

# Characterization of Alteration Minerals within a Volcanic Dome of the Paipa Geothermal System, Boyacá, Colombia

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**Keywords:** Geothermal, hydrothermal alterations, hydrothermal fluids, clay minerals, Paipa Geothermal Area.

## ABSTRACT

This research contributes to the knowledge of the petrographic, compositional and alteration mineral characteristics of the felsic volcanic rocks and igneous bodies in the Paipa Geothermal System (PGS). The investigation is carried out through optical microscopy analysis, mineral geochemistry, and X-ray diffraction (XRD) analysis. The rock samples in the Alto de los Godos sector are classified as trachytes and latites, with predominance of anorthoclase over albite. Within the clay fraction, the mineral association halloysite-kaolinite-illite-montmorillonite is recognized as an alteration product of the argillic and intermediate-argillic types, formed in acid-to-neutral pH environments and relatively low temperatures. The clay fraction samples reflect favorable crystallization conditions. The alteration species are associated as a product of thermal contribution by hydrothermal fluids which result in the neo formation of clay minerals.

## 1. INTRODUCTION

An important aspect in the characterization of a geothermal system is the mapping of hydrothermal manifestations (heated ground, soil steaming, fumaroles, boiling mud, altered areas) because they are usually the first evidence of the presence of a geothermal anomaly. In these environments, primary minerals tend to be altered to secondary ones, usually depending on temperature, permeability, pressure, fluid composition, initial rock composition and duration of hydrothermal activity. Therefore, the study of alteration minerals, integrated with geochemical information, provides information on physical-chemical processes in the system that lead to water-rock interactions and allows to interpret the temporal evolution and the current state of the geothermal system.

The Paipa Geothermal System (PGS) is located at the eastern cordillera of Colombia, south of the city of Paipa, 180 km from Bogotá with a surface area of 130 km<sup>2</sup> (Figure 1). It is considered an important area for the direct and indirect uses of the geothermal resource, with an altitude between 2500 and 2700 m s. n. m which corresponds to cold climate, with temperatures varying between 7 °C and 20 °C. There is currently a conceptual model of the PGS published by *Servicio Geológico Colombiano* (Alfaro et al., 2017) which includes a 3D geological-geophysical model, that integrates geology, density and magnetic susceptibility data with complementary information from other works such as petrographic characterization of shallow wells in the area of El Durazno, fluid geochemistry, hydrothermal alteration and magnetotelluric survey. This model describes the main elements of the geothermal system such as heat source, reservoir characteristics, caprock, and recharge zones. This research seeks to contribute to the knowledge of the characteristics of the caprock and the surface hydrothermal alteration minerals.

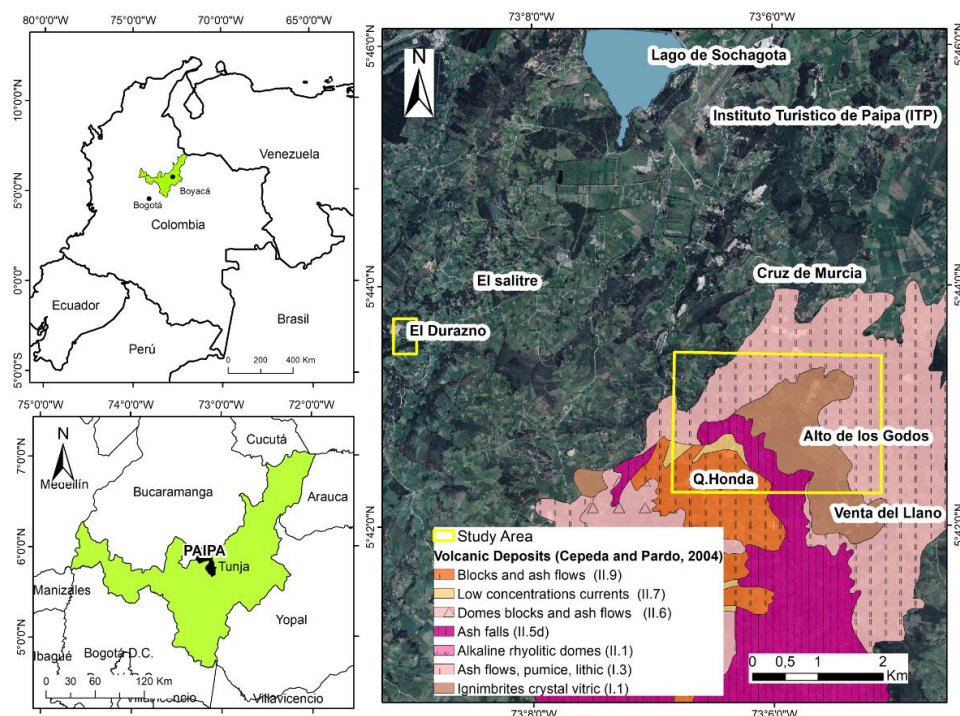


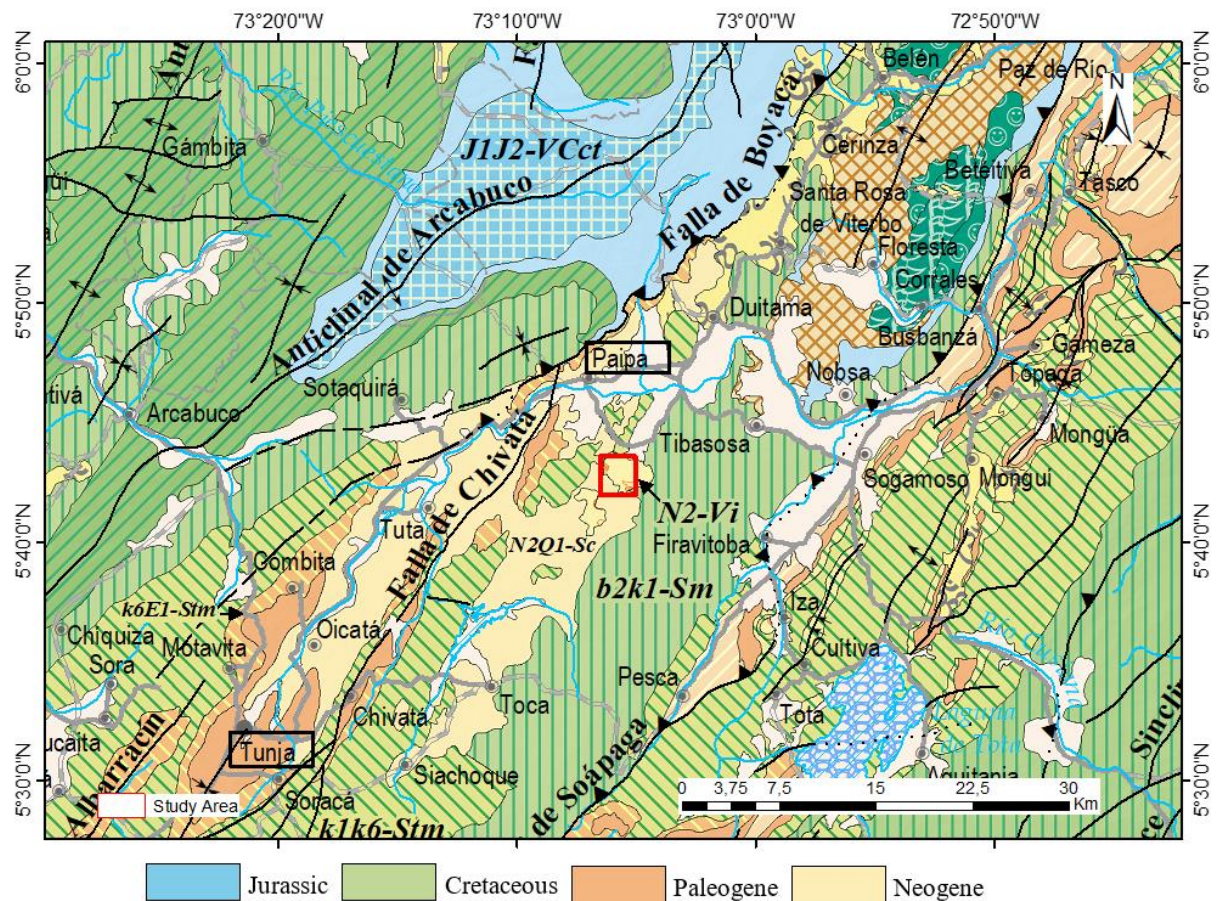
Figure 1: Location of the study area. Modified from Rueda (2017), Cepeda and Pardo (2004)

To confirm the geothermal potential of the PGS in terms of electricity generation, deep exploration wells are required to validate the geological model and allow the measurement the temperature of the fluids in the reservoir. One of the targets in the conceptual model (Alfaro et al., 2017) includes a 500-m-deep well. If these studies are carried out, the estimation of the geothermal potential will be more accurate. At present, the possibility of using the resource deals with direct uses, taking into account the well-known springs with temperatures of up to 70 °C. Among the industries that can make use of this heat in their production processes are the agricultural and fruit-dehydration plants, as well as manufacturers of heat pumps for living spaces and greenhouses.

This work presents the results of the characterization of the alteration minerals from petrography and X-ray diffraction chemistry (DRX) analyses.

## 2. GEOLOGY

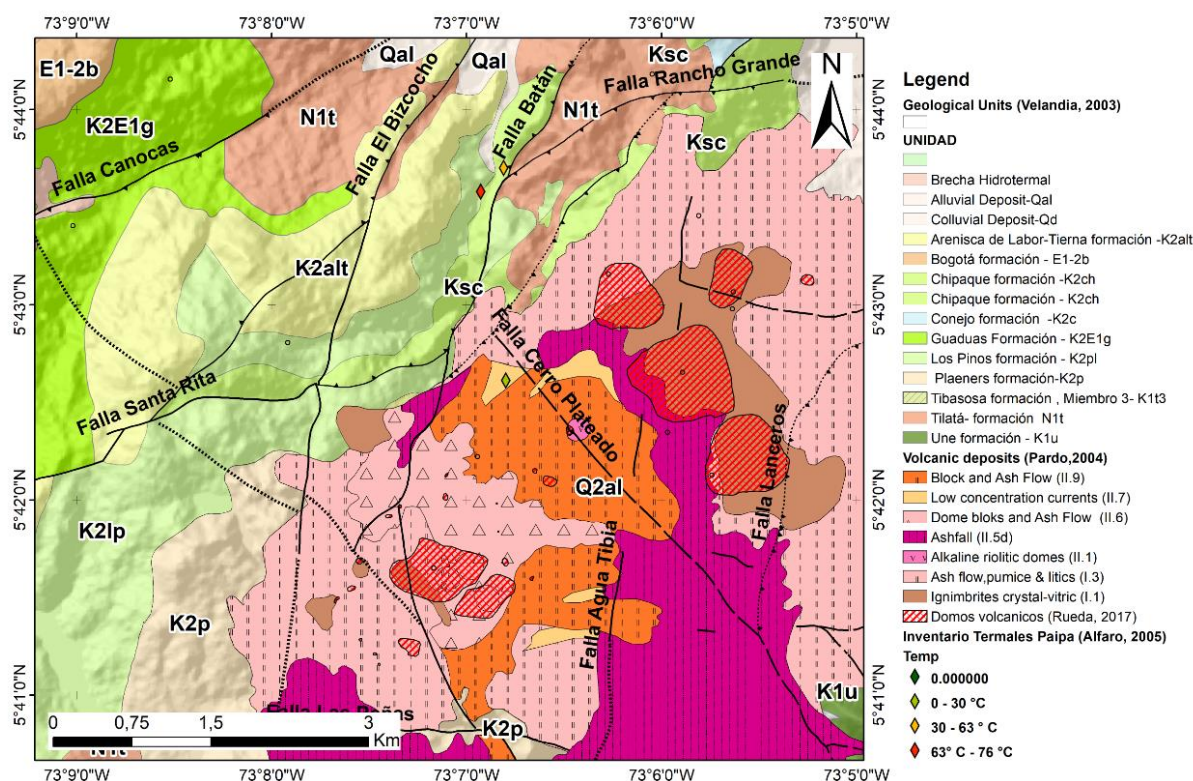
The PGS was formed within the compressive tectonic environment of the Eastern Cordillera, between the Boyacá and Soapaga thrust faults. The basement in this area is composed of metamorphic and sedimentary rocks of Paleozoic age, as well as intrusive and extrusive igneous bodies of Jurassic age that form the Floresta Massif to the NE of Paipa. In addition, Jurassic sedimentary rocks outcrop from regional structures such as the Arcabuco anticline and sedimentary sequences of Cretaceous, Paleogene and Neogene ages (Velandia, 2003) (Figure 2).



**Figure 2: Regional geology map. Modified from Gómez et al. (2005).**

Locally, felsic volcanic rocks (rhyolites and alkaline trachytes) have been documented (Cepeda and Pardo, 2004); igneous bodies of intrusive nature with porphyritic texture and dome morphologies (Rueda, 2017), and a volcanoclastic deposit informally called El Durazno that is characterized by its advanced argillic and intermediate-argillic alterations (Rodríguez and Valero, 2015) (Figure 3).





**Figure 3: Geological map of the Paipa area. Modified from Gómez et al. (2015) and Rueda (2017).**

### 3. METHODS

This study was carried out in four stages: (1) bibliographic information as well as the various relevant maps were compiled; (2) field campaigns, that included site and sample selection and geomechanical characterization; (3) laboratory stage, which integrated petrographic analysis, X-ray diffraction (DRX), and mineral chemistry; (4) data processing, which included calculation of weathering indexes and geothermometry.

#### 3.1 Bibliographic information

##### 3.1.1 Reference information and mapping.

Location maps of the sampling points for petrographic analysis and X-ray diffraction were based on coordinates taken in the field with a hand-held GPS receiver, base images were obtained using Google Earth Pro and the Basemap tool from ArcGIS. Regional and local geological maps were simplified versions from those published by Servicio Geológico Colombiano (Gómez et al., 2005).

#### 3.2 Stage 2-field work

##### 3.2.1 Site and sample selection.

The sampling sites were defined according to the distribution of volcanic rocks published by Cepeda and Pardo (2004), specifically, in the Alto de los Godos sector. In the field, the reconnaissance of the PGS was carried out and the best rock exposures in quarries and road cuts were identified. Subsequently, the sites with the highest degree of hardening were selected and a total of nine (9) samples were obtained for petrographic analyses in the Alto de Los Godos area, these samples were also analyzed by the X-ray diffraction method (DRX).

#### 3.3 Stage 3-laboratory work

##### 3.3.1 Petrographic analysis.

Petrographic analysis was performed with a light-polarizing microscope (both transmitted and reflected light) using 300 field views per thin section at standard 4x zoom. From this analysis, information is obtained on the mineral associations and the modal proportion of each of the mineral phases, additionally it allows detailed description of textural aspects of shapes, sizes, and spatial relationships among grains. This allows classifying the rocks and to qualitatively establish formation conditions.

##### 3.3.2 X-ray diffraction (DRX)

X-ray diffraction analysis was performed in the Lithogeochemical Characterization Laboratory at Universidad Nacional de Colombia-Sede Bogotá with the BRUKER D2 PHASER device. The samples were analyzed through both disoriented and oriented aggregate techniques.

### 3.3.3 Mineral chemistry

The electronic microprobe analysis is a technique of high precision and sensitivity used for qualitative and quantitative analyses, which involves bombarding a mineral specimen with a fine electron beam in order to measure the wavelength and intensity of X-rays and the intensities of secondary electrons and backscattered electrons. The characteristic X-rays generated in the sample are detected by wavelength dispersing spectrometers (WDS). The qualitative analysis is carried out by comparing the intensities of the characteristic elementary lines with those emitted by the standards, which are mostly pure elements or components of known composition (Castellanos and Ríos, 2005).

### 3.4 Stage 4-processing

For the calculation of weathering indexes, the database of whole-rock geochemistry by Rueda (2017) was used. Then, a brief description is made of the indexes and the standard equations used (Nesbitt and Young, 1982; Irfan, 1996, 1999; Fedo et al., 1995; Cox et al., 1995).

#### 3.4.1 Mineral chemistry and calculation of weathering indexes.

The Chemical Index of Alteration (CIA) of Nesbitt and Young (1982), calculated from equation 1 is necessary to determine the degree of weathering in the rocks, that is, it measures the degree to which feldspar minerals have become aluminous weathering products. The proportions of the CIA in feldspar and rocks of fresh origin are typically ~ 50, while those of residual weathering, such as kaolinite and gibbsite can reach values of ~100:

$$\text{CIA: } [ \text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) ] \times 100 \quad (1)$$

The values of CIA reflect the removal of unstable mobile cations (Ca, Na, K) in relation to highly immobile or stable residual constituents (Al, Ti) during weathering. Low values of CIA indicate absence of chemical alteration and therefore may reflect cold / arid conditions. CIA = 50-60 indicate an incipient weathering, CIA = 60-80 indicate intermediate weathering and CIA > 80 extreme weathering (Nesbitt and Young, 1982). The effects of weathering can also be evaluated using the Chemical Index of Weathering-CIW in molecular proportions, calculated from equation 2:

$$\text{CIW: } [ \text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O}) ] \times 100 \quad (2)$$

This equation is more appropriate to understand the extent of plagioclase alteration alone since K<sub>2</sub>O is subtracted from Al<sub>2</sub>O<sub>3</sub> in the numerator and denominator of the CIA equation. The CIA and CIW values are interpreted similarly with a value of 50 for the upper unheated continental crust and about 100 for highly degraded materials with complete removal of alkaline and alkaline earth elements.

The degree of chemical weathering can also be estimated using the modified plagioclase index alteration (PIA) equation to control plagioclase (Fedo et al., 1995). The alteration index (PIA) is calculated according to the following equation in molar proportions:

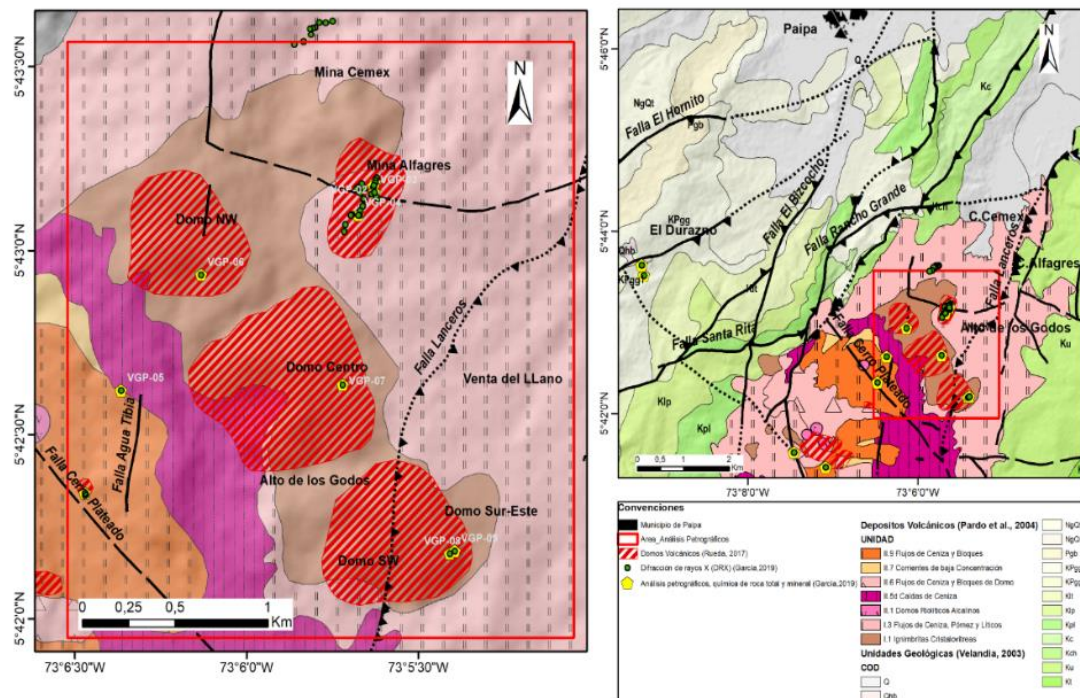
$$\text{PIA} = 100 \times ((\text{Al}_2\text{O}_3 - \text{K}_2\text{O})) / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} - \text{K}_2\text{O}) \quad (3)$$

Large PIA values (> 84) would indicate intense chemical weathering, while low values (~ 50) are characteristic of fresh rocks.

## 4. RESULTS AND DISCUSSION

The rocks from the Alto de Godos area in the PGS (figure 4) were classified according to the mineralogy (table 1) in the range of trachyte - latite (figure 5) with predominance of anorthoclase over albite. In the clay fraction, the mineralogical association halloysite-kaolinite-illite-montmorillonite was identified as alteration products of the argillic and intermediate-argillic types, formed in acid-to-neutral pH environments and at relatively low temperatures. The CIA values for samples of the Paipa domes vary between 55.18 and 58.73 indicating a low degree of weathering, whereas values of PIA vary between 56.26 and 61.75, reflecting a moderate chemical alteration. The petrographic and DRX analyses carried out for the clay fraction suggest favorable crystallization conditions.

Within the Alto de los Godos sector are the quarries ALFAGRES, CEMEX, domes NW, Centro, SE, and SW as illustrated in the figure 4.

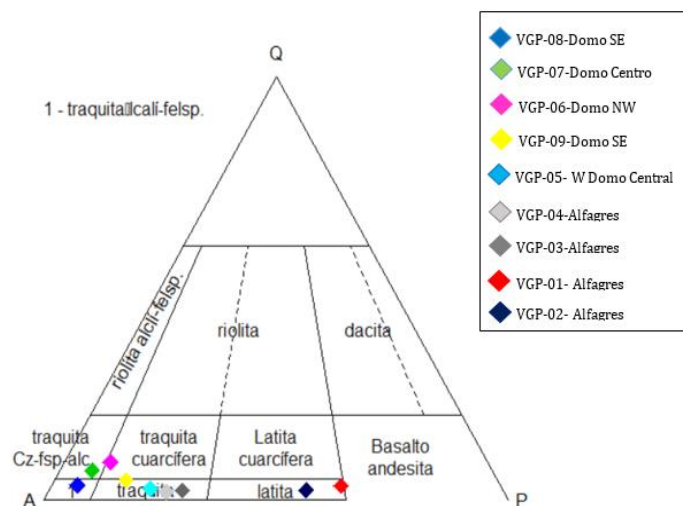


**Figure 4: Location map of the sampling points for petrographic and X-ray diffraction analyses (DRX). Datum WGS\_1984. simplified from Cepeda and Pardo (2004), Velandia (2003), and this work.**

**Table 1. Classification of rocks (Streckeisen, 1979).**

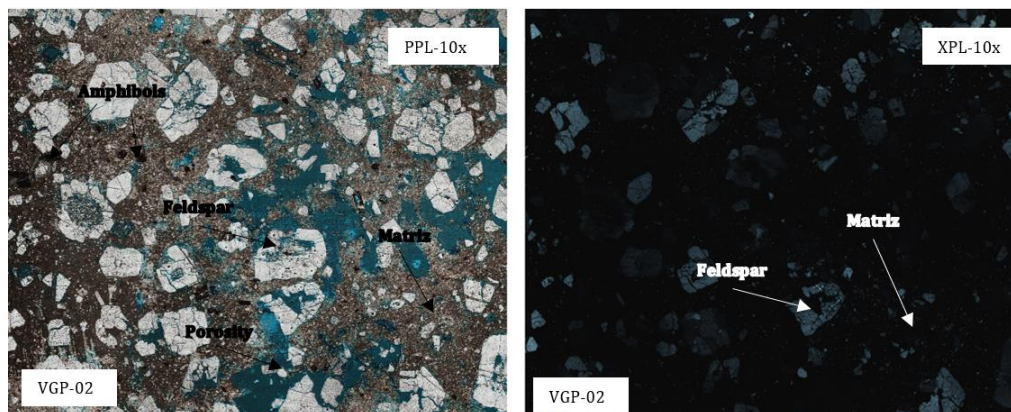
Sample	Minerals			Classification
	%Quartz (Q)	% Alkaline feldspar (A)	%Plagioclase (P)	Streckeisen (1979)
VGP-01	3.35	34.32	62.31	Latite with argillic alteration
VGP-02	2.3	42.3	55.2	Latite with argillic alteration
VGP-03	2.2	69.02	28.7	Trachyte with argillic alteration
VGP-04	1.77	72.69	25.53	Trachyte with argillic alteration
VGP-05	2.61	75.74	21.6	Trachyte with argillic alteration
VGP-06	8.86	81.12	9.92	Quartz Trachyte with argillic alteration
VGP-07	6.97	86.04	6.97	Alkaline quartz trachyte with argillic alteration
VGP-08	3.44	91.03	5.51	Alkaline trachite with argillic alteration
VGP-09	4.7	79.9	15.4	Trachyte with argillic alteration





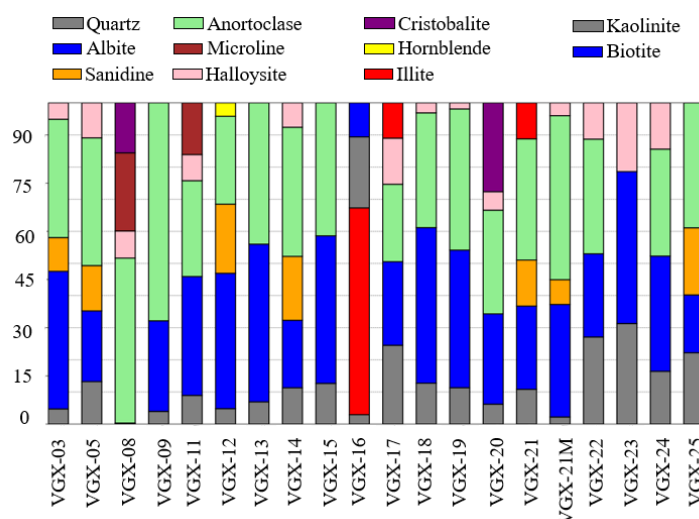
**Figure 5: Classification diagram (Streckeisen, 1979). Rocks from the Alto de los Godos area.**

In figure 6, the photographic scans of the section are presented. In each one, the main constituents are highlighted, in PPL XPL. In the sections, the pores and voids are observed with blue resin, which makes possible the identification of the primary and secondary porosities.



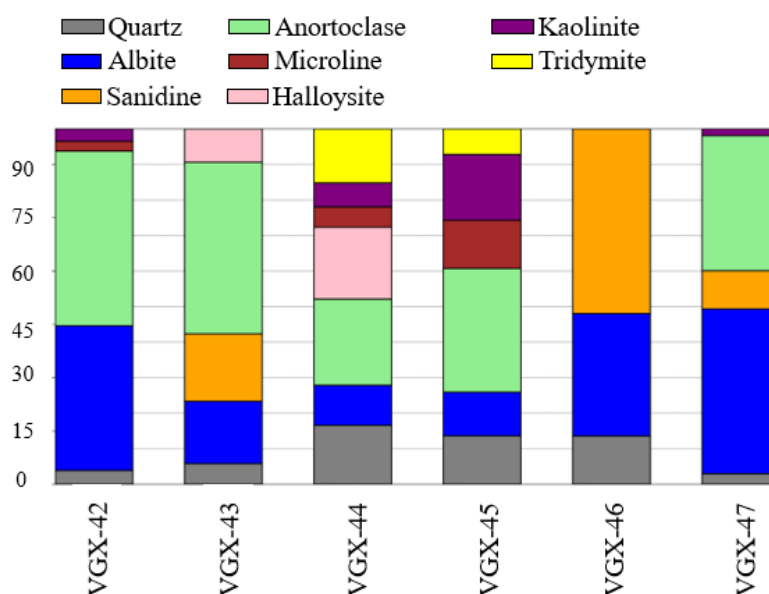
**Figure 6: Scanned thin section VGP-01, Alto de los Godos area.**

Petrographic analysis was complemented with X-ray diffraction analyses. The results of the quantification of disoriented mineral powder samples show a predominance of anorthoclase, albite and quartz, and sanidine, halloysite, microcline, kaolinite and illite in minor proportions, with biotite and hornblende occasionally reported, as shown in figures 7 and 8.



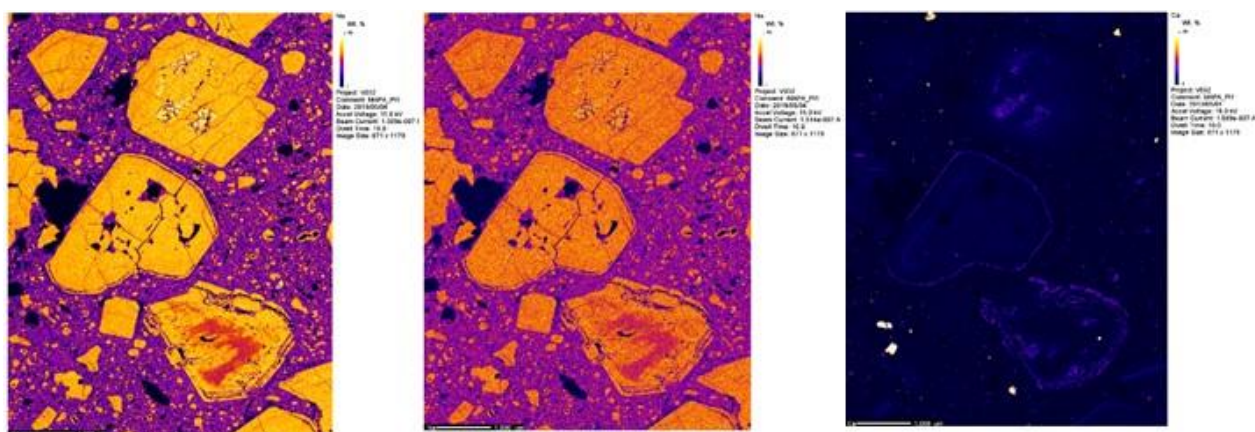
**Figure 7: Bar charts of percentages of minerals obtained in the quantification, ALFAGRES area.**

In the Alto de los Godos area, the main mineral phases found were anortoclase, albite, K-feldspar, and quartz. In addition, clay minerals were identified as kaolinite, halloysite and illite, as can be seen in figure 8.



**Figure 8: Bar charts of percentages of minerals obtained for the SE Dome samples, Alto de los Godos area.**

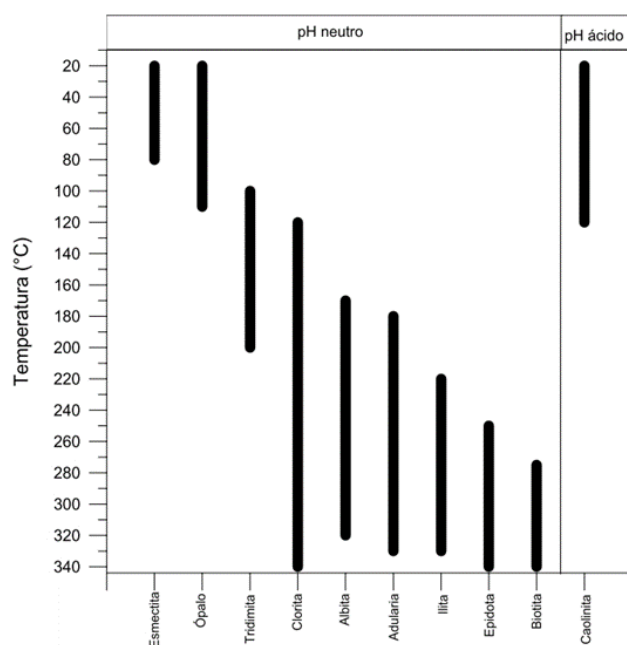
The investigation is further complemented with compositional maps and element profiles at different resolutions carried out mainly on feldspar and plagioclase phenocrysts. The elements identified in each set of maps were calcium, potassium, sodium, aluminum, iron, magnesium, silica (Figure 9).



**Figure 9: Compositional map for feldspar phenocrysts, sample VGP-08, Alto de los Godos area. Elements analyzed were Na, Ca, and K.**

The integration of the results obtained from the analysis of X-ray diffraction (XRD) through the disoriented aggregate and oriented sheet techniques allowed the identification of the mineralogical association in the clay fraction, composed mainly of kaolinite, illite and halloysite. Subsequent treatments with ethylene glycol and 500 ° C calcination allowed recognition of interlayered illite-smectite. The presence of quartz and potassium feldspar as predominant minerals is consistent with the petrographic description that classifies rocks in the range of trachytes-latites. On the other hand, there are secondary minerals occasionally reported such as hydromagnesite and brookite, which are related to areas of hydrothermal alteration, brookite in particular is a mineral that is formed during dissolution and precipitation processes related to the solidification of magma in preexisting rock fissures. The presence of clay minerals from the smectite group in the Matarredonda quarry (also known as ALFAGRES quarry) is an indicator of temperatures < 200 ° C formed under acid alkaline conditions with intermediate pH.

Figure 10 shows the mineral temperature and pH ranges for hydrothermal alteration minerals and the corresponding temperatures of the PGS obtained for accidental lithics (xenoliths) by petrography and electron microprobe analyses (Alfaro, 2005). High-temperature alterations are related to the system at depth, whereas the presence of kaolinite and iron and aluminum oxides residues are related to surface weathering processes.



**Figure 10: Temperatures and pH conditions for hydrothermal alteration minerals in the PGS. Taken from Alfaro (2005).**

An integrated proposal based on petrological analysis, X-ray diffraction (DRX) and mineral chemistry is presented in table 2. The minerals referenced include both main crystalline phases and alteration minerals, this information complements the knowledge about the argillic intermediate-argillic type alterations of the shallow PGS.

**Table 2. Primary and secondary minerals identified within the shallow PGS. Source: This work.**

Location /unit		Type of sample and rock	Primary Minerals	Secondary Minerals
Alto de los Godos	ALFAGRES quarry	Deposit /Dome	<ul style="list-style-type: none"> <li>• Anortoclase</li> <li>• Sanidine</li> <li>• Microcline</li> <li>• Albite</li> <li>• Quartz</li> <li>• Biotite</li> <li>• Amorphous</li> </ul>	<ul style="list-style-type: none"> <li>• Halloysite 10 A and 7A</li> <li>• Kaolinite</li> <li>• Zeolite</li> <li>• Smectite</li> <li>• Illite</li> </ul>
	CEMEX quarry	Volcanoclastic deposit	<ul style="list-style-type: none"> <li>• Anortoclase</li> <li>• Albite</li> <li>• Quartz</li> </ul>	<ul style="list-style-type: none"> <li>• Smectite</li> <li>• Illite</li> <li>• Kaolinite</li> <li>• Montmorillonite</li> </ul>
	SE Dome	Dome, clay material in fractures	<ul style="list-style-type: none"> <li>• Anortoclase</li> <li>• Sanidine</li> <li>• Albite</li> <li>• Quartz</li> </ul>	<ul style="list-style-type: none"> <li>• Illite</li> <li>• Halloysite 10 A</li> <li>• Sericite</li> <li>• Kaolinite</li> <li>• Tridymite</li> </ul>

## CONCLUSIONS

Porphyritic and fragmented textures were identified in rocks under study, with voids filled by clay minerals, and mafic minerals replaced by oxides. The main minerals found were plagioclase, feldspars, amphibole, and quartz; apatite and zircon as accessory minerals, and clays and iron oxides as alteration minerals. The clay minerals located in the matrix, show good degree of crystallization and are assumed as a byproduct of hydrothermal events. The nuclei of the zoned feldspar phenocrysts have high sodium contents, evolving to a higher potassium content at the edges. This compositional difference could be associated with mixture of magmas. The volcanoclastic deposits and domes are associated to an efficient seal of the shallow PGS by a rocky massive or hardened deposit or a combination of the two, this is inferred by the presence of alteration minerals, mainly clay minerals, which favor an impermeable



layer that insulates hot fluids migrating towards the surface. This hypothesis is supported by the lack of surface expressions of thermal activity such as springs and heated ground in the Alto de los Godos area of the PGS.

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