Vol. 4, No. 10 October 1994

GSA TODAY

A Publication of the Geological Society of America

Gold Degassing and Deposition at Galeras Volcano, Colombia

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Figure 1. The active cone within the Galeras crater looking west on January 25, 1993; the inner crater is about 500 m in diameter, and the cone height is about 150 m. Large andesite blocks as much as 5 m high were mostly vented during the July 16, 1992, explosion of the plug dome. Small fragments of hydrothermally altered vent breccia are also found on the cone. Deformes Fumarole (200 °C) is the highly focused magmatic gas plume on the left edge of the inner crater.

ABSTRACT

Analyses of hydrothermally altered rocks, vein ore, 1992–1993 andesite, 200–360 °C fumarole discharges, and fumarole sublimates show that Galeras volcano has deposited Au in past hydrothermal events and that solidified andesite and magmatic volatiles contain Au at levels of about 0.015 mg/kg and 0.04 mg/kg, respectively. Although the S in Galeras magma is relatively reduced, shallow decompression releases gases containing SO_2 that disproportionate with water to form H_2SO_4-rich fluids. The hydrothermal environment in country rocks surrounding the magmatic conduit is best described as "high-sulfidation" and provides favorable conditions for deposition of Au, Cu, and other metals; it is entirely possible that a gold-enargite deposit has already formed during the complex hydrothermal evolution of Galeras. Flux estimates for SO_2 discharged by the volcano and for SO_4 discharged by large acid springs flanking the volcano indicate that Galeras is releasing 0.5 kg/d Au to the atmosphere and is probably depositing >0.06 kg/d (>20 kg/yr) Au inside the volcanic edifice. If such flux rates remained continuous, a moderate-sized precious-metal deposit (>200 t contained Au) would form in only 10 ka.

INTRODUCTION

Throughout history, no metal has been more desired or described than gold (Boyle, 1987). Economic geologists have long recognized the association of precious metal deposits and exhumed volcanoes. Epithermal gold deposits associated with obvious volcanism are now broadly classified as low-sulfidation (adularia-sericite) types, in which the principal mineralizing fluid is meteoric water, and high-sulfidation (acid-sulfate or alunite-kaolinite) types, in which the primary fluid is magmatic water (Heald et al., 1987; Hedenquist, 1987; Rye, 1993). Geologic and geochemical characteristics of high-sulfidation Au deposits have been recently tabulated by White (1991). Such deposits generally contain substantial Cu as enargite and other sulfosalts and develop in relatively acid environments where alunite, kaolin, pyrophyllite, and diaspore may be stable (Knight, 1977). High-sulfidation deposits most commonly form in the higher levels of stratovolcanos and flow-dome complexes of andesitic to rhyolitic composition (Sillitoe and Bonham, 1984), although the largest bulk-mineable gold deposit of this type occurs in a maar-diatreme complex (Vennemann et al., 1993). Degassing shallow magma is presumed to be the primary source of S, Cl, F, Cu, and Au responsible for acidification, alteration, and ore formation in high-sulfidation deposits (Brimhall and Ghiorso, 1983; Giggenbach, 1992; Rye, 1993; Hedenquist et al., 1993).

The highly active Colombian volcano, Galeras (Figs. 1, 2), provides an ideal setting in which to better understand these processes. We have analyzed samples of rocks, veins, sublimates, acid springs, and high-temperature fumarole discharges (≤360 °C) from the volcano. Our results show that Au and Cu not only were deposited in past hydrothermal events, but are degassing from shallow magma. In this paper we discuss geochemical processes involved with Au transport from magma into hydrothermal fluid, calculate flux rates of Cu and Au associated with recent eruptions and acid spring discharges, and speculate on the present formation of gold-enargite deposits at Galeras.

GALERAS VOLCANO

Galeras volcano (4200 m) is a composite andesitic stratovolcano located in the northern Andes volcanic chain of southern Colombia (Fig. 2). Galeras is historically the most active volcano in Colombia, having erupted many times since first observed by Europeans in 1554. After 40 yr of dormancy, Galeras became active in March 1988, and its close proximity to the city of Pasto (300,000 people) led to its eventual choice as a "Decade Volcano" (Muñoz et al., 1993; Stix et al., 1993). A small but catastrophic explosion on January 14, 1993, killed six scientists

Galeras *continued on p. 244*

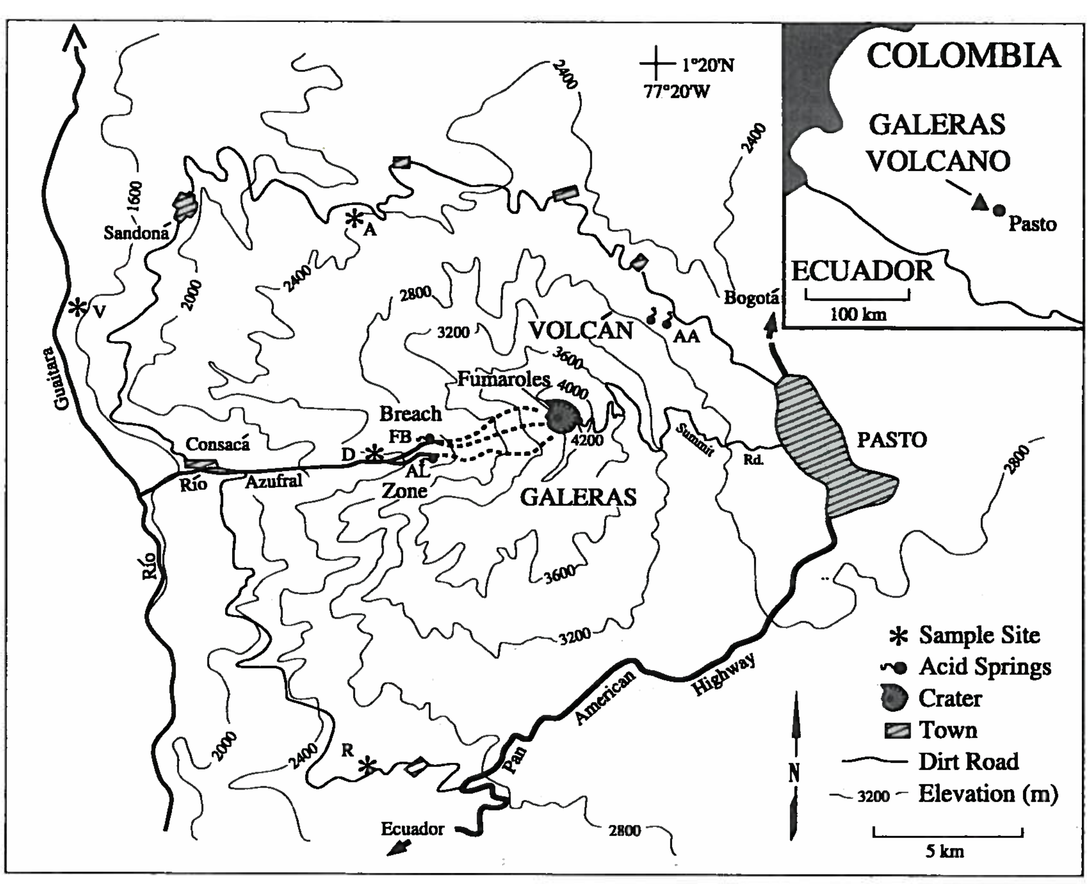

Figure 2. Map of Galeras volcano region, Colombia, showing significant features. Symbols: A = dated olivine andesite flow (0.686 ± 0.012 Ma); R = dated biotite rhyolite tuff (0.288 ± 0.034 Ma); D = altered porphyritic dacite; V = gold-bearing quartz-dolomite-sulfide-sulfosalt vein; AA = Aguas Agrias springs; AL = Alicamancha springs; FB = Fuente Blanca springs.

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who were participating in an international workshop to study Galeras.

Recent eruptive history, tectonic setting, and bedrock geology of Galeras have been described previously (Calvache and Williams, 1992; Stix et al., 1993; Murcia and Cepeda, 1991). Although much is known about the eruptive history of the past few thousand years, little is known about the earlier volcanic events. Two $^{40}Ar/^{39}Ar$ dates we obtained for a thick andesite flow on the lower north flank of the volcano and for a widespread rhyolite tuff beneath the southern flows of the summit (A and R in Fig. 2) suggest that most of the present edifice has formed since 0.7 Ma. This volcanic pile overlies Precambrian metamorphic rocks to the south and Cretaceous ophiolites and subordinate Miocene sedimentary rocks to the north.

The summit of Galeras displays several nested craters (1–2 km wide) that have undergone sector collapse, forming a breach zone to the west. The breach zone is drained by the Río Azufral (Sulfur River). Within this crater area is an active cone with a central vent about 500 m in diameter at the east end of an andesite flow erupted in 1866 (Figs. 1 and 3). A plug dome grew in the central vent during 1991 but was destroyed by a violent explosion on July 16, 1992 (Stix et al., 1993). The explosion of January 1993 produced ash containing fragments of fresh andesite and hydrothermally altered rocks from the conduit. The fresh lavas and ash are porphyritic, calc-alkaline andesites (57–59 wt% SiO_2) containing phenocrysts of plagioclase, clinopyroxene, orthopyroxene, magnetite, ilmenite, and sparse resorbed olivine. A variety of textures including sieve texture and reverse zoning in plagioclase and reverse zoning and mantling of one pyroxene by another suggest that mixing of similar batches of basaltic andesite and andesite was an important process in development of the Galeras magma chamber (Stimac and Pearce, 1992). Stix et al. (1993) demonstrated that the solidified andesite is relatively rich in Cl and F, but depleted in S. The andesite from the plug dome contains <1% metasedimentary xenoliths composed of quartz, biotite, cordierite, and banded pyrrhotite (Goff et al., 1993).

High- and low-temperature fumaroles (60–360 °C in early 1993) discharge near the margins of the active central vent (Fig. 1). The hottest fumarole (Besolima, 340–360 °C) produces vapor containing 90 mol% H_2O. The $\delta D/\delta^{18}O$ and ^3H values of this water show that it is 80% magmatic water and 20% meteoric water <1 yr old precipitated on the crater (Goff et al., 1993). The noncondensible gases consist of 75.3% CO_2, 12.3% SO_2, 5.2% H_2S, 3.7% HCl, 0.4% HF, 2.3% H_2, 0.5% N_2, 0.03% CO, and 0.000% O_2 (all mol%). Carbon, sulfur, and helium isotope results show that the fumarole gases are primarily magmatic in origin (Williams et al., 1993; F. Goff and G. McMurtry, unpub. data). Warm acid springs (≤29 °C) of SO_4-Cl–rich composition discharge from the eastern flank (Aguas Agrias group) and western breach zone (Río Azufral groups) of the volcano at elevations of 2400 to 2800 m. The Río Azufral springs issue from and just below the contact of 1866 lava and underlying andesitic flows and volcaniclastic deposits. The $\delta D/\delta^{18}O$ and ^3H values of acid spring waters show that they are composed of >95% meteoric water ≤20 yr old (Goff et al., 1993). The geologic setting and geochemistry of the acid springs that are the source of the Río Azufral show many similarities to the Loowit hot springs in the breach zone of Mount St. Helens (Shevenell and Goff, 1993).

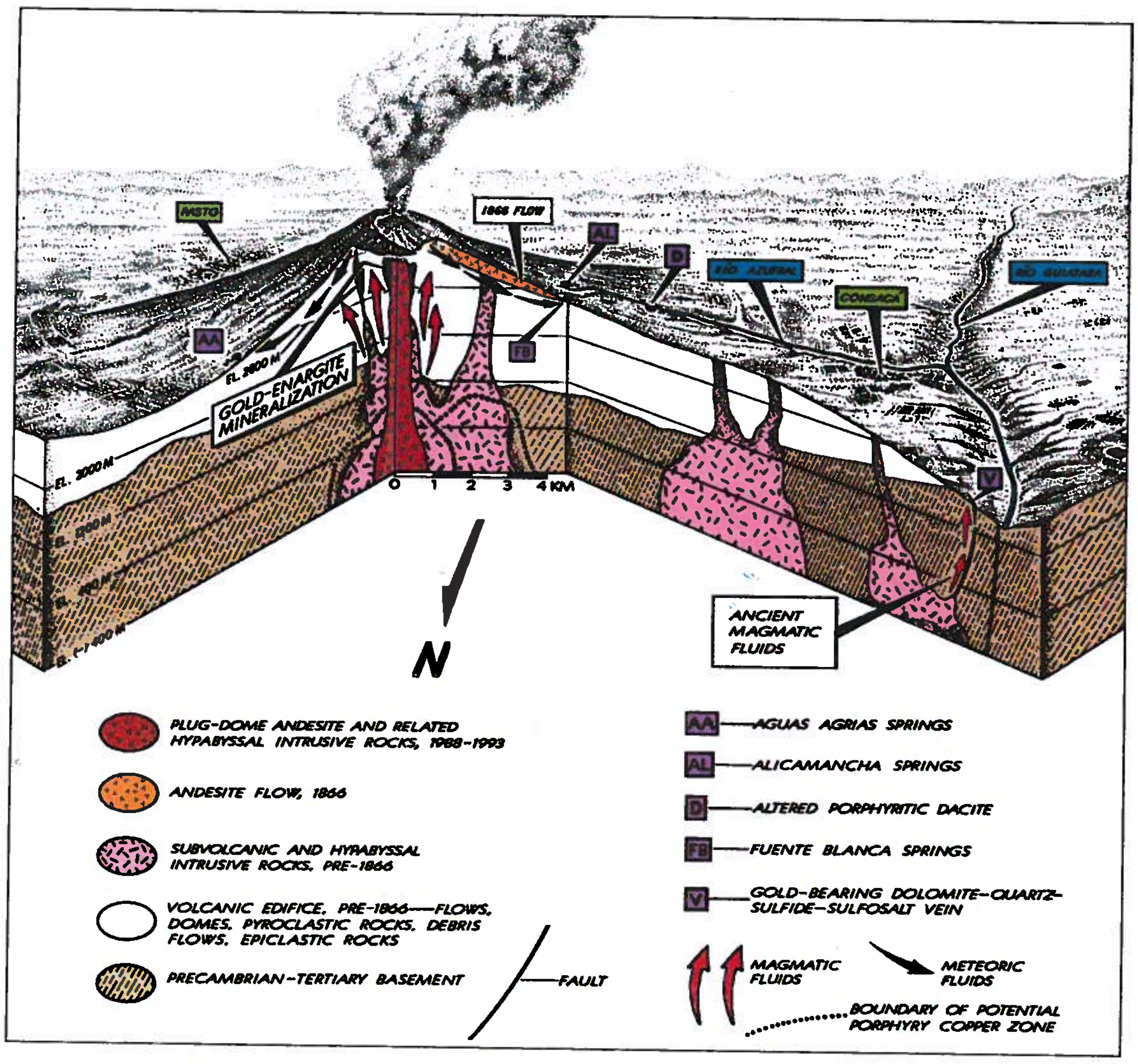

Figure 3. Modified cutaway perspective drawing of Galeras volcano (viewed from the north) showing the basic geology and configuration of a shallow hydrothermal system. Magmatic volatiles mix with young, near-surface groundwaters to form acid springs (Goff et al., 1993). Magmatic fluids discharging inside the volcano create high-sulfidation conditions favorable for deposition of Au and Cu (Hedenquist et al., 1993). Altered rocks around the volcano's conduit probably show chemical and mineral zonations typical of "acid-sulfate" precious-metal deposits as described by White (1991) and Rye (1991); such deposits are commonly associated with deeper, coeval, porphyry copper mineralization. Ancient magmatic fluids derived from a proto-Galeras intrusion are envisioned as responsible for bonanza gold mineralization now exposed on the western flank of Río Guitara. Vertical exaggeration at the Galeras summit is about 1.5x.

GOLD AND ASSOCIATED METALS

Samples described herein were collected during the three-week period after the explosion of January 1993. Chemical analyses of Au and related metals from Galeras rock and fluid samples were performed by two different laboratories (methods are given in Table 1). Mineral phases and compositions were determined by petrographic microscope, X-ray diffraction (XRD), scanning electron microscope (SEM), and electron microprobe. Small fragments of hydrothermally altered andesite breccia litter the active cone and surrounding areas and probably represent country rock encircling the magmatic conduit, which was excavated during past explosions. The breccia is replaced by quartz, gypsum, anhydrite, alunite, and pyrite (5–10 mode %) and has up to 2.5 mg/kg (ppm or g/t) Au. Outcrops of intensely altered, quartz-plagioclase porphyritic lava (dacite?) representing older Galeras volcanism are exposed along the Río Azufral about 2 km west of the Fuente Blanca springs (D in Fig. 2). Alteration minerals consist of quartz, sericite, chlorite, and pyrite, and specimens of this rock contain minor Au (0.2 mg/kg).

A spectacular but previously undescribed (Murcia and Cepeda, 1991), gold-bearing, quartz-dolomite-sulfide-sulfosalt vein cuts Miocene sedimentary and Quaternary (?) volcaniclastic rocks 16 km west of the Galeras summit (V, Fig. 1). The vein, where exposed by a small "glory hole" on the east side of the Río Guaitara, trends northwest and is up to 3 m wide; its length and depth remain to be determined. Dolomite, the earliest vein-forming phase, is partially replaced by finely crystalline quartz along with sericite, a trace of chlorite, and localized traces of hematite. Ore minerals consist of pyrite, chalcopyrite, tetrahedrite, enargite, and sphalerite as well as megascopically visible, late-stage electrum (85%–91% Au, Fig. 4). Grab samples of ore from this vein run about 20 mg/kg Au, whereas high-grade chunks contain up to 270 mg/kg Au (7.8 oz/t)! Ion microprobe analyses of coexisting pyrite yield concentrations of 0.5–0.8 mg/kg Au (see Larocque et al., 1994, for analytical parameters). The youngest vein-forming phase is kaolin, deposited in small vugs following gold precipitation.

Figure 4. A 0.32 mm electrum nugget perched on a striated pyrite cube in a quartz matrix from a vein 16 km west-northwest of the Galeras summit (field of view is 0.68 cm wide). Associated minerals include chalcopyrite, tetrahedrite, enargite, and sphalerite. (Photo by Wes Martin, Salt Lake City.)

Figure 5. Photomicrograph of coexisting magnetite-pyrrhotite-Cu, Fe monosulfide in a clinopyroxene phenocryst from the July 1992 Galeras andesite (reflected light, Nomarski lens, 0.18 μm field of view).

Fluid inclusions in samples of the early dolomite are large (commonly 20 μm) and abundant, but they are exceedingly sparse and small (mostly <3 μm) in the sulfide-, sulfosalt-, and gold-stage replacement quartz. Fifteen primary inclusions trapped during crystal growth (Roedder, 1984) in dolomite yield homogenization temperatures (T_h) ranging from 116 to 132 °C (mean = 129 °C). Five primary inclusions in quartz have T_h between 163 and 173 °C (mean = 168 °C). The local geologic setting and youth of the host rocks require that at this level of exposure, these two vein minerals and accompanying metallic phases were precipitated at relatively shallow depth, perhaps 1 km or less. Accordingly, the corresponding reconnaissance T_h values for our samples approximate true entrapment temperatures (Roedder and Bodnar, 1980). The data suggest that the quartz, sulfides, sulfosalts, and gold were deposited at temperatures slightly below the typical range for high-sulfidation precious-metal systems (200–300 °C; e.g., Hayba et al., 1985). This tentative conclusion is consistent with the abundant relict presence of vein dolomite, a carbonate that would readily dissolve in the acidic solutions characterizing high-sulfidation deposits.

A sublimate sample consisting mostly of soluble sulfates and sulfur

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TABLE 1. CHEMICAL ANALYSES OF GOLD AND RELATED ELEMENTS IN ROCKS, SUBLIMATE, MAGMATIC FLUID, SULFUR, AND ACID SPRING WATERS, GALERAS VOLCANO, COLOMBIA

Sample no.	Description	Au (ppm)	Ag (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	As (ppm)	Hg (ppm)	Sb (ppm)	Se (ppm)	Comments
Various Rocks and Sublimate											
F93-7(B)	Pyritic breccia	2.59±15%	<0.2	34	17	6	35	0.044	<5	—	50 g sample
F93-7(L)	Pyritic breccia	0.40±0.4	19	33	14	10	20	<0.05	<1	7	100 mg fragment
F93-11(B)	Altered dacite	0.22±15%	<0.2	20	30	64	86	0.02	<5	—	50 g sample
F93-11(L)	Altered dacite	0.15±0.07	13	18	36	56	80	<0.05	<1	0.1	100 mg fragment
F93-15(B)	Gold vein, ore	22.3±10%	7.3	430	20	220	165	<0.01	156	—	50 g sample
F93-15(L)	Gold vein, high-grade	269±13	30	300	15	210	190	<0.05	—	0.7	100 mg fragment
F93-16(L)	Fumarole sublimate	0.03±0.02	5.5	21	3.4	32	44	0.8	<1	24	250 mg sample
F93-21b(B)	Xenolith, bulk	0.048±25%	<0.2	345	6	18	<5	0.174	<5	—	45 g sample
F93-21b(L)	Xenolith, pyrrhotite	<0.05±0.05	45	1390	6	52	30	<0.14	<1	25	50 mg separate
Fresh Andesite											
F93-17(B)	7/92 2-px andesite	0.030±25%	<0.2	28	2	38	5	<0.01	<5	—	50 g split of XRF sample
F93-21a(B)	7/92 2-px andesite	0.015±50%	<0.2	25	3	34	<5	<0.01	<5	—	50 g split of XRF sample
Ave. of 4(B)	7/92 2-px andesite	0.016	<0.2	30	3	35	5	<0.01	<5	—	—
F93-3(B)	1/93 andesite ash	0.007±50%	<0.2	31	5	25	<5	<0.01	<5	—	50 g split of XRF sample
Magmatic Fluid and Sulfur											
GV93-33(L)	Deformes Fumarole	<0.05±0.05	—	0.19	—	—	116	0.04	0.010	0.022	T = 207 °C; total discharge
GV93-33(L)	Deformes Fumarole	23±11	34	40	<10	<60	57	23	11	55	T = 207 °C; sulfur ppt
GV93-35(L)	Besolima Fumarole	<0.05±0.05	—	0.38	—	—	165	0.01	0.010	<0.001	T = 358 °C; total discharge
GV93-35(L)	Besolima Fumarole	3±2	3	115	5	<20	290	26	26	240	T = 358 °C; sulfur ppt
GV93-36(L)	Besolima Fumarole	0.07±0.05	—	0.23	—	—	152	0.05	0.014	<0.001	T = 342 °C; total discharge
GV93-36(L)	Besolima Fumarole	9±3	6	70	7	<20	400	<1?	23	180	T = 342 °C; sulfur ppt
Acid Springs and River											
GV93-5(L)	Agua Agrias #2	<0.002±0.002	<0.001	0.12	0.005	1.09	0.090	0.001	<0.001	<0.001	T = 29.0 °C; pH = 2.3
GV93-6(L)	Agua Agrias #1	<0.002±0.002	<0.001	0.06	<0.002	0.87	0.004	<0.001	<0.001	<0.001	T = 27.4 °C; pH = 2.5
GV93-20(L)	Fuente Blanca	<0.002±0.002	<0.001	0.05	<0.002	0.08	<0.05	—	<0.001	<0.001	T = 21.8 °C; pH = 4.8
GV93-24(L)	R. Azufral, F. Blanca	<0.002±0.002	<0.001	0.05	<0.002	0.10	0.05	—	<0.001	<0.001	T = 19.7 °C; pH = 4.4

Note: B after sample number indicates analysis by Bonder-Clegg (Sparks, NV); Au by fire assay; Hg by cold vapor AA; others by ICP. L after sample number indicates analysis by P. Trujillo and D. Counce (LANL); Au, Ag, Cu, Pb, and Zn by graphite furnace AA after dissolution in aqua regia and HF (if needed); As, Hg, Sb, Se by hydride generator method.

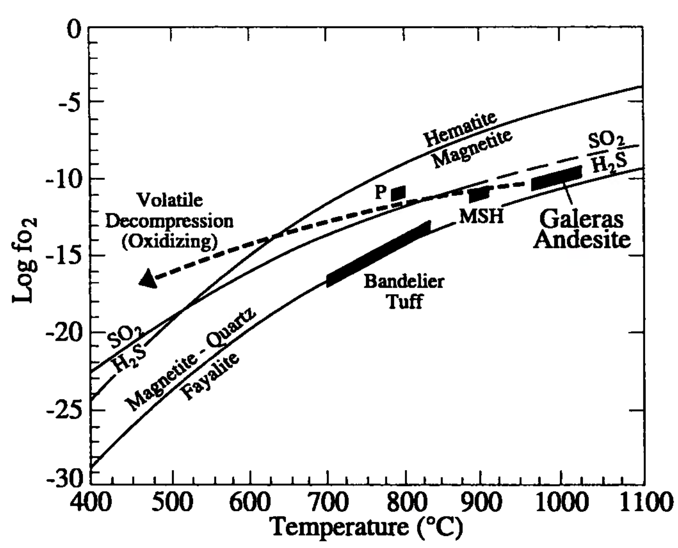

Figure 6. Plot of log f_{O_2} vs. temperature showing redox conditions of 1992 Galeras andesite. Although only sulfide phases are present in the solidified andesite, shallow decompression of magma causes released volatiles to become SO_2-rich with falling temperature. Conditions for the Bandelier Tuff (Valles caldera) are from Warshaw and Smith (1988). MSH = 1980–1986 Mount St. Helens dacite; P = 1991 Pinatubo dacite (modified from Rutherford, 1993; Rye, 1993).

Galeras *continued*

from Deformes Fumarole (200 °C) contains detectable Au. A bulk sample of metasedimentary xenolith from 1992 Galeras andesite also contains detectable Au, although a pyrrhotite separate does not. Ion-microprobe analysis of the pyrrhotite indicates that Au content is <0.050 mg/kg. Most of these samples contain Cu, Ag, and varying amounts of relatively volatile As, Hg, Sb, and Se. Contents of Cu are generally greater than those of Pb and Zn, a feature common to high-sulfidation Au deposits (White, 1991).

Four samples of fresh andesite from the July 1992 explosion contain an average of 0.016 mg/kg Au, whereas the ash from January 1993 contains 0.007 mg/kg Au. One sample of andesite (analyzed twice) contains 0.030 ± 0.002 mg/kg Au. For comparison, Mount Erebus anorthoclase phonolite contains 0.023 mg/kg Au (Kyle et al., 1990). These values are considerably higher than the mean value of 0.00054 mg/kg Au recently reported for a suite of 23 "relatively silicic intermediate rocks" (Connors et al., 1993) and suggest that Au content in any given magma is highly unpredictable, or possibly that extremely young, fresh specimens quenched near their vents have Au contents more representative of initial values.

Total discharge samples of magmatic fluid from high-temperature fumaroles were collected through Ti tubing into special evacuated glass bottles filled with ~100 ml of 4N NaOH (Trujillo et al., 1987; Fahlquist and Janik, 1992). After the gases were determined, splits of the caustic solutions were analyzed for selected metals. Results indicate that the magmatic fluid contains Au at levels of ≤0.07 mg/kg (≤0.07 g/t). Magmatic fluids were also condensed in glass tubes immersed in crushed ice and water. Some elemental S precipitates during condensation and partially scavenges metals, particularly volatile elements, Cu, and Au. Although the S analyses are not quantitative (about 0.009 to 0.035 g S precipitates from 50 ml of condensate), the S analyses verify that Au is present in the magmatic fluid at concentrations >0.006 mg/kg. In contrast, the acid springs flanking Galeras contain <0.002 mg/kg Au and low levels of the other metals.

MAGMATIC AND HYDROTHERMAL CONDITIONS

The temperature of July 1992 Galeras andesite magma during eruption was 1000 ± 50 °C, determined from both two-pyroxene and Fe-Ti oxide geothermometry (Lindsley and Anderson, 1983; Ghiorso and Sack, 1991), and the log f_{O_2} was −10.8 to −9.7. Coexisting blebs of magnetite, pyrrhotite (Fe[0.96]S), and Cu, Fe monosulfide in clinopyroxene phenocrysts place the log f_{S_2} at −0.7 to −0.9 (Toulmin and Barton, 1964) and show that the S in the magma was relatively reduced (Fig. 5). Many arc magmas straddle the SO_2-H_2S boundary, whereas continental ignimbrites like the Bandelier Tuff tend to lie well below this boundary (Fig. 6), although the state of S in any given magma will be controlled by temperature, pressure, melt composition, and total S (Hattori, 1993). Magmatic vapors released from solidifying andesite in the conduit (and, previously, the plug dome) undergo rapid decompression, causing H_2S to partially convert to SO_2 (Fig. 6; Rye, 1993). As a result, the magmatic vapors become oxidizing (high-sulfidation). Below temperatures of 400 °C, SO_2 disproportionates in the presence of water to H_2SO_4 and H_2S (Rye, 1993); thus, an extremely acid environment develops around the magmatic conduit.

We have not identified a separate Au-rich phase in Galeras andesite, but it is most likely carried in sulfide phases and magnetite in the magma (Connors et al., 1993) as well as the xenoliths. During shallow degassing, some Au partitions from magma into vapor and is probably transported as $HAu(SH)_2$ (Giggenbach, 1992) or AuS (Symonds and Reed, 1993). The solubility of the first phase in SO_2-rich vapor at 400 °C (Fig. 7) is compatible with Au values that we measured in the total discharge samples (≤0.07 mg/kg).

Although many tons of magmatic volatiles are lost to the atmosphere at Galeras (Stix et al., 1993), SO_4-rich acidic fluids invade and attack country rocks around the conduit, as evidenced by hydrothermally altered rocks around the vent and in exploded ejecta. A probable path line (1) for present Galeras hydrothermal fluid (Fig. 7) shows that the solubility of Au decreases dramatically going from submagmatic conditions around the conduit to conditions represented by the acid springs on the flanks of the volcano. Most of the Au is precipitated in rocks such as the pyritic breccia (Table 1) surrounding the conduit. Another path line (2) shows that the Au-bearing

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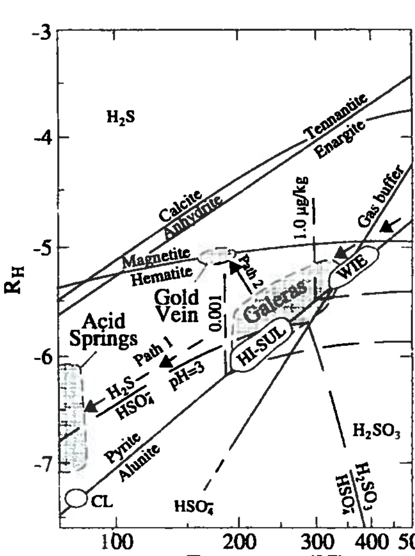

Figure 7. Redox potential ($R_H = f_{H_2}/f_{H_2O}$) vs. temperature (modified from Giggenbach, 1992). The heavy line designated "gas buffer" represents magmatic fluid (H_2S + H_2SO_3), and Au solubilities are in µg/kg of $HAu(SH)_2$. Open envelopes show conditions for White Island "acid-sulfate" ejecta (WIE), for typical acid crater lakes (CL), and for high-sulfidation Cu-Au deposits (HI-SUL) as defined by Hedenquist et al. (1993). Shaded envelopes show probable conditions surrounding the conduit within Galeras, the range of conditions represented by the acid springs, and conditions represented by the Au vein west of Galeras. Path 1 shows a probable transition from magmatic fluid to the acid springs. Falling temperature causes Au deposition in the region surrounding the conduit. Path 2 shows a hypothetical transition from high-sulfidation conditions to conditions represented in the gold vein during progressive neutralization of fluid.

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TABLE 2. CONCENTRATONS AND FLUX RATES OF SELECTED CONSTITUENTS IN ACTIVE CRATER PLUME AND ACID SPRINGS, GALERAS VOLCANO, COLOMBIA

Constituent	Galeras Volcano,* active crater		Río Azufral† Fuente Blanca Gp.		Río Azufral§ Alicamancha Gp.		Agua Agrias# Springs 1 and 2	
	conc. (mg/kg)	flux (t/d)	conc. (mg/kg)	flux (t/d)	conc. (mg/kg)	flux (t/d)	conc. (mg/kg)	flux (t/d)
SO_2	38,000	500	1,260	42.3**	650	12.4**	~4,500	~0.3**
H_2S	8,700	115	—	—	—	—	—	—
HCl	6,800	89	220	11.3††	58	1.7††	~575	~0.04††
CO_2	160,000	2,100	—	—	—	—	—	—
As	144	1.89	≤0.05	≤0.0025	—	—	≤0.09	≤4x10-6
Cu	0.27	0.0036	0.05	0.0025	0.008	0.0002	~0.09	~4x10-6
Au	0.04	0.0005	—	—	—	—	—	—
Hg	0.03	0.0004	—	—	—	—	—	—

* Flux of 500 t/d assumed; other fluxes calculated from ratios of unknowns to SO_2.
† Estimated discharge is 50,000 t/d.
§ Estimated discharge is 30,000 t/d.
\# Estimated discharge is 80 t/d; fluxes calculated from average concentrations of both springs.
** Measured analyte is SO_4; flux is recalculated as SO_2.
†† Measured analyte is Cl; flux is recalculated as HCl.

quartz vein west of Galeras could be generated by progressive neutralization of metal-rich acidic solutions from earlier magma-hydrothermal events in the evolution of the volcano.

The position of the gas buffer, compositions and temperatures of fumarole discharges, and coexisting phases in the pyritic breccia require that conditions around the conduit are very close to the pyrite-alunite join (Fig. 7). The envelope marked "HI-SUL" (Fig. 7) represents high-sulfidation Cu-Au deposits as defined by Hedenquist et al. (1993) and implies that such deposits must have alunite, which, of course, many do. As the name suggests, however, high-sulfidation conditions are defined by the oxidation state of S (and the resulting acidity of the hydrothermal fluid). Extremely sharp chemical and mineral zonations typically are present in the exhumed conduits and fracture networks of high-sulfidation deposits (White, 1991). Deposition of Au and Cu under high-sulfidation conditions can take place without formation of alunite, and enargite can form in environments considerably less acid than those forming alunite.

FLUX RATES

Since 1988, emissions of SO_2 at Galeras have often exceeded 2000 t/d (maximum about 5500 t/d) but have generally decreased since early 1990 to values of typically 500 t/d (Stix et al., 1993; Fischer et al., 1994). No Cu/SO_2, Au/SO_2, or other metal ratios have been determined in the aerosols at Galeras. The concentration of Cu in the total discharge of three fumarole samples is 0.19 to 0.38 mg/kg (average 0.27 mg/kg). Although as much as 0.07 mg/kg Au apparently occurs in discharge samples, the average Au/Cu ratio of the S precipitates indicates an average Au content of 0.04 mg/kg. We realize that changes occur with time in the relative proportions of gases in Galeras fumarole discharges (Fischer et al., 1994), but these changes are small relative to water. Thus, we can calculate the approximate flux rates of selected constituents from the volcano assuming constant ratios of these constituents to SO_2 (Table 2). A constant flux of 500 t/d and concentration of 38,000 g/t SO_2 from Besolima Fumarole are used. The results show that very large amounts of CO_2, H_2S, and HCl are discharged with SO_2 and water. Nearly 2 t/d As are also discharged. Flux rates of Cu, Au, and Hg are roughly 3.6, 0.5, and 0.4 kg/d.

Although Au measurements in gases and aerosols are lacking at most volcanoes, the Au concentrations determined in the total discharge at Galeras are about four times higher than measured at White Island, a similar calc-alkaline volcano (Le Cloarec et al., 1989). The flux rate of Au at Mt. Erebus can be as much as 0.1 kg/d when the SO_2 flux is only 20 t/d (Meeker et al., 1989). Concentrations of Cu at Galeras are about five times higher than at White Island in comparable fumarole discharges, but Le Cloarec et al. (1989) have measured considerably higher flux rates of Cu in the aerosols (300 kg/d).

It is interesting to calculate the flux of magmatic volatiles into the Río Azufral, which drains approximately 99% of Galeras acid spring waters from remote locations 4.5 km west of the active crater (Fuente Blanca and Alicamancha). We determined approximate flow rates of 50 and 30 x 10^3 t/d for the two main branches of the Río Azufral fed by these springs, whereas the total flow rate of the Aguas Agrias group is merely 80 t/d. The SO_4 and Cl in these springs are derived from magmatic volatiles (SO_4/Cl recalculated as SO_2/Cl is similar to SO_2/Cl of fumarole discharges) even though, as at Mount St. Helens, the waters are dominantly meteoric (Shevenell and Goff, 1993; Goff et al., 1993). The flux of SO_2 and Cl from the Río Azufral springs is about 55 and 13 t/d or about 10% of the flux discharged at the volcano summit, assuming the latter is 500 t/d SO_2. By comparison, the measured discharge of thermal fluid into Loowit Creek, Mount St. Helens, was 18 x 10^3 t/d in 1989 (Shevenell and Goff, 1993), and the fluxes of SO_2 and Cl were 6.2 and 10.1 t/d, respectively.

The flux of Cu into the Río Azufral (2.5 kg/d) is actually larger than would be expected from the Cu/SO_2 ratio in the fumarole discharges. Hedenquist et al. (1993) noted similar findings in the acid springs of White Island and suggested that additional Cu was provided by isochemical dissolution of rock by acid waters. On the other hand, Au concentrations in the acid springs of Galeras are <0.002 mg/kg. Using an equivalent SO_2 flux of 55 t/d for all acid springs and a ratio for Au/SO_2 of 1.05 x 10^{-6} in the magmatic fluid, at least 0.06 kg/d or 20 kg/yr Au are being deposited in the hydrothermally altered volcanic rocks inside the volcano. If sustained, flux rates of this magnitude can produce moderate-sized Au deposits (>100 t contained Au) in geologically short periods of time (a few thousand years or less).

CONCLUSIONS

The temporal variation of Au concentration in the crater fumaroles and flux rate of magmatic volatiles in the acid springs are unknown, but Galeras has erupted often during the last few thousand years and has supplied magmatic components to the acid springs for at least several hundred years. At present, the volcano vents 0.5 kg/d Au to the atmosphere (based on SO_2 flux of 500 t/d) and is probably depositing at least 0.06 kg/d Au in altered rocks around the magmatic conduit (Fig. 3). Depositional conditions are best described as high-sulfidation and are similar to conditions described in classic "acid-sulfate," gold-enargite deposits within exhumed volcanoes (e.g., White, 1991; Rye,1993). The Au contents of hydrothermally altered rocks and veins in the volcanic edifice indicate that magmatic fluids have episodically deposited Au (as well as other metals) over many thousands of years, perhaps the past 700 ka.

Note Added in Proof: The leachate from dolomite in the gold-bearing vein west of Galeras was dated by M. Murrell (LANL) using the ^{234}U-^{230}Th disequilibrium method. Although the observed disequilibrium is only a few percent, it is clearly resolved using mass spectrometry. Given the usual assumptions about closed system behavior and low initial ^{230}Th, the apparent age of this sample is 520 ka (+110, –60; 2σ).

ACKNOWLEDGMENTS

This project would have been impossible without the help of Stan Williams and Tobias Fischer (Arizona State University), Marta Calvache and colleagues (Observatório Vulcanológico de Colombia del Sur, Pasto), and John Stix (Université de Montréal). Louis Cabri (Canada Centre for Mineral and Energy Technology) kindly provided standards for ion-microprobe analyses. Ken Wohletz, Peter Schiffman, and Eldridge Moores reviewed the manuscript. Funding came from the U.S. Department of Energy, Office of Basic Energy Sciences (Advanced Concepts) and from an LDRD grant (Magmatic Tritium), Los Alamos National Laboratory. Goff dedicates this paper to the memory of Aaron C. Waters, a professional and spiritual guide through many troubled times, a great teacher, and a lover of volcanoes.

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Manuscript received February 28, 1994; revision received April 7, 1994; accepted April 13, 1994 ■

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