

## Hydrothermal Alteration in the Geothermal System of the Irruputuncu Volcano Deep Well PGC-01, Northern Chile

Christian Betancourt, Jeanne Vidal, Diego Morata and Santiago Maza

University of Chile, Facultad de Ciencias Físicas y Matemáticas, Andean Geothermal Center of Excellence (CEGA), Plaza Ercilla 803, Santiago, Chile

chris.betanco@gmail.com

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### ABSTRACT

Numerous studies have shown the relationship between alteration mineralogy and the characteristics of a geothermal system, as well as the fluid-rock interaction processes. Various Ca-rich hydrated silicates as epidote, prehnite, zeolites, calcite and anhydrite, together with clay minerals, including diverse chlorite, illite and smectite interstratified, are the most currently developed secondary minerals observed in geothermal systems. These secondary minerals show a number of characteristics which, together with their formation and changes when exposed to different conditions, have been described as dependent on temperature, pH, fluid composition and lithology as the main factors. In this work we present the ongoing study of the alteration mineralogy associated to the geothermal system of the Irruputuncu. This is a currently active volcano with geothermal manifestations such as fumaroles near the craters and hot springs at their base. It is mainly composed by a mixture of andesitic to dacitic lavas and pyroclastic rocks, and built on top of various ignimbrites and older lava flows. Sampling from a continuous drill core gives the opportunity to explore and study how factors such as fluid composition, lithology and permeability are playing a role in the formation of different alteration minerals, and to see how they compare to known first order factors such as fluid temperature and pH. Petrography studies and X-ray diffraction data have shown the presence of calcite and anhydrite in association with mixed-layer clays, particularly illite/smectite, as the main secondary mineralogy. These results, together with a future fluid-inclusions and isotopes study, will allow us to constraint T, pH and fluid composition of the different hydrothermal event(s) developed in this geothermal volcano-related field.

### 1. INTRODUCTION

Currently, there is a constantly growing demand of energy in Chile and the world due to its increasing development. In this scenario, geothermal energy shows up as a viable alternative which is also clean and renewable. Even though Chile has a high geothermal potential (Lahsen, 1988; Aravena *et al.*, 2016), most of its geothermal systems haven't been carefully studied, and their particular characteristics and reservoir location are generally unknown.

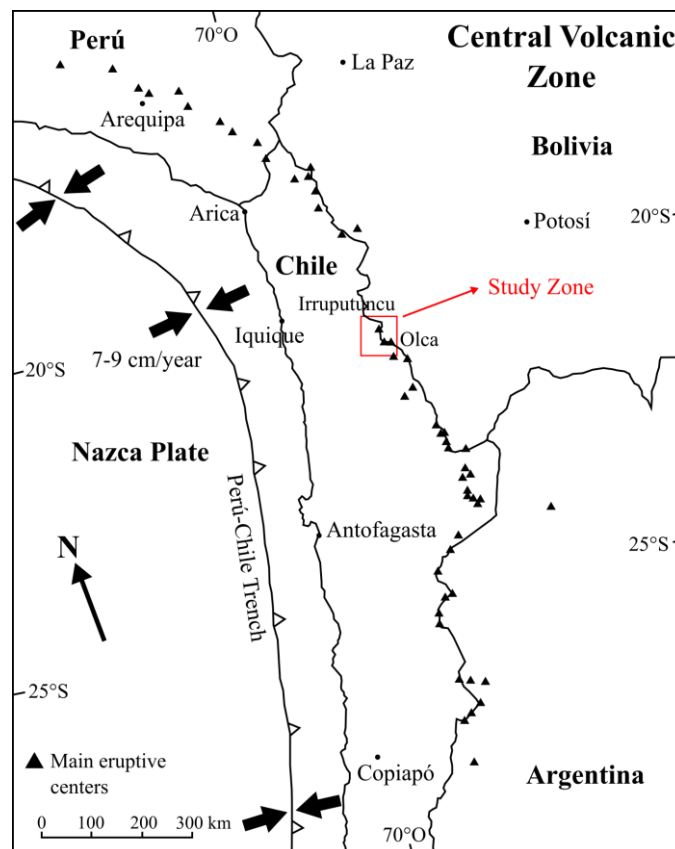
This is the framework in which this project is set, we seek to further study and develop the knowledge of geothermal systems in Chile. To achieve this, we are currently studying the hydrothermal systems associated to two active volcanoes in northern Chile, the Irruputuncu and the Olca volcanoes, from which samples were taken from 4 different boreholes previously drilled by the Doña Inés de Collahuasi Mining Company, two near the Irruputuncu and two near the Olca. The work presented here, focuses in the samples taken from one of the boreholes drilled near the Irruputuncu, labeled as well PGC-01.

The main focus of this study is to see how the different characteristics of a hydrothermal system impact in its alteration processes. To achieve this, we describe and characterize the petrology observed in the well, focusing in both the primary and secondary mineralogy, as well as the variations present along it. This will set the groundwork to further study the hydrothermal system, as it is part of a bigger project associated to the zone.

Particularly, what makes the study zone interesting and sets it apart from most hydrothermal systems, including those located in southern Chile, is the more felsic nature of its volcanism, as well as the presence of different lithologies such as lavas, ignimbrites and sandstones. These characteristics, presents a contrast with the usually basaltic systems that are more widespread in highly developed geothermal areas. That's why the study zone represents an excellent setting to study the effects of these attributes on hydrothermal systems, such as its chemistry or the alteration minerals formed in it.

### 2. GEOLOGICAL SETTING

The Irruputuncu volcano forms part of the Andean Central Volcanic Zone (CVZ) and is located in the border between Chile and Bolivia (figure 1). The volcanism in this zone occurs due to the subduction of the Nazca Plate beneath the South American Plate, and is characterized for presenting andesites, dacites and rhyolites as the dominant erupted rocks, as well as by the presence of extensive and varied pyroclastic deposits such as ignimbrites. Additionally, most of these deposits and outcrops are well preserved thanks to the hyperarid conditions associated with the zone (Stern, 2004).

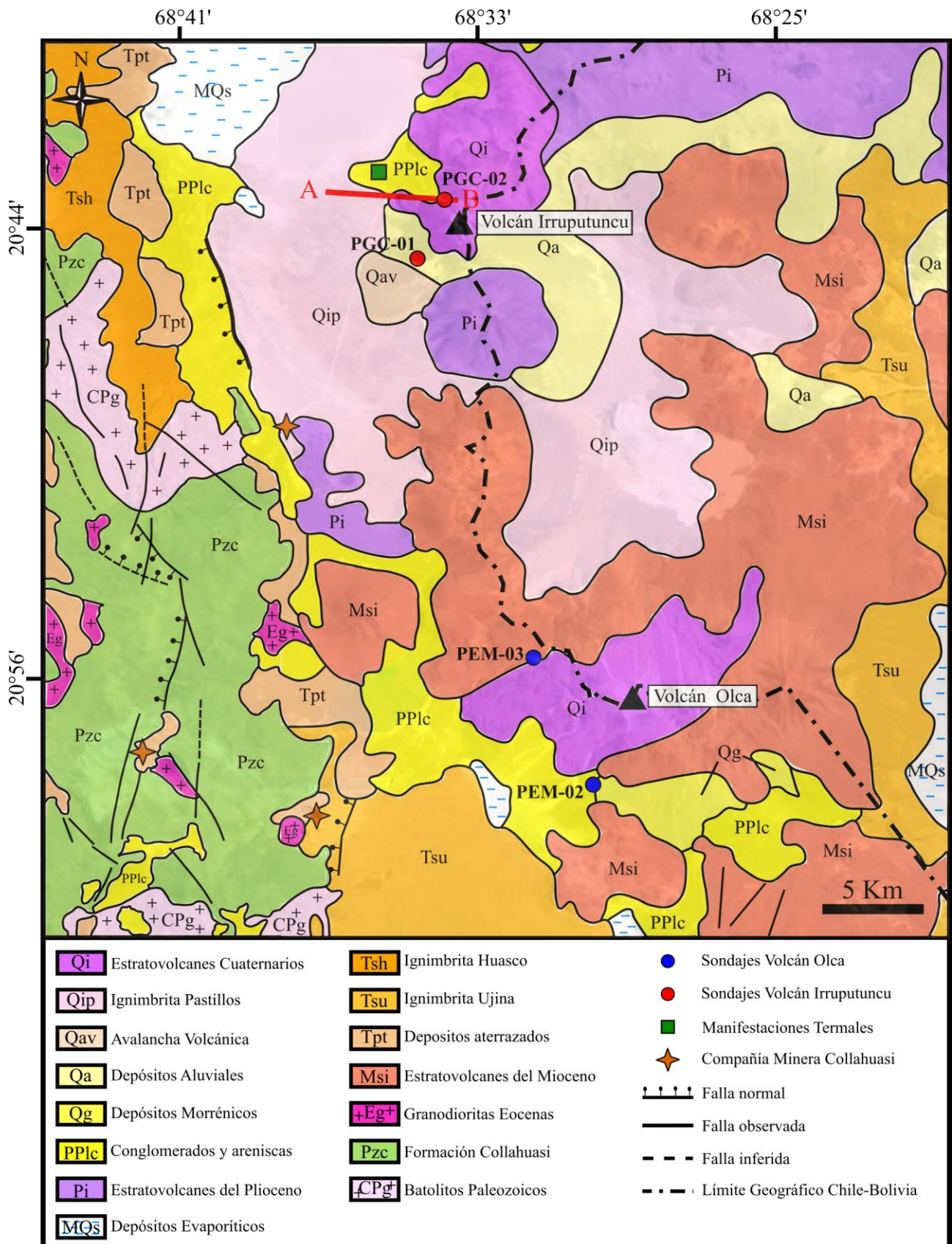


**Figure 1: Irruputuncu and Olca volcanoes located in the CVZ in the Andes Cordillera, in the limit between Chile and Bolivia. The area in the red square represents the study zone. Modified from Stern (2004).**

The Irruputuncu itself is a currently active volcano, with different hydrothermal manifestations such as fumaroles and hot springs (Hauser, 1997; Aguilera, 2008). It has been active since at least the last  $258 \pm 49$  ka (Rodríguez *et al.*, 2015; Wörner *et al.*, 2000) and, similar to most of the volcanoes of the CVZ, is comprised mainly by an intercalation of andesitic and dacitic lavas. Its edifice is built over the different ignimbrites present in the zone, such as the Pastillos Ignimbrite, the Ujina Ignimbrite and the Huasco Ignimbrite (Vergara & Thomas, 1984; Reyes *et al.*, 2011). The disposition of this ignimbrites, as well as the other geological units of the zone, can be seen in figure 2.

Though these ignimbrites are relatively similar between them, they present some differences that should be noted. The youngest one, Pastillos Ignimbrite, is divided in two members, with the upper member being dominated by cinerites and the lower member being mainly tuffs and laharic deposits with low welding. Underlying this, in concordance is the Ujina Ignimbrite, which has a basal section, as well as sporadic lenses, of disaggregated pyroclastic material. The upper section of the ignimbrite is comprised mainly of welded tuffs. Finally, in discordance, is the Huasco Ignimbrite, which is a dacitic to rhyolitic tuff that varies from partially to totally welded (Vergara & Thomas, 1984).

The basement in the zone corresponds to the Collahuasi Formation, which is a mainly a volcanic unit of andesitic to rhyolitic compositions, intercalated with lenses of sedimentary rocks. It is divided in three members, with the lower member consisting of rhyolites and dacites, the middle member being mainly andesites, and the upper one comprised again by rhyolites and dacites. The sedimentary intercalations are observed along all three members and consist mainly of non-fossil sandstones and conglomerates. The estimated thickness of this formation is  $\sim 3200$  m, with  $\pm 1100$  m corresponding to the upper member,  $\pm 400$  m to the middle and  $\pm 1700$  m to the lower member (Vergara & Thomas, 1984).



**Figure 2: Geological map of the study zone. Marks represent the 4 wells, as well as the locations of the Doña Inés de Collahuasi Mining Company mine sites. Modified from Vergara & Thomas (1984).**

Finally, previous geophysical studies in the zone have shown the presence of a high resistivity zone below the Irruputuncu, which was associated to the presence of a geothermal reservoir. This zone is below a relatively shallow low resistivity zone which in hand was associated to a clay cap. An example of these studies can be seen in figure 3 and its location is shown in figure 2.

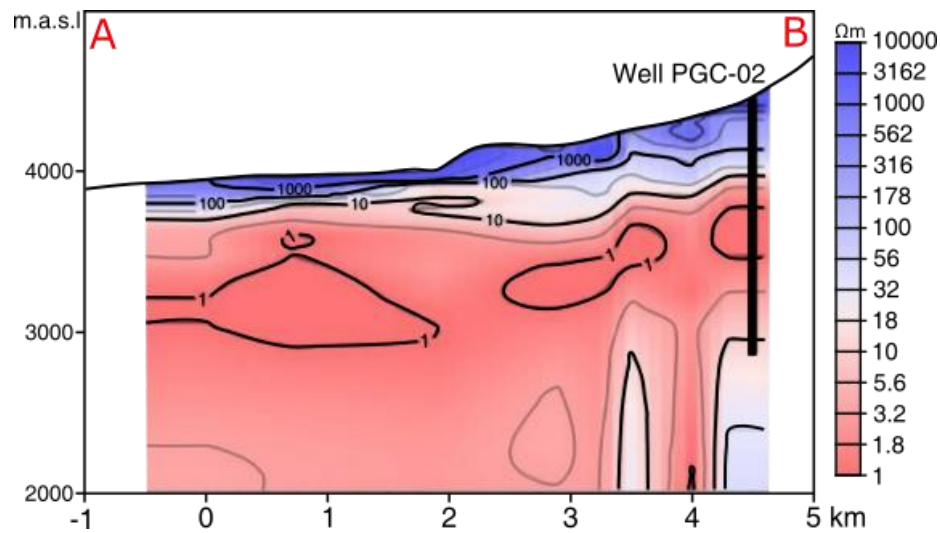


Figure 3: MT resistivity profile near the Irruputuncu volcano. Modified from Reyes *et al.*, (2011).

### 3. METHODOLOGY

In the framework of this project, 273 samples have been taken from 4 different boreholes which were previously drilled by the Doña Inés de Collahuasi Mining Company in the study zone (figure 2). From these samples, 55 were taken from the PGC-01 borehole, and correspond to the ones considered for this study. These samples were chosen according to their lithology and the presence of hydrothermal alteration, selecting those that presented a change in lithology, alteration or presented zones of interest such as veins or amygdaloids.

After selecting the samples, one or more polished thin sections were made from them, in order to further study their lithology. This was accomplished by doing a description of the samples using the petrographic microscope, in which we were able to recognize the different minerals and textures present in the rocks, as well as any particular features of the sample.

The mineralogical analysis was further developed through the use of a scanning electronic microscope (SEM) and x-ray diffraction (XRD). SEM was mainly used to study the different textural and morphological characteristics of the minerals, as well as to obtain the broad chemistry of certain minerals. The XRD was used mainly to identify the clay fraction present in the samples. The separation of the clays, as well as its analysis, was done using the procedures and methodology described by Moore & Reynolds (1997).

Petrographic microscope, SEM analyses and separation of clay fractions were performed in the Geology Department of the University of Chile, using the equipment and laboratories provided by the Andean Geothermal Center of Excellence (CEGA). XRD analyses were realized in the Laboratory of Crystallography and X-ray Diffraction of the University of Chile, using a Bruker D8 Advance diffractometer.

### 4. RESULTS

#### 4.1 Hand Sample Description

From a macroscopic perspective, the variations present along the well are rather subtle. Most of the well consists of consolidated rocks, with colors ranging in tones of grey or, in particular cases, slightly more purple. Nevertheless, there are some zones along it that show unconsolidated and extremely friable rocks, with all of them being found above the 270 m of depth. Examples of both type of rocks can be seen in figure 4.

In the case of the consolidated rocks, most of them show a pyroclastic texture with lithic fragments of size between 0.5 and 15 cm immersed in a finer ash matrix. Although, crystals are also visible in most samples, identifying them reliably in hand sample is impossible. Differentiating between pyroclastic units is also difficult in hand samples since most of them look relatively similar. Some of the observed differences are subtle variations in color, lithic fragments and crystals. Besides these pyroclastic units, samples resembling sedimentary rocks start to appear, starting at a depth of 387 m and up until the last samples taken at 428 m. These samples, in contrast with the pyroclastic rocks described above, have a much finer grain size, a better selection and have a slightly more purplish color.

Regarding the alteration present in the samples, most of them don't look heavily altered, preserving most of their original features. In cases where alteration is present and visible in hand sample, it's usually seen either on veins or in the matrix. In the case of the veins, there are different fillings depending on the samples, but it's not possible to identify the mineralogy. On the other hand, when the alteration is observed in the matrix, this makes its usually whiter colors take more yellow or green tones.





**Figure 4:** Here we show two examples from the PGC-01 well. Image (A) represents the consolidated samples which are most common along the well, while (B) is an example of the unconsolidated samples found in specific zones.

#### 4.2 Primary Petrography

As it was mentioned in the hand samples description, the well is mostly comprised of either pyroclastic or sedimentary rocks. This is further noticeable when studying the polished thin sections under the microscope, where both rock types are clearly evident.

Starting with the pyroclastic rocks, most of these samples are rather alike, presenting similar mineralogy, textures and lithic fragments. In general, most of them can be classified as crystalline tuffs, but still, there are some subtle differences that allow recognizing different units in this group.

In the case of the mineralogy, the most widespread and common mineral is plagioclase, followed by biotite. Both are present in almost all of the samples and represent the greater proportion of the crystals. Other primary minerals, such as hornblende, quartz and feldspar are also common, but are rather not present in all of the samples in the case of hornblende or, in the case of quartz and feldspar, represent a low number of the crystals. In general, mineral crystals comprise around 40-60% of the samples, with the rest of it being the ash matrix and lithic fragments.

Beside crystals, the pyroclastic rocks also show lithic fragments in almost all of the samples, which usually vary in size, quantity and in composition. The size of these fragments, as seen on hand samples, go up to ~15 cm while on the microscope fragments as small as 1 mm can be recognized. Regarding quantity, it varies greatly between sample and different units, but it is usually less than 20% of the sample. The composition of the fragments, on the other hand, is either andesitic or dacitic lavas, with both showing a noticeable porphyritic texture. The andesitic fragments have plagioclase, biotite and hornblende phenocrysts immersed in an intergranular groundmass, while the dacitic fragments usually display plagioclase and feldspar phenocrysts in a felsitic groundmass.

Lastly, all of the samples show a pyroclastic texture, as it has been said before, but some of the samples also present varying amounts of spherulitic and axiolitic textures. These textures are seen on glass rich or welded tuffs, which are more common in the first 200 m of the well. Other common textures that can be seen in most of the samples are minerals zoning and reabsorption, which are usually seen in plagioclase and quartz respectively.

On the other hand, sedimentary rocks in the well are observed starting at 387 m depth down until the last sample taken at 428 m. These rocks are comprised mainly of relatively well-rounded crystals of quartz and feldspar, with a varying amount of well-rounded lithic fragments (10-25%) depending on the sample.

#### 4.3 Alteration Petrography

There are varying degrees of alteration present in all of the samples taken from the well, with the main differences between them being the mineralogy present, its intensity and its style. Examples of these alteration can be seen in figure 5, while a summary of it is shown in figure 6, as well as the samples taken and the primary lithology of the well.

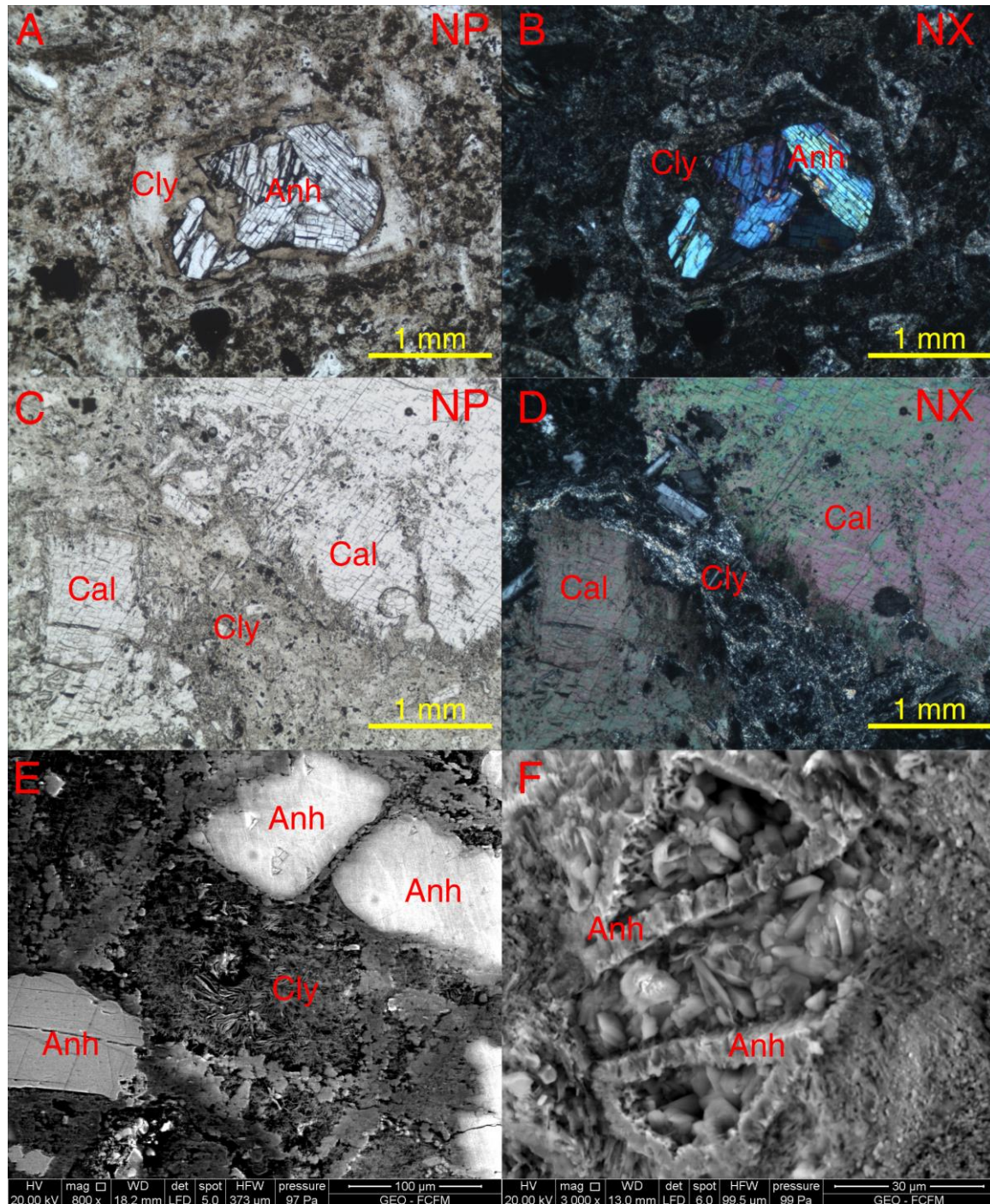
In the case of the mineralogy, the most common and widespread secondary minerals are calcite, anhydrite and clays. Calcite is present in most of the well, either replacing primary minerals, mainly plagioclase, or filling veins and vesicles. Anhydrite, on the other hand, starts appearing predominantly below 200 m depth, and becomes a constant part of the alteration from that point onward. As calcite, anhydrite is seen as either replacement of primary minerals or filling veins and vesicles. In the case of clays, they are seen in most of the samples replacing the glass and crystals present in the matrix, and in some samples, they can be seen replacing primary minerals. XRD analysis showed that the clays present in the samples are chlorite, illite and kaolinite, as well as different interstratifications of illite/smectite (I/S) and chlorite/smectite (C/S). Other alteration minerals present in the samples, but not as commonly or widespread as the ones mentioned above are quartz, epidote, gypsum, chalcedony and pyrite. Quartz and chalcedony can be seen filling veins in some samples, with quartz sometimes replacing the matrix along with clays, while epidote is seen only below 387 m depth as fine grains and in extremely small amounts. Lastly, pyrite is seen either replacing some of the mafic minerals or filling veins.

Regarding the alteration intensity and style, there are two really distinct groups that can be recognized in the samples. The first one corresponds to a low intensity and selective alteration that can be seen throughout all of the samples. This affects predominantly the glass matrix of the samples and, in a lesser degree, the mafic minerals. It's composed mainly of clays and calcite, while at deeper



levels anhydrite also starts to appear. It increases gradually towards greater depths, but it's a relatively subtle increase and tends to be overridden by the second type of alteration. This one is a high intensity and selective alteration which, unlike the low intensity alteration, is located in limited zones scattered along the well. In these zones, the primary minerals, as well as the textures, start getting obliterated by the alteration, making them harder to recognize, only with plagioclase retaining most of their integrity. The secondary minerals associated to the high intensity alteration are usually the same as the low intensity but are notably more developed.

Finally, as mentioned before, there are several veins along the well filled by different secondary minerals. Not only do they vary in terms of mineralogy, but also in their orientations. Most of the veins present a vertical to sub vertical orientation and are filled generally with anhydrite, and in particular cases, quartz and/or pyrite. Still, some horizontal veins were also recognized with similar filling than the previous ones, with the exception of pyrite.



**Figure 5: Examples of the alteration mineralogy in different samples as seen through petrographic microscope (A, B, C & D) and SEM (E & F). Images (A) and (B) show the complete replacement of a mafic mineral by anhydrite in its core and illitic minerals in the rims, while (C) and (D) show calcite filling spaces and illitic minerals replacing the matrix. Images (E) and (F) also show the replacement of primary minerals by illitic minerals and anhydrite. Abbreviations: Anh=anhydrite, Cal=calcite and Cly=illitic mineral.**

## 5. DISCUSSIONS

### 5.1 Physicochemical Conditions

The secondary minerals observed in the well are able to shed some light into the characteristics of the mineralizing fluids, such as temperature, pH and chemistry. This is thanks to the high amount of studies conducted in hydrothermal systems that have shown the relation between alteration minerals and the fluids that formed them (Browne, 1978; Hedenquist *et al.*, 1989; Reyes, 1990; Moore *et al.*, 2001; Moore *et al.*, 2008; Milicich *et al.*, 2018), particularly those in veins, since they usually precipitate directly from the fluids.

Starting with the temperatures, many of the minerals present in the well, such as calcite and quartz, fail to help constraining them since they can be found at a wide range in hydrothermal systems. Nevertheless, minerals like chalcedony, as well as the presence of interstratified smectite, usually reflect formation temperatures below 200°C (Hoffman & Hower, 1979; Inoue *et al.*, 1991; Abid *et al.*, 2004), which in part is consistent with the relatively low intensity of alteration observed along the well. On the other hand, epidote is a mineral associated to higher temperatures (>180°C), but the crystals observed could be classified as “incipient” epidote (Reyes, 1990), which reflects the lowest formation temperature for this mineral. Still, the appearance of epidote correlates with a higher depth, which should also mean slightly higher temperatures. Similar to epidote, the presence of clays such as chlorite and illite are usually associated to higher temperatures in hydrothermal systems (Lowell & Guilbert, 1970; Tittley *et al.*, 1986; Meunier, 2005), but its appearance along the well seems to indicate that other factors such as lithology could be controlling its formation (Lopez-Munguira *et al.*, 2002; Meunier, 2005; Vázquez *et al.*, 2014). Lastly, anhydrite is also a mineral that can be found at a wide range of temperatures, yet in hydrothermal settings, it is most commonly associated with temperature above 200°C (Muramatsu *et al.*, 2000), which contrasts with the temperatures mentioned above, especially in samples at lower depths. This could indicate that formation of anhydrite in this system is controlled by other factors, such as fluid chemistry, rather than temperature.

In the case of the fluid composition, most of the alteration suite reflects a more neutral pH for them, with the exception of the kaolinite found at ~260 m depth. Even though kaolinite is usually associated to a more acid alteration (Reyes, 1990), its limited appearance could be controlled by a lithological component rather than the fluid composition (Arostegui *et al.*, 2006; Vázquez *et al.*, 2014). The presence of anhydrite on the other hand indicates that the fluids that formed them were highly oxidizing in nature, yet its disappearance at shallower parts of the well, which matches with the appearance of pyrite veins in some samples. This could reflect a shift in the fluids composition towards a more reducing nature during its ascension.

### 5.2 Fluids Origin

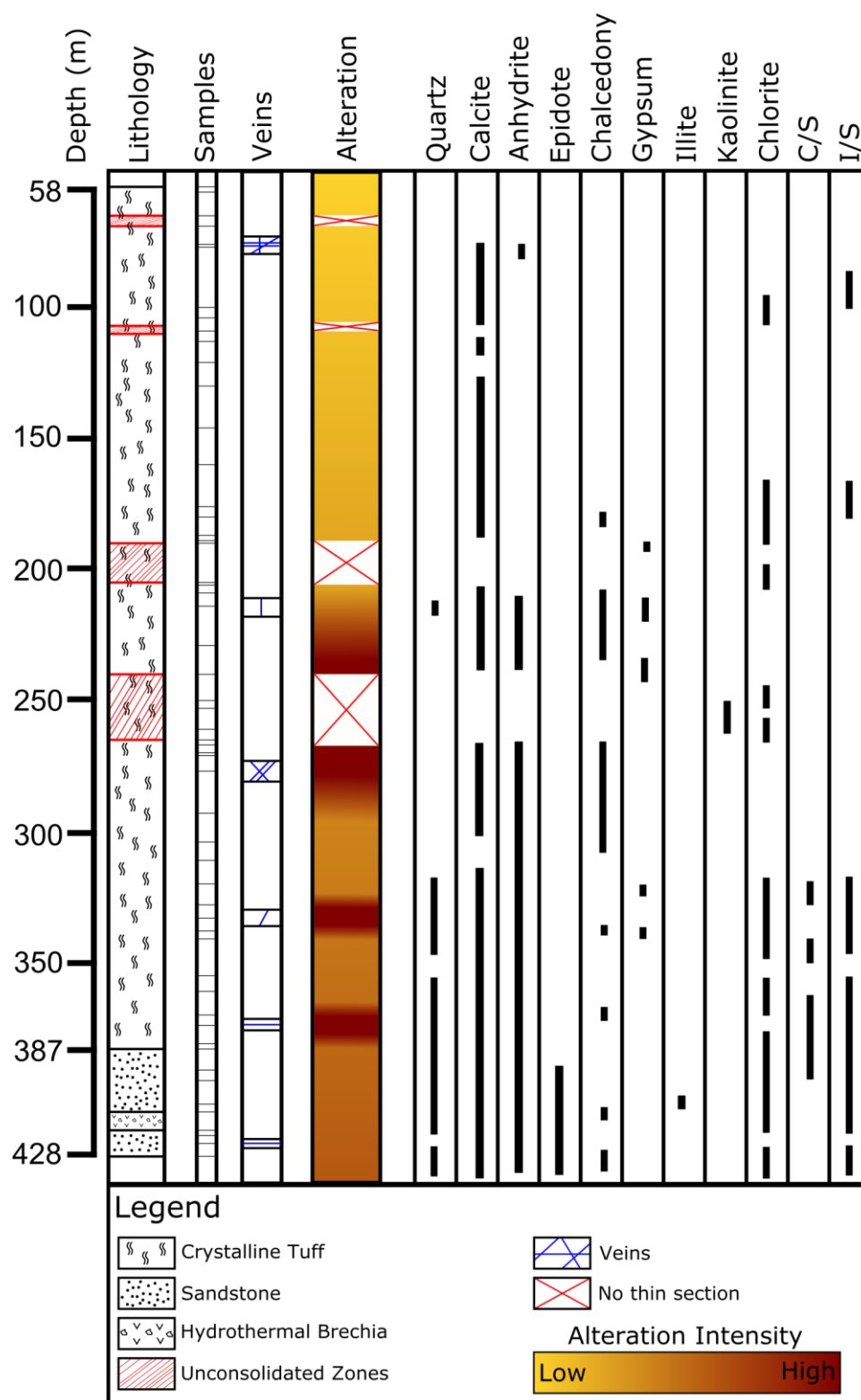
Even though it's hard to determine the origin of the fluids without further studies, the fact that anhydrite is such a widespread and common mineral along the well give us some indication regarding which the main input in the system could be. The formation of this mineral is tied to highly saline and S-rich fluids (Bock, 1961; Dixon *et al.*, 2015), which could be explained more easily by the presence of a mainly magmatic fluid rather than a meteoric one. Still, this can also be explained through a meteoric recharge influenced by the presence of the Coposa Salt Flat in the study zone, which could also provide the fluids required to form anhydrite without the need of a predominantly magmatic input.

### 5.3 Alteration Control

The style, intensity and mineralogy of the alteration observed in the well indicate that temperature isn't the main control during its formation, or at least is as important as features such as fluid chemistry, lithology and primary permeability (Arostegui *et al.*, 2006; Vázquez *et al.*, 2014).

For fluid chemistry, the main example of its importance is the presence of anhydrite, which as it has been said above, its formation temperature is usually higher than the range proposed for the well. This means that, in the case of anhydrite, the fluid chemistry could be playing more important role than temperature, which explains why it develop so easily in the 100-200°C range (Bock, 1961; Dixon *et al.*, 2015).

Likewise, the alteration intensity and style also seem to be heavily controlled by factors other than temperature. Most of the samples where veins are present the host rock alteration changes drastically, increasing notoriously its intensity in their vicinities. In these zones, samples start getting obliterated and crystals replacing the primary mineralogy are better developed, which in part shows the importance of these higher permeability zones as controllers of the alteration, even though is only locally. This is also true in most of the samples near zones of unconsolidated rock, which could indicate that these zones also represent a higher permeability regime in comparison to the rest of the well.



**Figure 6: Lithology, samples taken, distribution of secondary minerals and alteration intensity observed in the PGC-01 well. Veins presence is also shown with their broad orientation.**

## 6. CONCLUSIONS

The hydrothermal alteration observed in well PGC-01 reflects the significance of other factors besides temperature in the formation of secondary minerals. The presence of most of them, as well as the intensity and style of the alteration, indicate that they formed at temperatures below 200°C, yet minerals associated with higher temperatures, such as anhydrite, are common along the well. This leads to the assumption that other factors must be playing a significant role in the formation of this minerals. In the case of anhydrite, fluid chemistry could be the main determinant on whether it develops, while the presence of kaolinite in a rather neutral suite reveals that lithology could also be playing an important role. The same goes to the intensity of the alteration, were the primary permeability and the presence of veins seems to be a significant factor in how it develops.



Nevertheless, the conclusions presented here still require further work in order to be conclusive. As mentioned previously, this work is the beginning of a series of studies that will be developed in the 4 wells obtained from the zone, which will help us further into understanding the geothermal systems associated to the Irruputuncu, as well as the Olca. Likewise, it will also give us more information on how the different variables present in both systems are affecting its alteration and whether they are as important as temperature.

## ACKNOWLEDGMENT

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