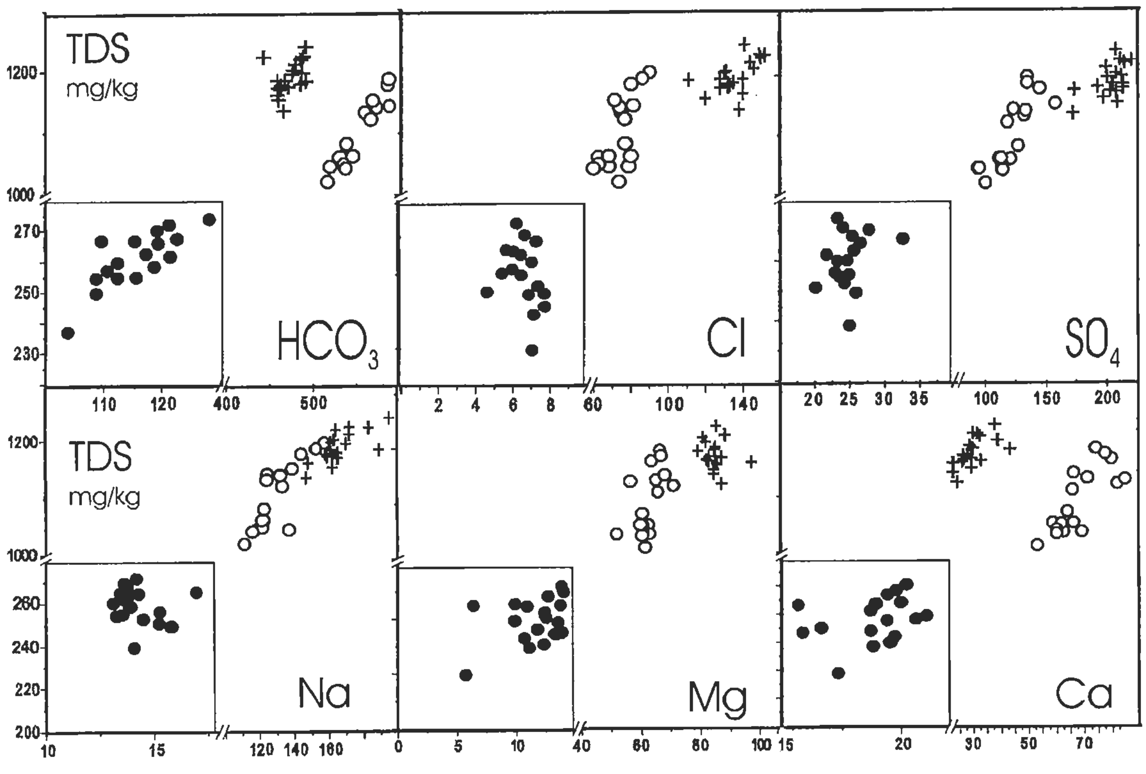

Figure 6. Correlations between TDS (total dissolved solids) and major ions in spring waters (mg/kg). Filled symbols - LU spring; open symbols - SC spring, and crosses - SA spring. Note the break on the TDS axes. For the SA and SC springs a positive correlation between TDS and all ions except Mg, corresponds to dilution by surface water. For the LU spring, only HCO_3 correlates with TDS (see text for further explanation).

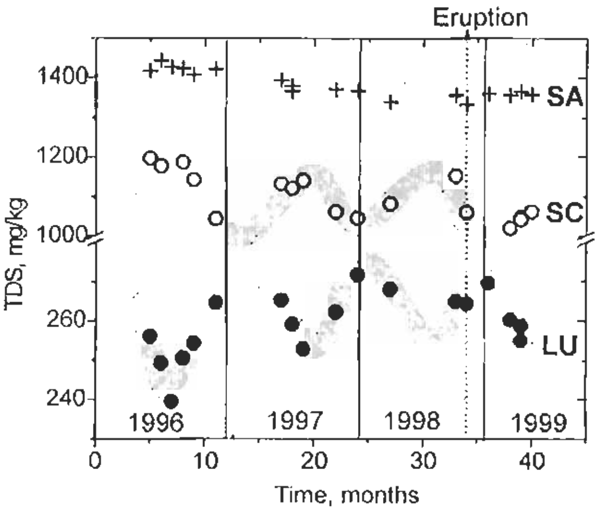

Figure 7. Variations over time for TDS. The seasonal variations in TDS are shown by stippled bands for Lu and SC springs. Gentle decreases in TDS for SA and SC springs correlate with decreases in HCO_3 and Cl (Figure 8). However, for the LU spring, an apparent slight increase in the TDS-values correlates positively with HCO_3 and negatively with Cl. For symbols see Figure 6..

major cations (Ca and Na) and anions (Cl, HCO_3, and SO_4) for SA and SC springs indicates a simple dilution with surface water. For the LU spring, only variations in HCO_3 and Ca are responsible for changes in TDS. Concentrations of other components in the LU waters do not correlate with TDS, and thus the salinity of the LU waters is not controlled by simple dilution, but by another mechanism related to the rock-water interaction.

Variations in TDS and Cl concentrations over time are opposite for the La Lumbre (LU) cold spring and both San Antonio (SA) and Santa Cruz (SC) warm springs (Figures 7 and 8). The salinity of SA and SC waters gradually decreased during the three years of observations. There were no significant changes preceding the eruption. The "saw-like" shape of variations in TDS for the SC water is related to seasonal variations, with rainwater dilution of the spring discharge during the wet season.

It is not clear why the composition of the shallow, very diluted water of the LU spring shows the trends in TDS plotted in Figure 7. As for the SC water, seasonal variations can be seen for TDS of the LU spring.

A possible explanation of the trends in TDS for SA and SC springs may be relaxation of the system to a basic level after the 1994 eruption. If so, TDS after the 1998-1999 eruption will increase up to some maximum values and then again will gradually decrease. These springs (SA and SC) have a deep source of the salinity, from a hydrothermal aquifer, with a much longer recharge time than water from the LU spring. Down-flowing, surface LU waters should be affected by volcanic gases within a part of the recharge area that is close to the summit of the volcano. Therefore, an increase in TDS in the LU water, which is directly related to an increase in the HCO_3 concentration, may be directly connected with the activity of the volcano.

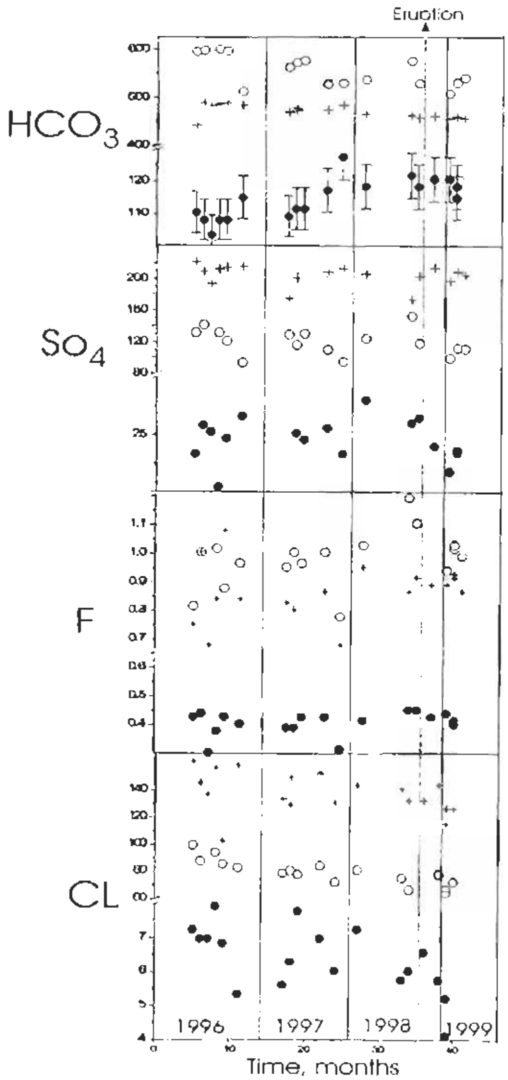

Figure 8. Variation over time in anion concentrations (mg/kg) for mineral springs. 5%-error bars are shown for the HCO_3 concentrations. Step-wise changes in the HCO_3 concentrations for the LU spring may be related to the interaction of the recharging water with volcanic fluids.

It may be suggested also that behavior of the salinity in the Colima spring waters reflects some regional climate variations and does not reflect possible changes in the local hydrological system of the volcano before the eruption.

ANIONS

It can be seen in Figure 8 that Cl and HCO_3 concentrations in SC and SA springs show a general, very gentle trends of dilution with time, corresponding to the trend for TDS (Figure 7). Variations in bicarbonate concentrations of the LU water are responsible for the rising of TDS of the LU spring. A step-wise 10%-enrichment in HCO_3 of the LU water occurred in the middle of 1997. The concentration of Cl in the LU spring shows an opposite trend for that of TDS.

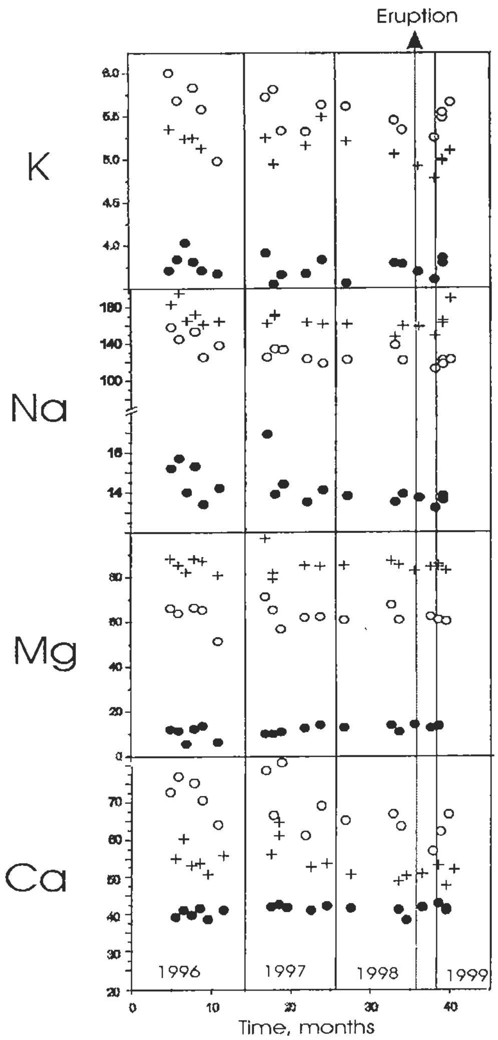

Figure 9 .Variations over time in cation concentrations (mg/kg) for mineral springs.

SO4 and F concentrations do not show any special trend for all three springs.

CATIONS

Variations of Na, K, Ca, and Mg with time are shown in Figure 9. Again, for major cations, Na and Ca, a dilution trend can be seen in SA and SC waters corresponding to the trend of the TDS data. For the LU spring variations in Na follow those in Cl, but both are opposite to the TDS trend. Concentrations of Mg in all three springs, and Ca and K in the LU spring, do not show any systematics trends during the time of observation.

RATIOS

Declining trends in Cl/F ratios (Figure 10) for the SA and SC springs correspond to general Cl, F and TDS trends for these springs, whereas the more significant lowering of the Cl/F ratio for the LU spring reflects the behavior of Cl concentrations in the LU waters (Figure 7). The same cause must be responsible for the trends in Ca/Cl and Mg/Cl for the very diluted water of the LU spring. A sharp depletion in Cl after the eruption started is reflected in increased Ca/Cl and Mg/Cl ratios.

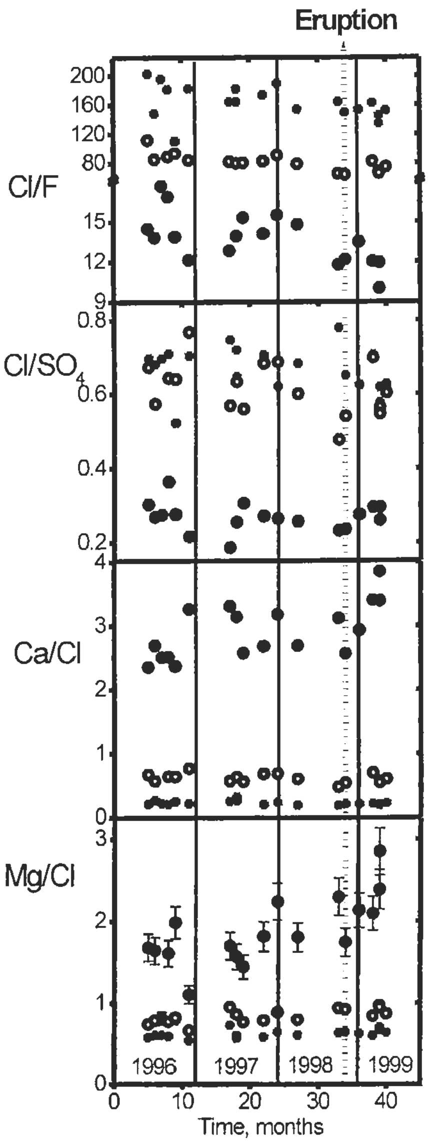

Figure 10. Variations in weight ratios of major components for the mineral springs over time. 10%-error bars are shown for the Mg/Cl ratio. An increase in the Mg/Cl and Ca/Cl ratios in the LU waters most probably reflects a decrease in the Cl concentrations.

PARTIAL PRESSURE OF CO_2 AND pH

Field and laboratory pH data differ by approximately 0.5 pH units and the pH_{lab} data do not show temporal trends for the nearly neutral SA waters and slightly acidic SC and LU waters (Figure 11). Therefore, variations in PCO_2 can be attributed to variations in pH and to trends in HCO_3, since PCO_2 was calculated from carbonate equilibrium at the

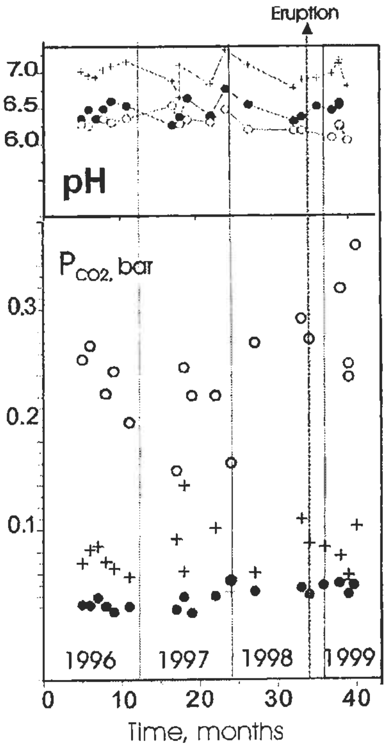

Figure 11. Variations in pH and calculated PCO_2 over time in mineral springs. In the middle of 1997, approximately 1.5 years before the eruption, a stepwise increase in PCO_2 can be seen for the LU and SC springs (see text).

sampling temperature:

$$PCO_2 = 0.018 \cdot m_{HCO_3} 10^{-pH} Kh \cdot K_1^{-1}$$

where K_1 is the first dissociation constant for H_2CO_3, and Kh is Henry's constant for CO_2, both at the sampling temperature, and $mHCO_3$ is the concentration of HCO_3 in mole/kg. The PCO_2-trend for the LU spring mimics its HCO_3 trend (Figure 8). The V-shaped trend for PCO_2 in the SC spring (Figure 11) has a minimum, again, approximately 1.5 years before the eruption, coincident with the step-wise increase in HCO_3 concentrations and PCO_2 for the LU spring. It may be suggested that both waters were affected by some change within the recharge area, close to the Colima crater.

BORON

The boron concentrations in all three springs are very low, typically less than 0.5 mg/kg on average (Figure 12). A two-three-fold jump in B occurred three months before the eruption in all springs. The reason for this simultaneous enrichment is not clear. It can be suggested that the main B contribution occurred from the shallow groundwaters within the recharge area close to the summit of the volcano, where boron entered the water after release from volcanic fluids. Relatively strong seismic events recorded in June and July 1998 were located inside the volcano edifice (G. Reyes, personal communication) and attributed to fracturing of the old lava plug. Probably these events are responsible for the boron enrichment of the down-going ground waters. However, it is not clear why these waters did not become enriched in other magmatic components like Cl, S, and F. A possible explanation is that boron was transported to ground water by the water vapor, which had separated from a liquid "brine", and for some reason, this "brine" did not interact directly with down-flowing shallow ground waters. But if so, why was there no further enrichment in B (and other "magmatic" species) after the eruption started and the total gas flux increased many times (see below). Nevertheless, the observed sharp enrichment in B three months before the 1998 lava emerged looks like a real precursor of the eruption.

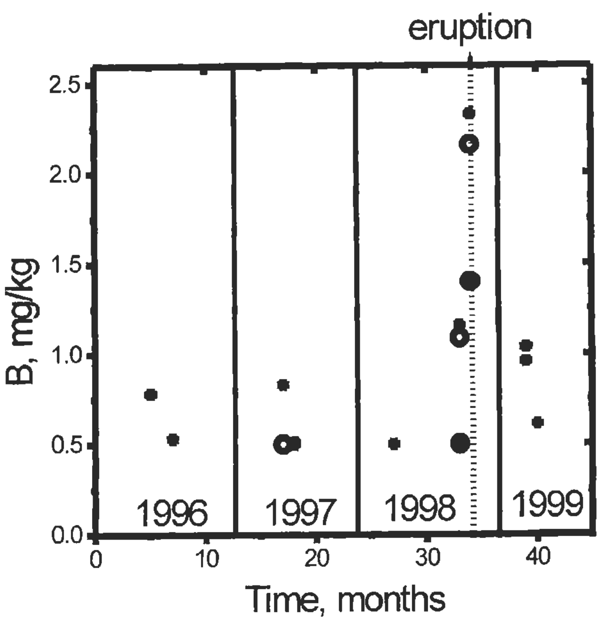

Figure 12. Variations in boron concentrations over time in mineral springs. A peak in the boron concentration occurred 3 months before the eruption.

SUMMARY OF THE SPRING CHEMISTRY

In general, there were few noticeable changes in the spring chemistry during three years before the 1998-1999 eruption. Variations in most elemental concentrations and pH were at background levels. The observed trends of dilution for SA and SC springs probably relate to some regional hydrological changes. There are two notable features in the behavior of the LU and SC springs: stepwise increases in the HCO_3 concentrations and calculated PCO_2 1.5 years before the eruption, and a short, sharp peak in B concentration 3 months before. Both are distinguishable and above background fluctuations and analytical error levels. The LU spring discharges very diluted, shallow groundwater. We suggest that the observed changes in HCO_3 , PCO_2 and B concentrations in

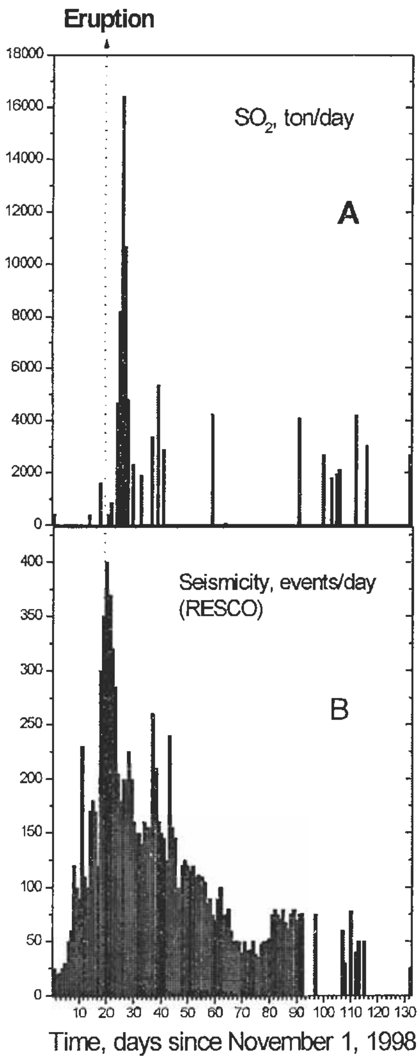

Figure 13. COSPEC data of the SO$_2$ flux (metric tons per day) and seismicity (events per day, G.Reyes, personal communication) before and during the 1998-1999 eruption. From 1995 to October 1998, SO$_2$-flux was either less than 100 t/day or below the detection limit of the COSPEC (~50 t/d).

the LU waters are connected with the activity of the volcano, because the LU waters obviously have a short recharge time and a part of its recharge area is close to the volcano crater. Changes in B concentrations for SA and SC springs, as well as PCO$_2$ for the SC spring are probably connected with changes in the diluting ground water that admixed with the deeper water near the surface.

It should be noted here, that the increase of PCO$_2$ in groundwaters discharging on the volcano slopes before an eruption can be considered as a reliable precursor. Bonfanti and collaborators (1996) have observed significant variations of PCO$_2$ in cold springs at Mt. Etna half a year before the 1991-1993 eruption over a large net of hydrochemical monitoring around the volcano. There are many differences between Mt. Etna and Colima volcanoes, nevertheless such a system of monitoring including water discharges and soil gas survey in favorable sites is recommended for Colima volcano.

SO$_2$-EMISSION RATE

Data on the SO$_2$ output in metric tons per day are presented in Figure 13 together with a companion plot of seismic events per day (G. Reyes, RESCO, personal communication). The first COSPEC data for the emission rate of SO$_2$ from Colima volcano were reported by Casadevall and collaborators (1984). In February, 1982, during the effusive 1981-1982 eruption, the volcano discharged 320 ± 50 t/d of SO$_2$. S.Williams (unpublished, 1990) reported a value of 600 t/d for SO$_2$ emission rate, measured during the effusive stage of the 1991 eruption. Since 1995 until October 1998, our values of the SO$_2$ output has not exceeded 150 t/d and often was below the detection limit of the instrument, less than 30 t/d. Even at the time of a few seismic swarms in 1997 and in the summer of 1998 no values higher than 150 t/d were obtained. On October 30th, 1998, for the first time during the last three years, a value of 400 t/d was recorded. On November 18, two days before the first lava appeared, a record SO$_2$-flux for Colima volcano value of 1,600 t/d was measured. This was a real short-term precursor to the eruption. A week after, on November 26, the volcano discharged more than 20,000 t/d of SO$_2$ - a maximum flux value, that coincided with a maximum of seismic activity (Figure 13). Lower values, but still very high for the Colima volcano, from 2,000 to 5,000 t/d were measured during the eruption until April 1999.

According to unpublished data of C. Navarro, the effusive stage of the eruption lasted until the end of January, in total 66 days, with a total volume of lava released estimated at about 40x106 m^3 or, on average, $0.6\cdot10^6$ t/d. If we assume that 0.1 wt% of dissolved sulfur in the parental Colima magma (Macías *et al.*, 1993) was almost completely released during the eruption, it corresponds to approximately 1,200 t/d of SO$_2$ flux. This is considerably lower, by about four times, than the average measured value for the same period of time. Therefore, the problem of "excess volatiles" also exists for Colima volcano, as for many others (Williams *et al.*, 1990; Wallace and Gerlach, 1994; Giggenbach, 1996; Gerlach *et al.*, 1997).

CONCLUSIONS

A set of geochemical data for crater fumaroles at Colima volcano, mineral springs on the slopes of the volcano, and Colima's SO$_2$ output were obtained during the three years before the 1998-1999 eruption, which started on November 20th, 1998, and continuing during the eruption until March, 1999.

Strong fluctuations in the chemical composition of volcanic gases from the 800°C and 400°C crater fumaroles have masked any possible trends or peaks preceding the eruption. The only real precursor of the eruption in the volcanic gas geochemistry was the isotopic composition of hydrogen of the volcanic vapor; about 1.5 years before the eruption, the volcanic vapor became more enriched in deuterium with δD values varying from those assumed for the degassed lava to values in the range -30 to -25 ‰, accepted for subduction-type volcanic vapor.

Among the chemical constituents of mineral springs near the volcano, only the concentrations of boron and HCO_3 (and calculated partial pressure of CO_2) in the most diluted spring, discharged a shallow ground water may be considered as precursors. A stepwise 10%-increase in HCO_3 concentration and peaks of the boron concentrations 1.5 years and 3 months before the eruption, respectively, can be related to the interaction of volcanic gases with down-flowing groundwater within the recharge area, close to the volcano crater. But the boron "jump", in spite of being very spectacular, is not easily explained, because it was not accompanied by anomalies in the concentrations of other "magmatic" components like SO_4, Cl, or F.

The SO_2-flux measured by COSPEC showed a real short-term precursor to the eruption. It sharply increased from almost undetectable values to 1600 t/d a few days before the first lava appeared, and during the eruption was in a good correlation with seismicity. Between November 20th, 1998, and March, 1999, the average flux of SO_2 released from Colima volcano was estimated as 4,000 t/d, which is about 4 times higher than expected from the total lava output.

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