ALTERATION RELATED TO HYDROTHERMAL ACTIVITY OF THE NEVADO DEL RUIZ VOLCANO (NRV), COLOMBIA

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ABSTRACT

The hydrothermal activity in the NRV generates alteration characterized by mineral associations depending on a number of physic-chemical factors of the hydrothermal system. Petrography of unaltered rocks was used to establish the mineral assemblage prior to rock-fluid interaction. XRD was used in altered rocks, where it was not possible to recognize the alteration products. The observed mineral assemblages indicate advanced and intermediate argillic alterations, this and the observation of very low modal proportion of sulphates, sulphides and native sulphur in some areas could point to a low sulphidation zone. However, the proximity to the volcano and the presence of acid thermal waters and steam pose an apparent contradiction with an expected high sulphidation zone which is explained by climatic conditions, where excess water has dissolved and leached sulfides, sulphur and sulphates close to the volcano. Fault zones serve as conducts for fluid transport and have acid-sulphate mineral associations produced by atmospheric oxidation at the water table in a steam-heated environment of H2S released by deeper, boiling fluids or by the disproportionation of magmatic SO2 to H2S and H2SO4 during condensation of magmatic vapor plume at intermedia depths in magmatic hydrothermal environment in andesitic volcanic terrain characteristic of high sulphidation zones.

Keywords: Hydrothermal Alteration, Nevado del Ruiz, Volcano.

ALTERACIÓN RELACIONADA CON LA ACTIVIDAD HIDROTERMAL DEL VOLCÁN NEVADO DEL RUIZ, COLOMBIA

RESUMEN

La actividad hidrotermal en el NRV genera alteraciones caracterizadas por asociaciones minerales dependiendo de factores físico-quimicos del sistema. Petrografía de rocas inalteradas fue usada para establecer la asociación mineral antes de la interacción fluido-roca. DRX fue usada en rocas alteradas donde no se reconocen los productos de alteración. Asociaciones minerales observadas indican alteración argílica avanzada e intermedia, esto y la poca cantidad de sulfatos, sulfuros y azufre nativo en algunas áreas apuntaría a una baja sulfuración. Sin embargo, la proximidad del volcán y la presencia de aguas termales acidas y fuentes de vapor pone una contradicción con una zona esperada de alta sulfuración, esto se explica por las condiciones climáticas, donde el exceso de agua ha disuelto y lixiviado sulfuros, azufre y sulfatos cerca al nevado. Las falla sirven como conducto para el transporte de fluidos y tienen asociaciones minerales acido-sulfatadas producidas por oxidación atmosférica en la tabla de agua en ambiente de vapor-calentado originado por H2S liberado por fluidos en ebullición a profundidad o por la desproporción de SO2 magmático a H2S y H2SO4 durante la condensación de una pluma de vapor magnatico a profundidades intermedias en ambiente magmatico-hidrotermal en terreno volcánico andesítico característico de zonas de alta sulfuración.

Palabras clave: Alteración Hidrotermal, Nevado del Ruiz, Volcán.

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INTRODUCTION

The NRV has been widely studied because of its eruptive history and its location near major cities in Colombia. Numerous volcanologic and geophysic studies were done in the 80s and 90s (Jaramillo 1980, Thouret 1988, Schaefer 1995, Williams *et al*., 1990, Stix *et al.,* 2003 among others). In terms of the hydrothermal system, the first works were done by Sturchio *et al.* (1988) and Lopez (1992) who suggested the presence of three distinctive types of water (acid sulfate waters, bicarbonate and neutral chloride waters) and reported an apparent lack of mixing between the two water types. CHEC, 1983 summarizes one of the most completed geothermal research in the NRV.

Lopez (1992) noted that acid sulfate waters appear to be related to the north-west striking and seismically active Villamaria-Termales fault. She also found that the neutral chloride waters are clustered to the west and south-east of the volcano. The bicarbonate waters are more widespread.

A recent field campaign in the area (see FIGURE 1) allowed identifying argillic alteration (no differentiation was made between intermediate and advanced in field) and silicification with vuggy silica (found in a isolated outcrop affected by the Villamaria-Termales fault and near to a hot spring with 63°C in temperature). The focus of this paper is to analyze the observed alteration related to hydrothermal activity using X-ray diffraction, thin section petrography, and field observations, in order to understand the active geothermal system.

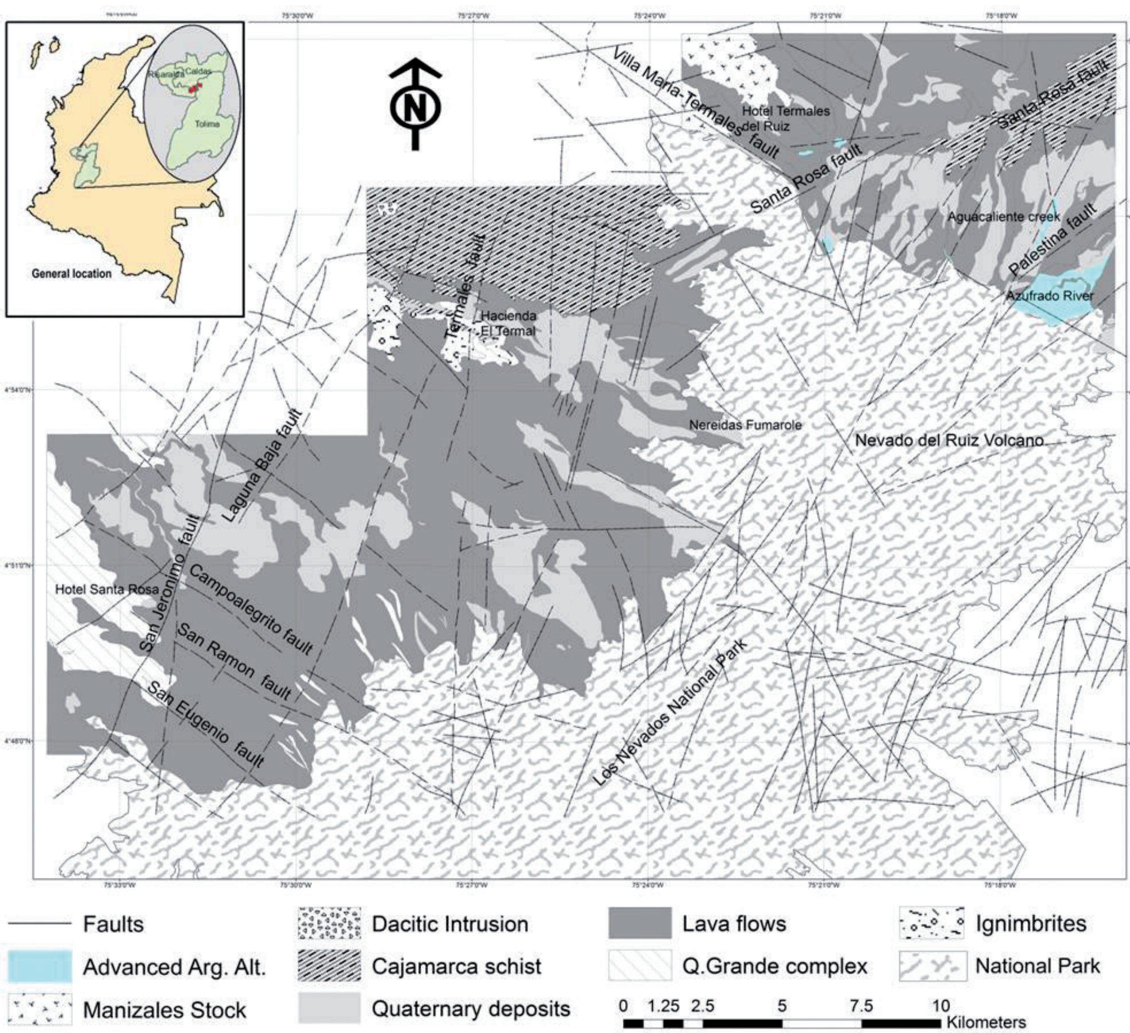

FIGURE 1. Generalized geologic map north and northwest of the Nevado del Ruiz Volcano showing sample localities mentioned in the text.

METHODOLOGY AND ANALYTICAL TECHNIQUES

Two areas, N and W of the volcano, were sampled. The areas are almost completely covered by pyroclastic deposits and residual soils, but some outcrops along roadways have exposed hydrothermally altered rocks. A total of 60 samples were collected from outcrops near hot springs in the two areas, of these, 10 representative samples were selected for petrographic analyses in thin section. Samples were initially described in the outcrop to identify potential mineral alterations and a complete macroscopic description was performed in the laboratory prior to thin sectioning and crushing for X-ray diffraction analysis.

Petrographic analyses of chosen samples consisted in textural description and mineral identification in both altered and unaltered rocks. Minerals were identified in hand sample, thin section and by XRD analysis in disoriented rock powder.

X-ray diffraction of powders was done on a Rigakudiffractometer, model RINT 2200, hosted at INGEOMINAS. This instrument has a configuration with K radiation of Cu , λ=1.54056 Å, 30 mA, and 40 kV; analysis were done in 2-theta geometry and Bragg–Brentano configuration, with a step size of 5 degrees/min and a step time of 0,02 degrees. Diffraction patterns were taken at room temperature, 20°C and an average 65% humidity. The mineralogy of some samples was also determined in the XRD labs of USGS (Denver, Colorado). Approximately 0.1 gram aliquots of each sample were mixed with 1 mL of water to create slurry that was tranfered to a glass petrographic slide and dried. A sample with an unusually high amorphous 'hump' was rescanned on a zero background slide to verify that the amorphous content was a component of the sample and not an artifact of the glass slide. XRD was performed using a Siemens D500 using Cu K-alpha radiation operated at 40 kV and 30 mA. The diffractometer is equipped with fixed slits and a graphite monochromater. Samples were scanned from 4 to 64 degrees two theta, at 0.02 degrees per step and a count time of 1 second per step.

GEOLOGICAL SETTING

NRV is located in the Central Cordillera of the Colombian Andes (4.90 °N and 75.32 °W). The maximum topographic elevation in the volcano is 5321 m. NRV belongs to the Ruiz-Tolima volcanic complex, in the central volcanic zone of Colombia, this volcano is the northernmost major active volcano of the Andean chain.

The Ruiz-Tolima complex was produced by repeated eruptions of andesite and dacite lavas and andesite pyroclastics. Initial volcanism in the area consisted of voluminous lavas of hypersthene-augite andesite and dacite now observed over most of the crest of the range (Herd, 1982).

NRV is a large and complex edifice constructed in three major phases over the past 600.000 to 1'200.000 years (Jaramillo, 1980; Thouret *et al*, 1988). The upper composite cone was built up from late Quaternary to Holocene; during that time, the emplacement of a series of lava flows and domes was followed by more destructive eruptions with pyroclastic flows (Thouret *et al*, 1988).

Field relationship and rock composition indicate that these rocks can be classified into two main groups, basalts and andesite porphyries (Jaramillo, 1980). The dominant composition of these lava flows are porphyritic andesites, with subordinate basalts.

The edifice of the NRV is built by andesite lava flows emplaced over an igneous and metamorphic country rock of schist from the Cajamarca Complex and tonalitic rocks from the Manizales Stock. These lithologies are overlayed by several pyroclastic deposits from later explosive eruptive phases, the lavas are composed by two pyroxenes andesites with local variations to basaltic andesites (FIGURE 2).

PETROGRAPHY AND XRD

Lava flows are mainly andesites and porphiritic andesites, but some differences in phenocrysts abundances are observed between ancient and young lava flows (Forero and Zuluaga, 2010). The rocks are hypocrystalline, with phenocrysts mainly of plagioclase and pyroxene in a glassy and cryptocrystalline matrix. The most important microstructure is allotriomorphic, with some euhedralphenocrysts. Poikilitic, glomeroporphyritic and cumulophyric microstructures were also identified. The phenocryst assemblage is plagioclase - augite - hypersthene, these minerals are usually present in glomerocryst assemblages as: 1. plagioclase, 2. augite-hypersthene-opaque, 3. augite-opaque and 4. plagioclase-augite-hypersthene-opaque (FIGURE 3)

Ancient lava flows usually show hydrothermal alteration, while young lava flows are usually unaltered; however, young lava flows show locally thin exudation layers in cooling fractures where sulfur, sulfates and salts have been deposited (FIGURE 4).

FIGURE 2. Outcrops of the Cajamarca complex schist (left) and the tonalitic Manizales stock (right).

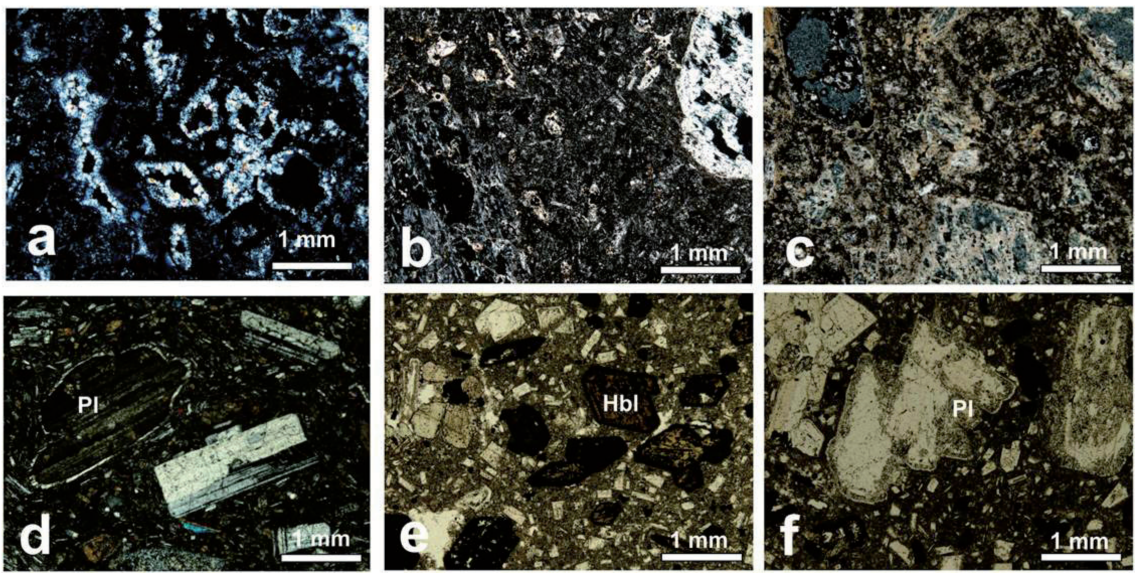

FIGURE 3. Photomicrographs of representative samples. **a)** sample GNR-JF-028A, **b)** sample GNR-007B and **c)** sample GNR-JF-004C are samples with advanced argillic alteration showing clay minerals and amorphous silica in a criptocrystalline mass. At the bottom left of photo a) it is possible to see a vuggy silica structure. **d)** sample GNR-JF-003A and **e)** and **f)** sample GNR-JF-025, photos of unaltered lava flows consisting of porphyritic andesites with plagioclase, pyroxene and hornblende phenocrysts.

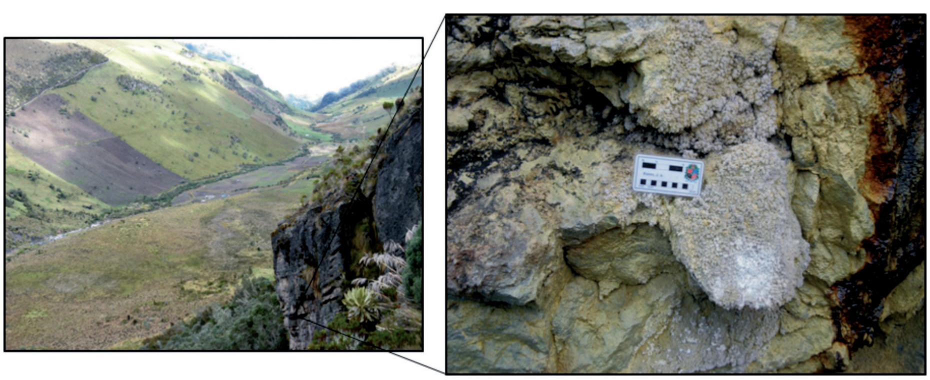

FIGURE 4. Panoramic view of Aguacaliente Creek (left) where an unaltered rocky escarpment shows evidence of mineral exudation with small crystals of gypsum (right, locality GNR-JF-114).

The most pervasively altered samples look as a criptocrystalline mass with clay minerals and amorphous silica, while samples moderately altered show relictic forms of preexisting minerals as plagioclase and pyroxenes, these minerals were replaced by kaolinite, albite and some other unidentified clay minerals in thin section, by XRD was possible to identify clay minerals using the methodology described by Thorez, J. 1976. The whole rock XRD analyses showed the presence of carbonates in hotel Termales and Santa Rosa hot springs. Clay minerals were not detected in these diffractograms (FIGURE 5).

TABLE 1 shows alteration minerals; from this table is clear the presence of three different paragenesis related to three ranges in pH of the fluid involved in the hydrothermal alteration process. Nereidas fumarole, La Gruta creek and Hotel Termales show an acid setting. Aguacaliente creek also shows an acidic setting in a location where a hot spring is currently active. The Azufrado river headwaters (La Hedionda and la Plazuela Creeks) shows a neutral environment. The neutral to alkaline settings are in Hacienda el Termal and Termales de Santa Rosa, where hot springs occur in schist.

TABLE 1. Minerals of hydrothermal alteration identified by X-ray diffraction analyses in samples from outcrops at Nevadodel Ruiz Volcano. Abbreviations: FN=Nereidas Fumarole, LG=La Gruta creek, TR=Hotel Termales del Ruiz, AC=Aguacalientecreek, Hed=La Hedionda creek, Plaz=La Plazuela creek, Azuf=Azufrado river, LB=Laguna baja, SR=Hotel Termales de Santa Rosa, HT=Hacienda el Termal, pp=precipítate, Alt. R.=Altered rock. Only the alteration minerals are reported.

Sample	956	955	954	953	115	978	981	983	985	963	958	958
Location	FN	FN	LG	TR	AC	Hed	Plaz	Azuf	LB	Sr	HT	HT
Sample type	pp	Alt. R.	Alt. R.	Alt. R.	Alt. R.	Alt. R.	Alt. R.	Alt. R.	Alt. R.	pp	pp	Alt. R.
Sulphur	■				■							
Alunite					■							
Woodhouseite						■		■				
Natroalunite				■								
Meta-alunogen		■										
Mercallite		■										
Jarosite			■	■								
Halloysite			■			■					■	
Kaolinite								■	■			
Anatase												
Cristobalite	■		■	■	■	■			■			
Quartz	■	■	■				■	■	■	■		■
Opal			■	■		■				■		
Tridymite			■	■	■					■		
Pyrite									■			■
Montmorillonite										■		
Smectite						■	■	■	■			
Illite-smectite							■	■				
Illite						■	■	■				■
Feldespar						■	■	■	■			
Clinochlore										■		■
Gypsum					■				■			
Calcite										■	■	■
Aragonite										■		

Acid (Sulphur–Pyrite); Neutral (Halloysite–Clinochlore); Alkaline (Gypsum–Aragonite)

HYDROTHERMAL ALTERATION

The main hydrothermal alteration in the surface of NRV is an extensive argillic zone that affects most ancient andesitic lava flows (augite-hyperstheneandesites). This alteration is observed at the Rio Azufrado valley that follows a north-northeast trend controlled by the dextral strike-slip Palestina fault system. Advanced argillic alteration is also observed along the Aguacaliente creek and in a 59 °C hot spring in the Marcada creek; in this area the alteration is covered by pyroclastic, lahars deposits, and by the ice cap at the highests elevations of the volcano (FIGURE 6).

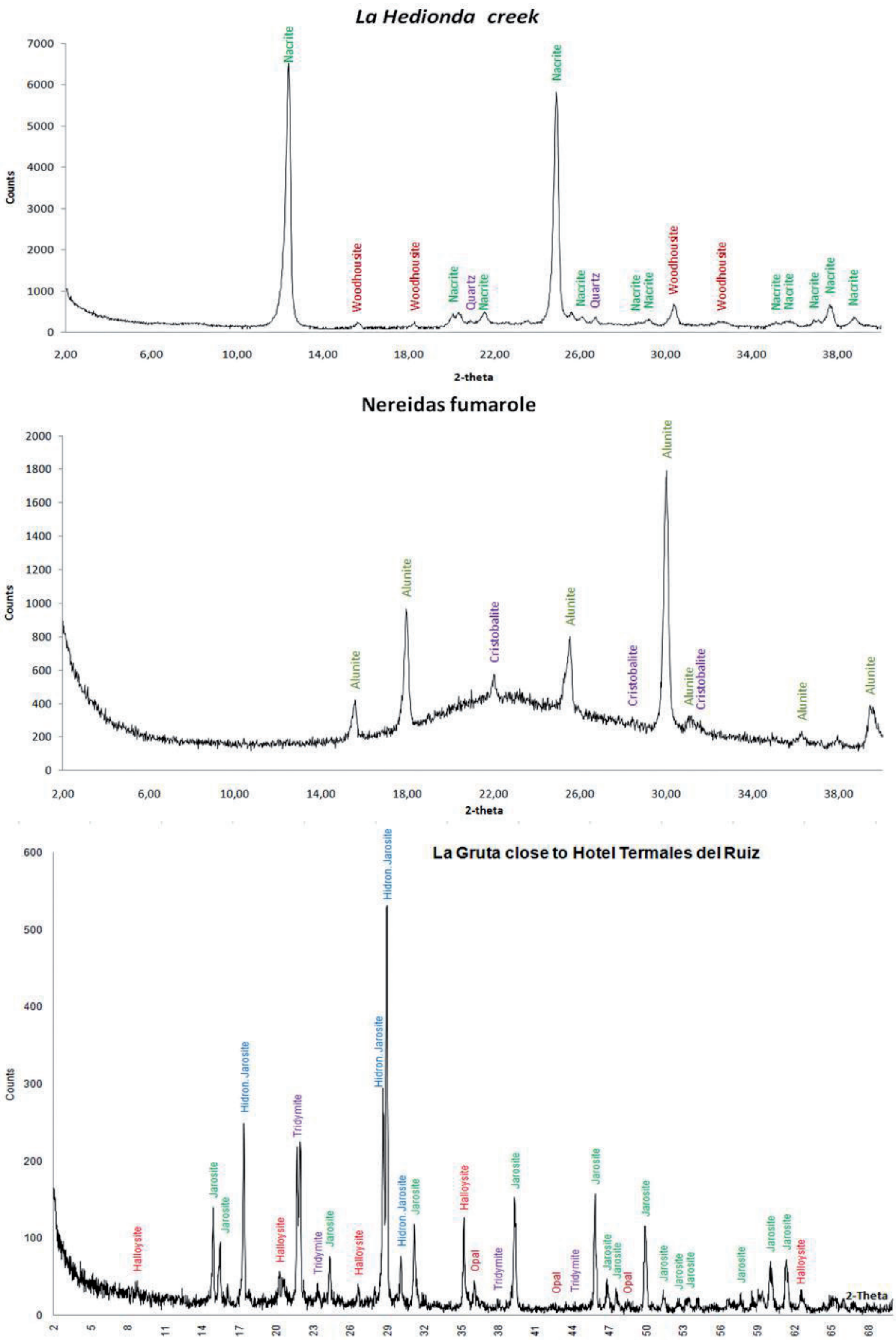

FIGURE 5. XRD patterns of samples in the area. JF-007B is a sample with advance argillic alteration and with soft sulfur sinters, H_2S fumes were also identified near the sample locality because of its typical smell. JF-035A is a sample from Nereidasfumaroles, this sample contains alunite, cristobalite and native sulfur. Sample JM-954 from la Gruta creek close to trend of Villa Maria – Termalesfault , this sample was taken from a big altered deposit.

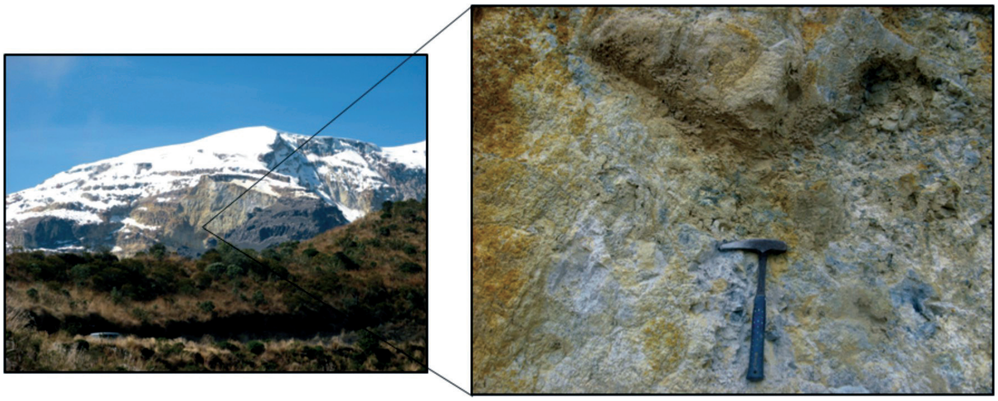

FIGURE 6. Outcrop locality GNR-JF-007, with intense hydrothermal alteration covered by ice cap. Left, panoramic view; right, detail of the outcrop. Yellowish material is a mixture of clays with jarosite and the white color is related to clay minerals like kaolinite, nacrite and dickite.

The advanced argillic alteration is characterized by an assemblage of *Amorphous silica* + *cristobalite* + *alunite* + *tridymite* + *kaolinite* + *quartz* + *jarosita* + *sulfur*; although, in some cases some of the mentioned minerals are absent.

In thin section the altered lava flows looks like a cryptocrystalline mass where clay minerals normally appear as massive fine aggregates mixed with shards. Relictic forms of prexisting minerals as plagioclase and pyroxenes are observed partially replaced by clay minerals and pyrite (a typical advanced argillic alteration assemblage).

Some soft silica-sulfur sinters are observed apparently aligned with the Palestina fault; additionally, in these places (La Hedionda, La Marcada and Aguacaliente creeks) characteristic odor to H_2S is perceived.

Silicification was identified in an isolated outcrop near to a hot spring (Hotel Termales del Ruiz) in the road El Arbolito - La Enea. This silicification appears to be structurally controlled by the Villamaria-Termales fault (FIGURE 7) because rocks' silicification is restricted to a vertical fracture (N72ºW). Silicification as small patches was also found at the bottom of the Azufrado River Valley near El Cerrito farm. Silicification is characterized by a slightly boxwork pattern, vuggy silica, relation to pyrite oxidation and association with clay minerals (mainly kaolinite).

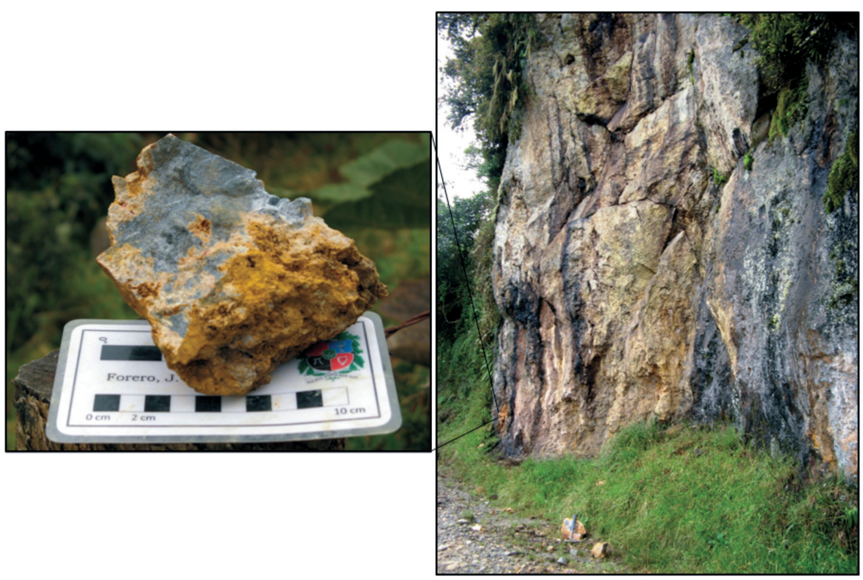

FIGURE 7. Silicification controlled by Villamaria-Termales fault system in locality GNR-JF-028, note the subvertically aligned oxidation pattern (right). In the left picture a hand sample (GNR-JF-028A) of silicified rock with a leached oxidation cap.

Intermediate argillic alteration was mapped together with advanced argillic alteration because of the difficulty in the differentiation of these two in hand samples. However, intermediate argillic alteration was identified using XRD analyses. This alteration is not common in the area, the best exposition is observed at the W part of NRV, in a road side isolated outcrop in the road Villamaria-Chorro Negro, near Laguna baja farm. The alteration is affecting schist and the overlying Rio Claro ignimbrites. The mineral assemblage is characterized by feldespar + quartz + cristobalite + smectite + kaolinite + pyrite.

Acid sulfate alteration is observed near to the La Olleta crater in the NRV; there, a paragenesis of amorphous silica, quartz, sulfur, alunite, mercallite and cristobalite was identified by XRD. In this place the alteration and precipitation occur in a restricted area, less than 500 m from a fumarole in a coluvial deposit. The water condensated from the steam has a pH of 2.

Local hydrothermal alteration and mineral precipitation is also observed in Hacienda el Termal; in this place, geysers coming out from schist of the Cajamarca complex are forming sinters of calcite with minor amorphous silica.

DISCUSSION AND CONCLUSIONS

The occurrence of kaolinite, alunite, cristobalite, opal, native sulphur, jarosite and pyrite allows identifying advanced argillic to intermediaargillic alteration in the NRV. Acid sulfate wall-rock alteration characterized by the assemblage alunite + kaolinite + quartz + pyrite results from leaching of fluids rich in H_2SO_4, near the alteration zone it is also possible to identify fumes of H_2S by its characteristic smell, this alteration is a subset of advanced argillic alteration and occurs in small restricted areas (e.g., near Nereidas Fumarole).

The advanced argillic alteration is the most widespread in the surface and helps to seal the rocks near the surface hindering fluid circulation. Rocks near the main faults (Villa Maria-Termales, Palestina and Santa Rosa) have enough permeability to allow fluid flow and therefore they play an important role in hydrothermal fluid circulation. An example of such behavior is seen in Aguacaliente creek and Nereidas fumaroles and other acidic hot springs, where past fluid flow produced advanced argillic alteration overprinted by acid-sulfate alteration; also in these areas it was observed other hydrothermal manifestations such as soft sulfur-silica sinters. The hydrothermal alterations in the area are typical of a low sulphidation setting, this observation contrast with the expected high sulphidation setting near the crater. The absence of higher amounts of sulfur minerals and the apparent low sulphidation could be explained by leaching in a wet weather condition with high rainfall typical of the Nevadodel Ruiz area.

The structural control of the advanced argillic alteration observed at the Rio Azufrado valley by the dextral strike-slip Palestina fault system strengthened the interpretation of Lopez (1992) who claims that this fault is a preferential path for magmatic fluids based on the observation that volcanic centers of Nevado del Ruiz, Nevado del Cisne and Nevado Santa Isabel are aligned with the Palestina fault. Isolated altered outcrops exposed at the Gualí River are also aligned with the Palestina-fault trend. Other pathway that may have played a key role in hydrothermal fluid circulation is the Villamaria-Termales fault as indicated by the observed silicification, hot springs and precipitation of sulphates and silica minerals in Hotel Termales del Ruiz and la Gruta creek.

ACKNOWLEDGMENTS

This work has been a product of geothermal exploration project with funding from COLCIENCIAS Universidad Nacional, ISAGEN and INGEOMINAS (Programa 762 del 2009, Código 1101-454-25657). The authors also thank the USGS (Denver) for their support in analyticval work. Authors thanks the Department of Geological Sciences of Universidad Nacional de Colombia which allowed the use of petrographic microscopes and other equipment.

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Trabajo recibido: Marzo 2 de 2011
Trabajo aceptado: Mayo 18 de 2011