

The relationship between fumarole gas composition and eruptive activity at Galeras Volcano, Colombia

Tobias P. Fischer Department of Geology, Arizona State University, Tempe, Arizona 85287-1404

Greg B. Arehart* } Argonne National Laboratory, CMT-205, Argonne, Illinois 60439

Neil C. Sturchio }
Stanley N. Williams Department of Geology, Arizona State University, Tempe, Arizona 85287-1404

ABSTRACT

Forecasting volcanic eruptions is critical to the mitigation of hazards for the millions of people living dangerously close to active volcanoes. Volcanic gases collected over five years from Galeras Volcano, Colombia, and analyzed for chemical and isotopic composition show the effects of long-term degassing of the magma body and a gradual decline in sulfur content of the gases. In contrast, short-term (weeks), sharp variations are the precursors to explosive eruptions. Selective absorption of magmatic SO₂ and HCl due to interaction with low-temperature geothermal waters allows the gas emissions to become dominated by CO₂. Absorption appears to precede an eruption because magmatic volatiles are slowed or retained by a sealing carapace, reducing the total flux of volatiles and allowing the hydrothermal volatiles to dominate gas emissions. Temporal changes in gas compositions were correlated with eruptive activity and provide new evidence bearing on the mechanism of this type of “pneumatic” explosive eruptions.

INTRODUCTION

Our five-year fumarole sampling program on the Decade Volcano, Galeras, has revealed intriguing variations in temperature, CO₂, total sulfur, HCl, and isotopic composition that appear related to the eruptive behavior of the volcano. A number of workers (e.g., Giggenbach et al., 1986, 1990; Hedenquist and Aoki, 1991; Chiodini et al., 1993; Hedenquist et al., 1993, 1994; Hedenquist and Lowenstern, 1994) noted similar variations in fumarole compositions produced by interactions of magmatic gas with low-temperature geothermal waters. We believe that the variations at Galeras are caused by sealing of the magmatic carapace (or fluid pathways) and consequent absorption of magmatic gas by the geothermal system. The sealing events are accompanied by pressure buildups that precede the Vulcanian eruptions.

Galeras is an active 4200-m-high andesitic stratovolcano in the Colombian Andes near the border with Ecuador. The city of Pasto (population 300 000) is located 7 km east of the active crater. Reactivation of Galeras was recognized in 1988 by increases in seismicity, gas emissions, and fumarole temperatures. Sulfur dioxide (SO₂) emissions reached a peak of ~5000 t/d in May 1989, when there was a small magmatic eruption emitting 400 000 m³ of ash (Williams et al., 1990; Cortés and Raigosa, 1994). A lava

dome was emplaced in October 1991, accompanied by another peak in SO₂ flux and Vulcanian explosions (Stix et al., 1993). An explosive eruption destroyed ~90% of this dome on July 16, 1992 (Gómez and Torres, 1993). An eruption on January 14, 1993, killed six scientists studying Galeras (Muñoz et al., 1993). Similar eruptions occurred on March 23, April 4, April 13, and June 7, 1993. Individual eruptions ejected ~100 m³ of material, and columns reached 2–7 km in height (Cortés and Raigosa, 1994).

SAMPLING AND ANALYTICAL RESULTS

Direct gas sampling of fumaroles has been performed sporadically since 1988, and in more detail prior to and following the July 16, 1992, eruption. In late 1988, the first sample was collected inside the crater (Crater fumarole). Since then, the majority of the samples have been collected at Deformes fumarole, which is located on the southwestern side of the active cone, outside the crater. In 1992 and 1993, samples were also collected at Besolima fumarole, on the northwestern side of the active cone, outside the crater on a fault dissecting the crater. Both fumaroles are within 50 m of the crater rim. Fumarolic gas was collected in evacuated bottles containing a 4 N NaOH solution. The acid gases (CO₂, SO₂, H₂S, HCl, HF) are absorbed into the solution and analyzed by ion chromatography and wet chemistry. The nonabsorbed gases (Ar, He, N₂, H₂, CH₄, CO) remain in the head space of the bottle and were analyzed by gas chro-

matography (Giggenbach, 1975). The dominant gas species of the fumarolic discharges is water (96.8 to 99.8 mol%), followed by carbon dioxide (CO₂), total sulfur (S_t = SO₂ + H₂S), and hydrogen chloride (HCl). Water from fumarolic vapor was condensed using an ice-water bath and analyzed by mass spectrometry for oxygen and hydrogen isotopic composition. The condensed steam was equilibrated with CO₂ for oxygen isotopes (Kishima and Sakai, 1980) and reduced with zinc for hydrogen isotopes (Coleman et al., 1982). Data are available from the GSA Data Repository.¹

DISCUSSION

Long-Term Variations

The time series of fumarole sampling during 1988–1994, in combination with SO₂ flux measurements by COSPEC, allows us to investigate long-term variations in magma degassing. SO₂ emissions at Galeras have been remotely monitored since early 1989 and show a pattern of decline from ~5000 t/d in late 1989 to <2000 t/d by the end of 1990. The SO₂ flux remained <1000 t/d through 1994; there were short-term variations prior to and following eruptions (Stix et al., 1993; Fischer et al., 1994). The decline in SO₂ flux since 1989 was interpreted as the result of a continuously degassing magma body. Melt inclusion and matrix glass data also showed that degassing of Galeras magma during 1988–1993 has reduced the H₂O, S, and Cl contents of the magma (Stix et al., 1993).

Fumarole compositions show variations between being magmatic, S_t + HCl dominated (S_t/CO₂ = 1.25 and HCl/CO₂ = 0.3), and being hydrothermal, CO₂ dominated (S_t/CO₂ = 0.14, HCl/CO₂ = 0.0012) (Fig. 1). The HCl content of the fumaroles decreases an order of magnitude as the gas composition changes from S_t + HCl dominated to CO₂ dominated. The S_t content decreases by a factor of five. Variations of HCl and S_t are larger when the composition is hydro-

¹GSA Data Repository item 9626 is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301. E-mail: editing@geosociety.org.

*Present address: Wairakei Research Centre, Institute of Geological and Nuclear Science, Private Bag 2000, Taupo, New Zealand.

Data Repository item 9626 contains additional material related to this article.

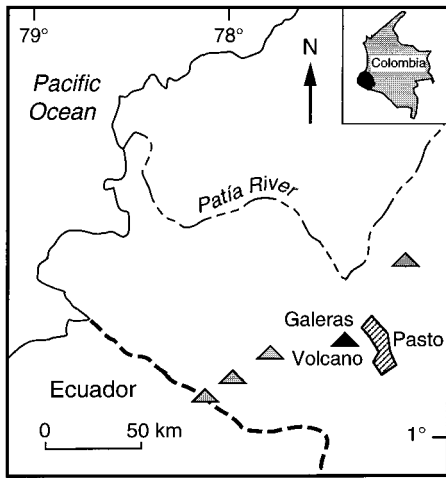


Figure 1. Location of Galeras Volcano and other active volcanoes of southwestern Colombia. City of Pasto (population ~300 000), capital of Nariño department, is outlined on map.

thermal than when it is magmatic. We suggest that the changes from magmatic to hydrothermal may represent times of maximum and minimum escape of magmatic gases through the sealed carapace. When escape is not possible, pressure may increase beneath the carapace, leading ultimately to a “pneumatic” eruption. In order to evaluate temporal changes of major fumarole gas species (H_2O , CO_2 , S_t , and HCl), the data are presented as ratios of C_i/C_{CO_2} (Fig. 2). C_i is the concentration of the particular gas species in mole percent. CO_2 is chosen as a reference because it is the least influenced by secondary processes, such as absorption into a liquid phase or interaction with wall rocks. Carbon dioxide, being the least soluble of the major volatiles in the melt, will degas more readily than H_2O , sulfur, and HCl in a cooling and solidifying magma body. During 1989–1994, the H_2O/CO_2 , S_t/CO_2 , and HCl/CO_2 ratios of fumarole gases show a minor, overall increase, most of the increase occurring between January, 1993, and August, 1994. The general increase in the ratios may be the result of continuous degassing of the magma. Prior to the eruption of July 16, 1992, there was a decrease in the ratios.

Short-Term Variations

Short-term variations in the chemical and isotopic composition of fumarole gases, prior to and following the eruption of July 16, 1992 (Fig. 3), are believed to represent changes related to processes which resulted in the eruption. The S_t/CO_2 ratios prior to and following the eruption show only minor changes, compared to those of the HCl/CO_2 ratio, indicating that each ratio is affected by different processes. The HCl/CO_2 ratio of volcanic gases has previously been inter-

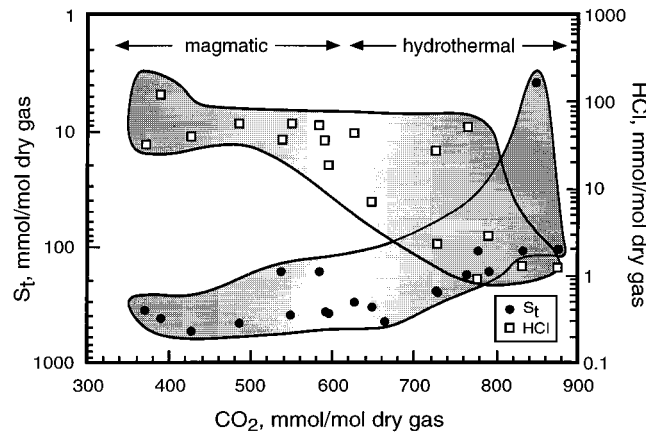


Figure 2. Variation of CO_2 , S_t , and HCl contents of Galeras fumaroles, expressed as mmol/mol dry gas, i.e., water-free composition of the sample. The y axes are log scales; S_t axis is reversed. Shown are “magmatic” and “hydrothermal” end member fields at Galeras. Magmatic gases are $S_t + HCl$ dominated; hydrothermal gases are CO_2 dominated.

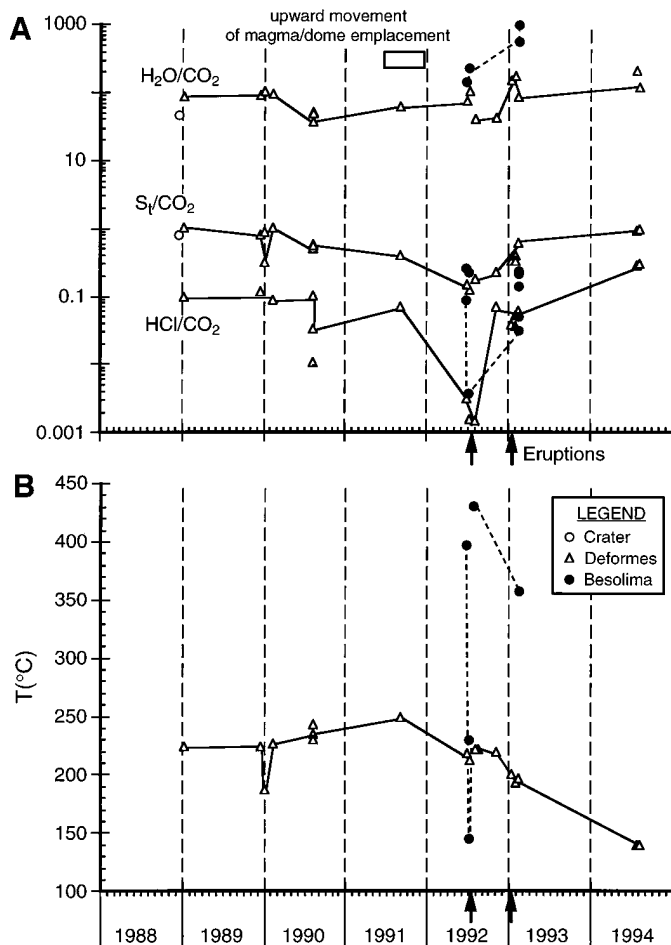
preted as reflecting processes which are associated with absorption of HCl by a liquid phase, whereas the S_t/CO_2 ratio is related to variations in the degree of degassing from the magma body (Giggenbach, 1983). Between June 25 and July 8, 1992, the HCl/CO_2 ratio of Besolima fumarole decreased an order of magnitude, from 0.09 to 0.003. Deformes also showed a decrease, from 0.003 to 0.001, during the same time period. At Deformes, the ratio remained unchanged shortly after the eruption and increased to 0.08 in November, 1992 (M. Martini, written commun.), a value similar to those of samples collected during 1989–1991. At Besolima, no sample had been collected until January, 1993, by which time the HCl/CO_2 ratio had increased to 0.02. Absorption of water-soluble magmatic gases into a liquid-dominated, hydrothermal environment can strongly influence the composition of the discharging fumarolic gases and thermal waters (Giggenbach et al., 1986, 1990; Hedenquist and Aoki, 1991; Chiodini et al., 1993; Hedenquist et al., 1993, 1994; Hedenquist and Lowenstern, 1994). Manifestations of the hydrothermal system at Galeras are large sulfate springs on the western side of the volcano (22 °C and pH 5) and smaller acid sulfate springs on the eastern side (29 °C and pH 2). A decline in HCl/CO_2 ratio in the fumarolic gas over a short time period is consistent with the idea of increased interaction of magmatic gases with a liquid-dominated hydrothermal system inside the volcanic edifice. The increase in interaction is also consistent with an increase in H_2O/CO_2 ratio of the gases prior to the eruption (Fig. 3A). Temperatures of fumarole gases also reflect variations in the extent of interaction of high-temperature magmatic gases with a lower-temperature hydrothermal system. At Besolima, the temperature was 397 °C on June 26, the date with the highest HCl/CO_2 ratio. It dropped to 230 °C on July 8, when the HCl/CO_2 ratio was lowest. After the eruption on July 27, the temperature reached 431 °C. Deformes

fumarole shows less-significant variations in temperature (Fig. 3B). The relative stability of Deformes temperatures may be the result of its more peripheral location on the active cone, as opposed to Besolima, which is located on a fault dissecting the crater.

Using δD as an indicator of the relative amount of meteoric water in the steam, and more negative values representing a more meteoric signature, we can investigate the variations related to the eruption of July 16, 1992 (Fig. 3C). Deformes δD values first increased then decreased prior to the eruption. After the eruption, on August 2, 1992, the δD value was the highest ever measured at Deformes, but declined to a low value on August 14, 1992. At Besolima, the δD value increased immediately prior to the eruption, although the temperature of the fumarolic gas was only 230 °C. δD remained high on July 27, immediately after the eruption, with a temperature increase to 431 °C. Gas samples for chemistry and for isotopes have not always been collected on the same day, making a direct comparison of the isotopic signature and the gas chemistry difficult. In general, there is no correlation between the amount of meteoric contribution to the fumarolic steam and the chemical composition of the fumarole gas. We believe that the variations of oxygen and hydrogen isotopes prior to July 16, 1992, are mostly related to very surficial processes, such as dilution by vaporization of surficial meteoric water at shallow levels. There are changes immediately prior to and following the eruption, but interpretation is difficult without further samples bracketing other Vulcanian eruptions similar to Galeras in 1992.

Total flux of the gas species can help further investigation of the processes leading to the eruption of July 16, 1992. We have shown that June 1992 marks a time of change of chemical composition of the fumarole gases. The SO_2 flux, measured by COSPEC, also changes significantly during that time; decreasing from 1600 t/d on June 25 to 400 t/d on July 7 (Fig. 3D). Using SO_2

Figure 3. Temporal variations in fumarole gas compositions and temperatures over period of December 1988 to August 1994. July 16, 1992, and January 14, 1993, eruptions are shown as arrows. **A:** C_i/C_{CO_2} ratios of fumarole gases, where C_i is water (H_2O), total sulfur ($S_t = SO_2 + H_2S$), and hydrogen chloride (HCl). Movement (August 1991) of magma that emplaced dome (October–November 1991) is shown as horizontal bars. **B:** Temperatures of fumaroles in °C.



flux and gas ratios of samples collected at Deformes, the CO_2 flux dropped from 4600 t/d on June 26 to 3100 t/d on July 8; the HCl flux dropped from 15 to 5 t/d. At Besolima, CO_2 dropped from 6100 t/d to 2000 t/d and HCl dropped from 530 t/d to 8 t/d over the same time interval. Therefore, the flux of all species decreased prior to the July 16 eruption and the compositions of the gases became more CO_2 rich. Immediately after the eruption, SO_2 flux remained low (~100 t/d on July 17), increasing to >500 t/d by the end of the month, followed by a decline to 100 t/d throughout August.

The decline in SO_2 flux prior to the March 23, 1993, eruption has been interpreted as caused by the retainment of magmatic gases due to a sealing process inside the volcanic edifice. Increased SO_2 flux immediately after an eruption could be related to re-opening of gas conduits during the explosive eruption. Fischer et al. (1994) and J. Stix (1995, personal commun.) showed that seismicity associated with these events is consistent with brittle failure of the sealed carapace at the top of the magma body. Once the strength of the impermeable seal has been exceeded, during an eruption, gas can freely escape through the permeable conduit and

interaction of gas with the hydrothermal system is minimized. We believe that this mechanism was also the cause of the larger eruption on July 16, 1992. The failure of gases to escape the volcano is reflected in the decline of the flux of all gas species during June and July, 1992, while ongoing degassing of the magma body is assumed to remain constant during the short time period. Retainment of magmatic gases below a sealing carapace will allow the hydrothermal system to dominate the gas chemistry by selective absorption of more water-soluble gas species, such as HCl . As a result, the HCl/CO_2 ratio declines. Immediately after the eruption, with the fluid pathways reopened, we expect the gas composition to return to pre-eruptive, open degassing composition of higher HCl/CO_2 ratios. Unfortunately, there were no gas samples collected immediately after the eruption. The sample, collected on August 4, 1992, shows essentially the same C_i/C_{CO_2} ratios as the sample collected just prior to the eruption. One explanation may be that, after the pressure release by the eruption and the reopening of the fluid flow paths, the hydrothermal system migrated deeper into the volcanic edifice and dominated the gas composition. In

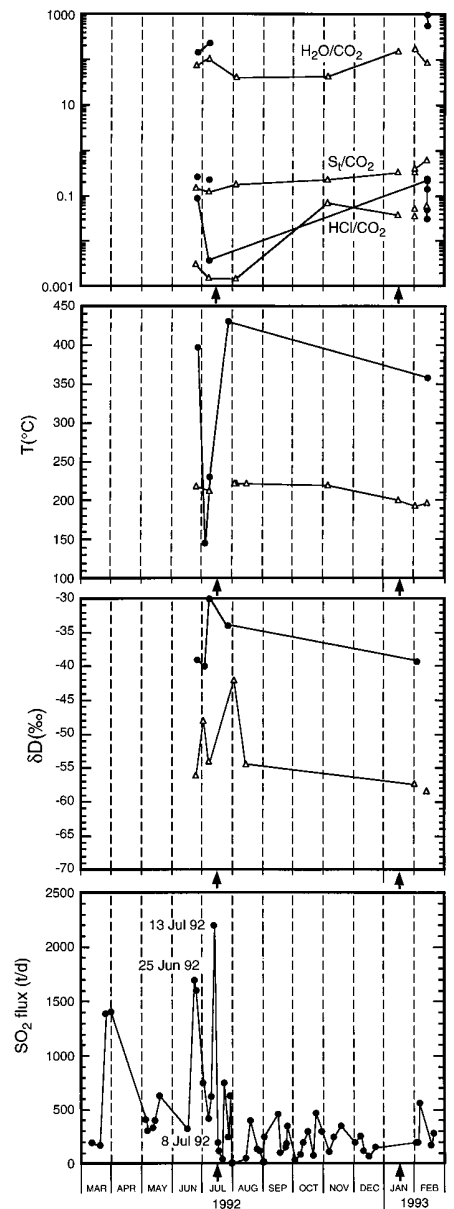


Figure 4. Temporal variations in SO_2 flux measured remotely by COSPEC, chemical and isotopic composition and temperatures of fumarole gases over period of March 1992 to March 1993. July 16, 1992, and January 14, 1993, eruptions are shown as arrows. Symbols as in Figure 2. **A:** C_i/C_{CO_2} ratios of fumarole gases. **B:** Temperatures of fumaroles in °C. **C:** δD of condensed steam in fumarole gases in parts per mille. **D:** SO_2 flux in metric tons/day.

November, 1992, the hydrothermal system had been sufficiently pushed back and the gas composition returned to pre-1992 values.

During times of increased interaction, the variations in the fumarole compositions and SO_2 flux are greater than during times of open, magmatic degassing, when gas compositions are $S_t + HCl$ dominated (Fig. 1). The greater variations may be due to pressure buildup and the impending eruption.

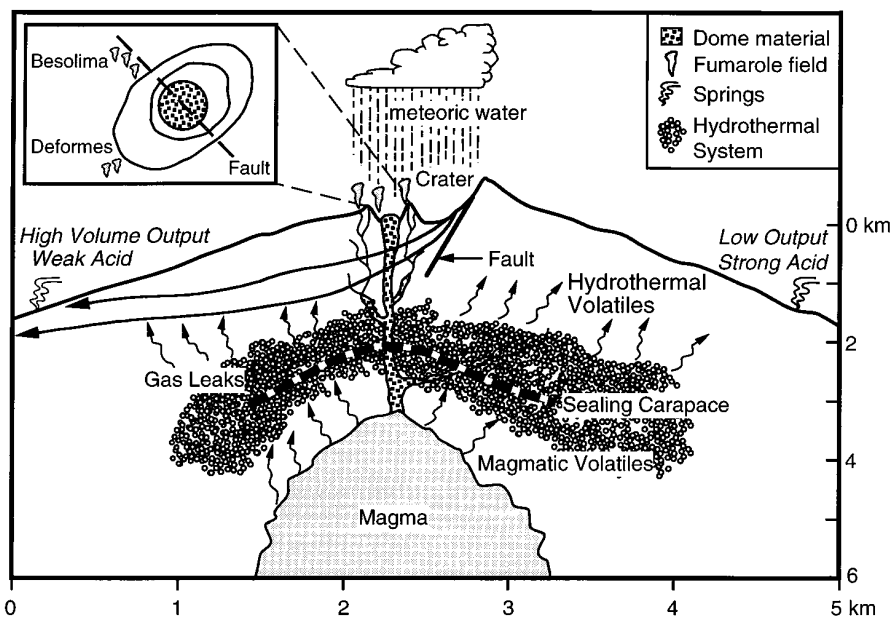


Figure 5. Schematic east-west cross section of Galeras Volcano, showing potential travel paths of fluids compatible with geochemical findings. Inset: Relative location of Deformes and Besolima fumaroles, outside of crater (with its inner crater and dome).

CONCLUSIONS

Through consideration of data available for Galeras fumaroles and eruptive activity from 1988 to 1994, we have inferred a mechanism that may change the gas composition of fumaroles during short time periods and is the cause of selective absorption of water-soluble gas species by a hydrothermal system. The extent of interaction between the magmatic gas and the hydrothermal system is related to the extent of magmatic gas retention by a sealing carapace which results in pressure buildup and eruption. This is illustrated schematically for Galeras in Figure 4. In detail, the sealing process could involve silica or other minerals by convecting liquids (Fournier, 1983). Two fumaroles reflect the sealing process and increased interaction with a hydrothermal system on different time scales and to different extents, due to their relative location on the active cone. The peripheral Deformes has lower temperatures, a more meteoric water isotopic signature, and allows the hydrothermal system to "invade" the magmatic gas conduits more easily than Besolima.

Monitoring of fumarole gas chemistry and temperatures is relatively inexpensive and provides a time-series data set that, in combination with seismicity and remotely measured SO_2 flux, allows better interpretation of all the data in terms of eruption forecasting. In addition, short-term versus long-term processes regarding the degassing behavior of the magma can be distinguished and contribute to the understanding of explosive eruptive events at active volcanoes.

ACKNOWLEDGMENTS

Supported by the U.S. National Science Foundation (Williams) and the Geosciences Research Program of the Office of Basic Energy Sciences, U.S. Department of Energy (Sturchio). We thank Dale Counce, Pat Trujillo, and Fraser Goff (Los Alamos National Laboratory) and Florence Smith (Argonne National Laboratory) for analytical assistance and discussions; the staff of the Observatorio Vulcanológico de Pasto, especially Marta Lucía Calvache V., for support in studying Galeras and SO_2 flux data; Marino Martini for the data of November 1992, and John Stix for the data of August 1992. Werner Giggenbach and Jacob Lowenstern are both appreciated for providing very helpful reviews and Sue Selkirk for her help with figures.

REFERENCES CITED

- Chioldini, G., Cioni, R., and Marini, L., 1993, Reactions governing the chemistry of crater fumaroles from Vulcan Island, Italy, and implications for volcanic surveillance: *Applied Geochemistry*, v. 8, p. 357-371.
- Coleman, M. L., Shepherd, J. T., Durham, J. J., Rouse, J. E., and Moore, G. R., 1982, Reduction of water with zinc for hydrogen isotope analysis: *Analytical Chemistry*, v. 54, p. 993-995.
- Cortés J., G. P., and Raigosa A. J., 1994, Aspectos relevantes de la actividad del volcán Galeras, Nariño-Colombia, febrero de 1989, mayo de 1994: INGEOMINAS, Centro de Observación Vulcanología y Sismología de Pasto, Internal Report, p. 14.
- Fischer, T. P., Morrissey, M. M., Calvache V., M. L., Gómez M., D., Torres C., R., Stix, J., and Williams, S. N., 1994, Correlations between SO_2 flux and long-period seismicity at Galeras volcano: *Nature*, v. 368, p. 135-137.
- Fournier, R. O., 1983, Active hydrothermal systems as analogues of fossil systems, in the role of heat in the developments of energy

- and mineral resources in the Northern Basin and Range Province: *Geothermal Resources Council Special Publication 13*, p. 263-284.
- Giggenbach, W. F., 1975, A simple method for the collection and analysis of volcanic gas samples: *Bulletin of Volcanology*, v. 39, p. 132-145.
- Giggenbach, W. F., 1983, Chemical surveillance of active volcanoes in New Zealand, in Tazieff, H., and Sabroux, J., eds., *Forecasting volcanic events*: New York, Elsevier, p. 311-322.
- Giggenbach, W. F., Martini, M., and Corazza, E., 1986, The effects of hydrothermal processes on the chemistry of some recent volcanic gas discharges: *Periodico di Mineralogia*, v. 55, p. 15-28.
- Giggenbach, W. F., García P., N., Londoño C., A., Rodríguez V., L., Rojas G., N., and Calvache V., M. L., 1990, The chemistry of fumarolic vapor and thermal-spring discharges from the Nevado del Ruiz volcanic-magmatic-hydrothermal system, Colombia: *Journal of Volcanology and Geothermal Research*, v. 42, p. 13-39.
- Gómez M., D. M., and Torres C., R. A., 1993, Aspectos relativos de la actividad del Volcán Galeras desde 1991 y estudios de algunos parámetros cinemáticos de las fuentes sísmicas de alta frecuencia: *Taller Internacional sobre el complejo volcánico Galeras*, Pasto, Colombia.
- Hedenquist, J. W., and Aoki, M., 1991, Meteoric interaction with magmatic discharges in Japan and the significance for mineralization: *Geology*, v. 19, p. 1041-1044.
- Hedenquist, J. W., and Lowenstern, J. B., 1994, The role of magmas in the formation of hydrothermal ore deposits: *Nature*, v. 370, p. 519-527.
- Hedenquist, J. W., Simmons, S. F., Giggenbach, W. F., and Eldridge, C. S., 1993, White Island, New Zealand, volcanic-hydrothermal system represents the geochemical environment of high sulfidation Cu and Au ore deposition: *Geology*, v. 21, p. 731-734.
- Hedenquist, J. W., Aoki, M., and Shinohara, H., 1994, Flux of volatiles and ore forming metals from the magmatic-hydrothermal system of Satsuma Iwojima volcano: *Geology*, v. 22, p. 585-588.
- Kishima, N., and Sakai, H., 1980, Oxygen-18 and deuterium determination on a single water sample of a few milligrams: *Analytical Chemistry*, v. 52, p. 356-358.
- Muñoz, F. A., and 11 others, 1993, Galeras Volcano: International workshop and eruption: EOS (Transactions, American Geophysical Union), v. 74, p. 281-287.
- Stix, J., and 10 others, 1993, A model of degassing at Galeras Volcano, Colombia, 1988-1994: *Geology*, v. 21, p. 963-967.
- Williams, S. N., and eight others, 1990, Premonitory geochemical evidence of magmatic reactivation of Galeras volcano, Colombia: EOS (Transactions, American Geophysical Union), v. 74, p. 690.

Manuscript received August 2, 1995
 Revised manuscript received January 1, 1996
 Manuscript accepted March 4, 1996