Eruption of the Nevado del Ruiz Volcano, Colombia, on 13 November 1985: Gas Flux and Fluid Geochemistry

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The 13 November 1985 eruption of Nevado del Ruiz volcano, in Colombia, released a small volume of pyroclastic material and a disproportionately large volume of volcanic gas. Before the eruption, summit fumarole gases became less water-rich, and the sulfur/chlorine ratio increased. Remote measurements of sulfur dioxide flux after the eruption indicated active degassing at levels associated with eruptive or inter-eruptive stages of other volcanoes. Thermal water analyses revealed increases in magnesium, calcium, and potassium and an increase in the magnesium/chlorine ratio, suggesting that these elements may have been leached from new magma. Ash leachate data showed sulfate and chloride concentrations and ratios that would be expected for the late stages of a major Plinian eruption. Water from the lahar contained high concentrations of sulfate and had a sulfur/chlorine ratio of 4.67, suggesting that water ejected from the crater lake and turbulent mixing of pyroclasts and glacial ice triggered the lahar. Microprobe analyses of pumice from this eruption and the most recent previous event showed similar mixed andesites. The uniform composition of the pumices and the unusually high ratio of gas to magma suggest that, although a new batch of magma triggered this eruption, the pumice that erupted may actually be old. Large volumes of new magma and glacial ice make the volcano dangerous and should stimulate development of an integrated long-term monitoring program to include Tolima volcano, 25 kilometers to the south.

N 13 NOVEMBER 1985, THE STRATovolcano Nevado del Ruiz erupted explosively and released a small volume of magmatic material and large amounts of magmatic gases. The volcano became seismically active in November 1984 (1) after a 140-year period of repose (2). Earlier eruptions between 1828 and 1833 and in 1845 were apparently minor, although eruptions produced a lahar (volcanic mudflow) in 1845 that swept down the east flank of the 5300-m-high volcano over the site of Armero (Fig. 1). The last major eruption of Ruiz occurred in 1595 with the production of an ash and lapilli layer and lahars (3). The premonitory activi-

Table 1. Gas geochemistry data from fumarole B inside the Arenas crater of the Nevado del Ruiz volcano, Colombia. Samples collected in evacuated Pyrex cylinder and analyses done by gravimetry, following methods of Giggenbach (9). Results expressed in percentages by weight. S in S/Cl expressed as SO_2 .

Date (1985)	H ₂ O	CO ₂	SO ₂	H ₂ S	HCl	S/Cl	S/C
24 September	97.31	1.15	1.47	0.068	0.0062	123	2.34
19 October	95.68	1.9	2.33	0.0798	0.0036	333	1.83
12 November	91.62	5.68	4.43	2.25	0.0058	395	1.43

Table 2. Flux data of SO₂ at the Nevado del Ruiz volcano, Colombia, and other active subduction zone volcanoes. Directly measured by COSPEC (except for 18 May 1980, which was inferred from ash leachate studies). For 18 November, n = 5; for 19 November, n = 2; and for 22 November, n = 2. Total error of COSPEC data is normally 10 to 15% (5).

Volcano	Date	SO ₂ flux (tons/day)	Nature of activity		
Nevado del Ruiz Nevado del Ruiz Nevado del Ruiz Mount St. Helens Mount St. Helens Masaya Mount Etna Mount Etna	18 November 1985 19 November 1985 22 November 1985 18 May 1980 25 May 1980 March-May 1980 1972–1978 July 1979 July 1979 July 1979	$\begin{array}{c} 40-240\\ 150-650\\ 1,500-10,000\\ 0.5\times10^6\ (11)\\ 2,500\ (11)\\ 30\ (12)\\ 200-300\ (13)\\ 1,000-3,000\ (14)\\ 6,000-12,000\ (14)\\ \end{array}$	Post-eruption degassing Post-eruption degassing Post-eruption degassing Climactic Plinian eruption Small Plinian eruption Phreatic eruptions Quiet degassing of lava lake Inter-eruptive degassing Violent ash eruptions		

ty before the November 1985 eruption included an increase in fumarolic discharge, minor phreatic eruptions, and wide deposition of sulfur over the glacier-clad summit region of the volcano (1). A notable ash eruption occurred on 11 September 1985, sending a few millimeters of ashfall 30 km to the northwest. Ash eruptions continued throughout September, before declining in October (1).

We report data on the geochemistry of fumarolic gases (including data taken from the crater the day before the eruption), remote sensing data on the rate of release of SO₂ after the eruption, post-eruption geochemistry of a thermal spring for which older data were published, analyses of leachates obtained from the ashfall of the 13 November 1985 eruption, analysis of the water contained within the main lahar, and microprobe data on the pumice ejected by the explosion [with a comparison to the most recent major pumice deposit (1595?)]. Fumaroles were sampled at the summit (Arenas crater) on 24 September, 19 October, and 12 November 1985 (4). Samples of fumarolic gases were collected in the field and analyzed by gravimetric methods. Remote sensing of SO₂ began on 18 November (5 days after the explosion) and continued on 19 and 22 November. These measurements were made by using a correlation spectrometer (COSPEC) (5) in an airplane. Thermal water samples were collected from the principal two acid sulfate springs of the Termales de Ruiz area (approximately 10 km northwest of the crater), which flow beneath a section of andesitic lava flows and which had been sampled in 1969 as part of a geothermal study (6). Ash leachates were prepared by the standard technique (7), by using deionized distilled water to wash soluble compounds from the surfaces of ash particles collected downwind of the volcano on 19 November (8). The lahar water was extracted by centrifuge from a bulk sample collected on 18 November in Arry ero. Pumice from the 13 November.⁴ posit was collected from the summit of the volcano, and representative lumps were analyzed by electron microprobe along with a lump of pumice collected from a major (35 to 50 cm thick) Plinian pumice-fall deposit that un-

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Table 3. Chemical composition of thermal waters from two vents (numbers are means of four analyses) at Termales de Ruiz (3400-m elevation on the western slope of Nevado del Ruiz volcano, Colombia). Results in parts per million; 1985 results by inductively coupled plasma (ICP) and checked by gravimetric methods; Li⁺ measured by atomic absorption (AA). Estimated ICP error, 5%; ion chromatography error, 10%; AA error, 5%; NA, not analyzed (*I5*).

	1040 (5)	21 November 1985				
Chemicals	1969 (5) (pH 1.50, 66°C)	Spring A (pH 1.45, 62.5°C)	Spring B (pH 1.45, 64.5°C)			
Na ⁺	465	445	512			
K^+	54	139	151			
Ca ²⁺	7.3	271	290			
Mg^{2+}	82.4	209	224			
Li [∓]	0.72	0.60	0.60			
Cl-	1,058	900	965			
SO4 ²⁻	10,060	7,570	8,125			
HCO3 ⁻	182	NA	NA			
HBO ₂ ⁻	23.53	NA	NA			
Al ³⁺	922	656	719			
CO_2		NA	NA			
S/CĪ	3.17	2.80	2.81			
Mg/Cl	0.078	0.232	0.232			

derlies the present-day soil (it is believed to be the product of the 1595? eruption). The fumarolic gas data are from fumarole B in the Arenas crater and include analyses of the ratio of total H₂O to active gases and the concentrations of SO_4^{2-} , Cl⁻, H₂S and CO₂ (Table 1) (9, 10).

Data on SO₂ flux from the Ruiz volcano, measured during the 10 days after the eruption, and data from other subduction zone volcanoes (11-14) are shown in Table 2. The first data from Ruiz, on 18 and 19 November, indicated a low average level of emission (150 metric tons/day), but by 22 November the flux had climbed to a high level of several thousand tons per day (the uncertainty of the flux reflects poor wind velocity data). The plume of gas was always rather small and white, rising a few hundred

Fig. 1. Generalized map of the area of west central Colombia with the volcanic complex of Nevado del Ruiz and associated modern cones. Tolima volcano had its most recent recorded activity in 1943, with additional eruptions in 1822, 1825, and 1826. Other vents are C.B., Cerro Bravo; S.I., Nevado de Santa Isabel; S.R., Paramo de Santa Rosa; and E.Q., Nevado El Quindio. COSPEC flights were generally made parallel to the Rio Magdalena or the Rio Cauca, depending on the wind direction. Sample sites include Termales de Ruiz, Alto de la Mona, and Honda.

meters over the crater with no visible ash content.

Data on the geochemistry of the natural hot springs at Termales de Ruiz from 1969 and November 1985 are summarized in Table 3 (15). The amount of SO_4^{2-} and Cl⁻ declined somewhat during these years but remained at high concentrations, and their ratio was essentially unchanged. Concentrations of K⁺, Mg²⁺, and Ca²⁺ increased significantly, while that of Al³⁺ declined over the same period. The Mg/Cl ratio increased from 0.078 to 0.232. The *p*H may be somewhat lower in 1985, but this is uncertain. The temperature of the water is approximately unchanged.

Results of partial analyses of leachates of ash (apparently not rained on) collected from the surfaces of leaves on 19 November in the town of Honda and at Alto de la Mona (downwind of the volcano) are presented in Table 4. The concentrations of SO_4^{2-} and Cl^- and the S/Cl ratio are similar to results obtained from samples of other magmatic eruptions (10). A sample of the water extracted from the lahar that flowed through Armero, the main lahar that descended from the volcano, was also analyzed. The results indicated a very high concentration of SO₄²⁻ (5375 ppm), a Cl⁻ concentration of 380 ppm, and a resultant S/Cl ratio of 4.67.

Microprobe analyses of representative pumice lumps (Table 5) showed that the bulk material erupted on 13 November was andesitic. Petrographic examination revealed the presence of plagioclase and pyroxene, with traces of hornblende and olivine. The pumice occasionally showed signs of physical mixing of distinct magma types. Melt inclusions were partially devitrified. The chemical and mineralogical composition of the pumice (bulk rock and glass septa) of 1595? is similar to that of the deposits of 1985.

The data presented indicate that the Ruiz

\$ Honda Manizales _С.В. Armero Termales de Ruiz 5°N uiz[●] Nevado S.I.△ del Ruiz Alto de la Mona S.R.∆ E.Q. $^{\Delta}$ Tolima Bogotá Bio 1990 50 km 75°₩

Table 4. Ash leachate data on ashfall from 13 November 1985 eruption. Collected on 19 November 1985 (before being rained on) in Honda and Alto de la Mona (8). Samples of bulk ash were washed for 1 hour in deionized distilled water (7); results in parts per million by weight of ash; SO_4^{2-} and Cl^- were analyzed by ion chromatography. Range in sulfate on the Alto de la Mona sample reflects uncertainty in reading record.

Chemicals	Honda	Alto de la Mona				
SO4 ²⁻	730	500 to 800				
Cl ⁻	1008	430				
S/Cl	0.24	0.39 to 0.62				

volcano has experienced a magmatic resurgence. The geothermal regime has probably been perturbed. The eruption released products (rock and gas) whose geochemical characteristics are similar to those of other subduction-related volcanoes.

Fumarolic gas condensate data, although few, are consistent with the introduction of a new gas-rich magma into the volcanic edifice before September 1985. Studies of similar situations (10, 16) at other volcanoes have shown that the total ratio of H₂O to active gas drops slowly as the S/Cl ratio increases rapidly before eruptions. This relation reflects the greater variation in the solubility of sulfur, as compared to chlorine, as a function of pressure. The predicted premonitory geochemical signals were well developed at Ruiz.

The SO_2 flux data showed that when the first measurements were made, the volcano was releasing gas at a rate similar to the early phreatic stage of activity at Mount St. Helens in the United States, or the very passive degassing of the old lava lake at Masaya in Nicaragua. This rate of emission contrasts sharply with the eruption itself, which apparently released 700,000 tons of SO₂ $(1\overline{7})$. As the week progressed, the rate of emission rose to levels associated with inter-eruptive phases of Mount Etna in Italy. Clearly, the level of SO₂ release was consistent with the near-surface active degassing of a large volume of magma. The data that week indicate that the volcano underwent an approximately 10-day period of reestablishing an equilibrium level of degassing after the explosive release of such a large amount of SO_2 . It is also possible that the presence of glacial meltwater acted as a buffer by dissolving most of the volcanic gases before the large flux finally exceeded this capacity, in a manner similar to the situation at the Soufrière St. Vincent volcano on the Windward Islands in 1971-1972 (18).

Thermal waters from Termales de Ruiz may show a response to magmatic resurgence. The high SO_4^{2-} values of 1969 implied that boiling was important in the

Table 5. Bulk compositions (percentages by weight) from "moving beam" electron microprobe average analyses of pumice in the form of pressed pellet and glass septa. Sample from 13 November 1985 was found near summit of Ruiz (28). Total iron expressed as FeO.

Analysis	SiO ₂	Al_2O_3	FeO	MgO	CaO	K ₂ O	Na ₂ O	TiO ₂	P_2O_5	Sum
			13	Novemb	er 1985					
Bulk composition	59.31	16.83	5.87	5.40	6.30	1.87	3.80	0.82	0.30	100.50
Glass septa	65.36	16.01	3.98	1.51	3.81	3.47	4.12	0.77	0.30	99.33
L L				1595	?					
Bulk composition	58.69	16.81	5.72	5.13	6.04	1.85	3.79	0.81	0.28	99.12
Glass septa	63.97	16.33	4.14	1.54	4.24	3.15	4.22	0.77	0.29	98.65

evolution of the geothermal fluids at Ruiz and that the system was unusually sulfurrich (19). The increases in K^+ , Ca^{2+} , and Mg^{2+} are as one would predict based on the leaching and volatilization of these elements from the host rocks (18, 20) or from new magma, and their increased abundance implies higher reservoir temperatures. Very similar Mg/Cl ratios have been observed at Ruapehu volcano in New Zealand (21), indicating increased interaction between H₂O and new magmatic material (and a greater eruption risk).

Ash leachate data from the two downwind samples are consistent with values from magmatic eruptions (11). During the 18 May 1980 climactic eruption of Mount St. Helens, S/Cl in leachates varied from approximately 1.0 to 0.8 in the initial directed blast and initial ashfall deposits and were 0.15 when ashfall finally ceased. Thus, the two concentration and ratio values from Ruiz are low but are similar to those for the late stages of a major Plinian eruption.

The water from the main lahar has a high concentration of SO42- and a high S/Cl ratio. These measurements indicate that the water is not simply melted ice but, rather, contains an important component of dissolved volcanic gases. This component may have resulted from the explosive ejection of the small lake observed in the Arenas crater of Ruiz in February and July 1985 (1) and on the day before the eruption. This hot acid (pH 0.2) water may have contributed to the rapid melt of the summit glaciers and provided the observed rates of SO_4^{2-} and Cl^- . Some of these compounds may have been contributed by the ash that fell on the summit region and stimulated melting or by the thorough mixing of pyroclasts and ice that took place during eruption of pyroclastic surges and flows (22). However, the relatively low ash leachate values suggest that the crater lake may have been the dominant source of the acids contained within the lahar. The mud derived by the scouring of the river canyons is not a reasonable source of SO_4^{2-} and Cl^- because it had a likely original concentration of these compounds 0.1 to 0.01 that of the Armero lahar (23). The sulfur noted on the surface of the

glaciers (1) cannot have contributed to the soluble SO_4^{2-} concentration of the lahar because it is relatively insoluble.

The microprobe and petrographic data, although cursory, reveal a remarkable similarity between the pumice ejected in 1985 and in the 1595? eruption. The 1985 pumice is a highly vesiculated andesite that shows evidence of having been held at very high (magmatic) temperatures for a long period (24). The hornblende is broken down to a fine-grained pyroxene assemblage, and the melt inclusions are, at least partially, devitrified. The two pumice lumps show very similar signs of contamination.

The total mass of ejected material was extremely small $[3.5 \times 10^{10} \text{ kg} (25)]$. The large mass of SO₂ released by the 13 November eruption is not consistent with the mass of ejected magma or even with reasonable estimates made elsewhere (26) of the ratios of magma degassed but not erupted to the volume erupted. The ratio of SO₂ released to magma erupted for Mount St. Helens was approximately 0.0023 and for El Chichón, in Mexico, was 0.0033 (27). Yet, the preliminary data at Ruiz indicate a ratio of 0.02, which is an order of magnitude greater.

In conclusion, the available data on diverse geochemical aspects of the volcano Nevado del Ruiz demonstrate that a volume of new magma rose into the volcano before September 1985. This intrusion probably caused the seismicity observed since November 1984, and triggered significant changes in fumarolic gases and the thermal and chemical revitalization of the summit-wide geothermal system. The post-eruption data on SO_2 flux indicate that a large volume of magma is still actively degassing beneath the summit. Thus, the potential exists for continued eruptions of a scale comparable to or larger than that which we have already witnessed. In view of the presence of approximately 90% of the original glacial ice, the potential for more lahars seems great.

The remarkable similarity in mineralogy and chemistry of the 1595? and 1985 pumices, coupled with the altered appearance of the 1985 pumice and the unrealistically large ratio of SO₂ released to magma erupted, leads us to speculate that at least some of the pumice and ash erupted in 13 November 1985 may have come from old magma in a summit magma chamber from the last major eruption (1595?). The driving force of the eruption was not that material but, rather, the rise of a new batch of magma into the volcanic edifice. The explosive release of its gases caused the recent eruption. In this speculative model, the pumice ejected is considered as accidental to the eruption (much like any older rock ripped from the conduit); the new magma has not yet erupted.

The Nevado del Ruiz volcano should be regarded as very dangerous. Our study demonstrates the value of geochemical monitoring of the combination of the summit gas plume, any accessible fumaroles, thermal waters, ash leachates, and lahar waters. These parameters should be included in a long-term monitoring program in order to minimize the risk posed to the region. The near synchroneity of activity at Ruiz and Tolima in the 19th century (2) should prompt similar monitoring at Tolima.

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sampled and as the system responds to changing enthalpy conditions over long periods of time. Be-cause of road destruction, Termales de Ruiz was the only well-characterized hot spring accessible in No-vember. The 1969 to 1985 differences are not easily explained by sampling differences or by analytical

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Insulin-Stimulated Hydrolysis of a Novel Glycolipid Generates Modulators of cAMP Phosphodiesterase

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Insulin action may involve the intracellular generation of low molecular weight substances that modulate certain key enzymes. The production of two substances that regulate the activity of adenosine 3',5'-monophosphate phosphodiesterase was evaluated in cultured myocytes by incorporation of radiolabeled precursors. Insulin caused the rapid hydrolysis of a chemically undefined membrane glycolipid, resulting in the production of two related complex carbohydrates as well as diacylglycerol. Both the glycolipid precursor and the aqueous products were monitored by labeling with radioactive inositol and glucosamine. Depletion of the labeled precursor and the appearance of labeled water-soluble products and diacylglycerol occurred within 30 seconds after hormone treatment and was followed by rapid resynthesis of the precursor. The aqueous products that were radioactively labeled appeared chromatographically and electrophoretically identical to phosphodiesterase modulating activities produced by insulin from the same cells. The purified radiolabeled and bioactive substances had similar chemical properties. Hydrolysis of the glycolipid precursor and subsequent generation of products could be reproduced by incubation of extracted lipids with a phosphatidylinositol-specific phospholipase C. These studies suggest that insulin stimulates an endogenous, selective phospholipase C activity that hydrolyzes a novel glycolipid, resulting in the generation of a complex carbohydrate-phosphate substance containing inositol and glucosamine that may mediate some of the actions of the hormone.

HE MOLECULAR MECHANISMS OF insulin action remain largely unexplained. Insulin binds to a heterodimeric cell surface receptor that contains a hormonally responsive tyrosine kinase activity in its β subunit (1). The ensuing changes in cellular metabolism are diverse, occurring within seconds or hours of the hormonereceptor interaction. The regulation by insulin of enzymes controlling intermediary metabolism is observed within minutes and is often the result of changes in the state of phosphorylation of the enzyme. However, the precise biochemical link between the activated receptor and enzyme regulation remains unknown. Several known substances have been proposed to act as second messengers for insulin, yet each has proved inadequate to account for the action of the

hormone (2). Recently, investigators have found (3) that some of the metabolic effects of insulin may result from the generation from the plasma membrane of an undefined substance or group of substances that regulate certain insulin-sensitive enzymes, perhaps through control of protein phosphorylation (4). These "mediator" activities were shown to be associated with a substance, or substances, that were water-soluble, nonnucleotide, and had an apparent molecular weight of 1000 to 2000 (3, 4). Although there were suggestions of a peptidic structure (3, 4), definitive information concerning the chemical identities of these substances has not been forthcoming.

We recently reported (5) the purification and partial characterization of two structurally related complex carbohydrate-phosphate substances produced from liver membranes that regulated the activity of the high-affinity adenosine 3',5'-monophosphate (cAMP) phosphodiesterase (PDE) in adipocytes. Both substances were apparently generated by exposure of membranes to insulin, and appeared to result from the phosphodiesterase-like cleavage of a novel inositol-containing glycolipid. Studies on enzymatic production of these activities with a phosphatidylinositol-specific phospholysine C (PI-PLC), and evaluation of chemical properties, suggested that these enzyme modulating activities were derived from substances that contained inositol and glycosidically linked glucosamine.

In the present studies the actions of insulin on the production of these carbohydrate substances were evaluated in the cultured murine myocyte line BC_3H1 (6). These cells become responsive to insulin when they differentiate after attaining confluence. We observed the insulin-sensitive incorporation of radioactive inositol and glucosamine into fractions separated by high-performance liquid chromatography (HPLC) that contain PDE-modulating activity. The production of these radioactive products mirrors that of the PDE-modulating activities, and appears to be due to the hydrolysis of a novel glycolipid precursor.

The purification of two liver-derived substances capable of modifying the activity of the high-affinity cAMP phosphodiesterase from adipocyte particulate fraction was recently reported (5). This procedure was modified for purification of similar substances from BC3H1 cells incubated with [³H]inositol or [³H]glucosamine. After in-

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