

First Results of the Vein Alteration in the Deep Well PGC1 of Irruputuncu Geothermal System, Andean Cordillera, Northern Chile

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ABSTRACT

The geothermal potential of the Irruputuncu active stratovolcano was explored with two magnetotelluric-transient electromagnetic campaigns as well as two deep exploration wells between 2009 and 2011. In this study, core samples from the first well PGC1 were investigated in order to estimate the hydrothermal alteration in the rock formations from 58 to 428m depth. The well intersects tuffs with fragments of andesitic and dacitic lavas and sedimentary rocks in the deepest part. X-Ray diffraction applied to the clay fraction allowed to identify the vertical distribution of the clay minerals along the well. In addition, microscopic observations of the alteration petrography give information about mineral parageneses associated to the hydrothermal events. The alteration petrography of core samples along the well PGC1 indicate a superimposition of several hydrothermal events. Quartz + Pyrite + Illite + R3 I/S ml + Chlorite + Corrensite + Anhydrite + Kaolinite + Opale observed are relicts of early hot stages (>150°C). Late stages lead to crystallization of Smectite + R1 I/S ml under temperatures close to the actual ones (≈150°C). These minerals are observed as replacement of vitreous matrix and selective or total replacement of primary minerals but also in veins. The hydrothermal history seems complex and dominated by various factor such as temperature, physico-chemical properties of the fluid chemistry, time... Further petrographic investigations should be carried out in samples in order to better understand the mineralogical relationships and better constrain the hydrothermal history in the Irruputuncu geothermal field.

1. INTRODUCTION

During the last 20 years, geothermal exploration has been very active in Chile with a desire for energy emancipation from importation of fossil fuels. The Andean geothermal potential is mostly linked to the volcanism generated as a consequence of the subduction of the Nazca Plate under the South America Plate. In 2010, two deep exploration wells were drilled in the flank of the Irruputuncu active volcano (Pica, Northern Chile). The present study focuses on the first mineralogical investigation of argillic alteration in the first exploration well PGC1.

Studies of several geothermal fields in the world indicate that clay minerals are widespread alteration products in most active and fossil geothermal systems. Because they are very sensitive to temperature, rock and fluid chemistry, time, fluid/rock (F/R) ratio, etc, they are good indicators of hydrothermal history of the geothermal field (Beaufort et al., 1996, 1992; Harvey and Browne, 1991; Inoue and Kitagawa, 1994; Inoue and Utada, 1983; Ji and Browne, 2000; Lonker et al., 1990; Mas et al., 2006; McDowell and Elders, 1980; Patrier et al., 1996; Roberson and Lahann, 1981; Simmons and Browne, 1998; Vazquez et al., 2014; Vidal et al., 2018). The temperature is a main parameter in the reaction progress of the clay minerals, but rock and fluid chemistry, time or F/R ratio also affect their structure (coherent domain size in c-direction, mixed layering) as well as their composition, texture and association with other hydrothermal mineral phases. Consequently, the properties of the clay minerals are potential markers of the past or present thermal conditions in which clays crystallized and could help to localize the zones of present-day and paleo permeability in the well.

The cored slim well PGC1 is a unique chance to observe the several stages of alteration in depth, poorly investigated in Chilean fields so far. This study presents the first geological results of the hydrothermal alteration. A special attention will be paid on clay minerals and alteration petrography linked to veins that intersected the core samples.

2. GEOLOGICAL SETTINGS

Irruputuncu (5163 m a.s.l) is an active stratovolcano of the Central Andean Volcanic Zone (CAVZ) in Northern Chile (Figure 1). It is mostly composed by dacitic lava flows, dacitic lava domes, block-and-ash and pyroclastic flow deposits, intercalated with minors tuffs and breccias (de Silva and Francis, 1991). It is one of the youngest active volcano with a production of andesitic to trachy-andesitic magmas over at least the last 258 ± 49 ka (Rodríguez et al., 2015). It presents two craters aligned NE-SW, the southernmost has a diameter of 200 m and is still being active with an intense fumarolic activity. The fumarolic discharges showed outlet temperatures ranging from 83°C to 240°C while gas phases consist of highly concentrated SO₂ and H₂S (Tassi et al., 2011). The chemical and isotopic compositions of these discharges were similar to other active volcanoes in the CAVZ indicating mixing between magmatic, hydrothermal and meteoric fluids. Inorganic and organic gas geothermometers for the H₂O-CO₂-CO-H₂, CO₂-CH₄ and C₂-C₃ alkenes-alkanes systems indicated equilibrium temperatures that exceed 500°C at the gas sources. These relatively high temperatures are in agreement with the presence of relevantly high concentrations of magmatic gas emissions, including SO₂. Superficial alteration associated to this fumarolic activity was not investigated yet in term of mineralogy. A 3-D inversion of TEM-MT has shown the presence of a high resistivity zone interpreted as a high temperature geothermal reservoir (>250°C, Reyes et al., 2011). This zone is below a relatively shallow low resistivity zone which in hand was associated to a clay cap.

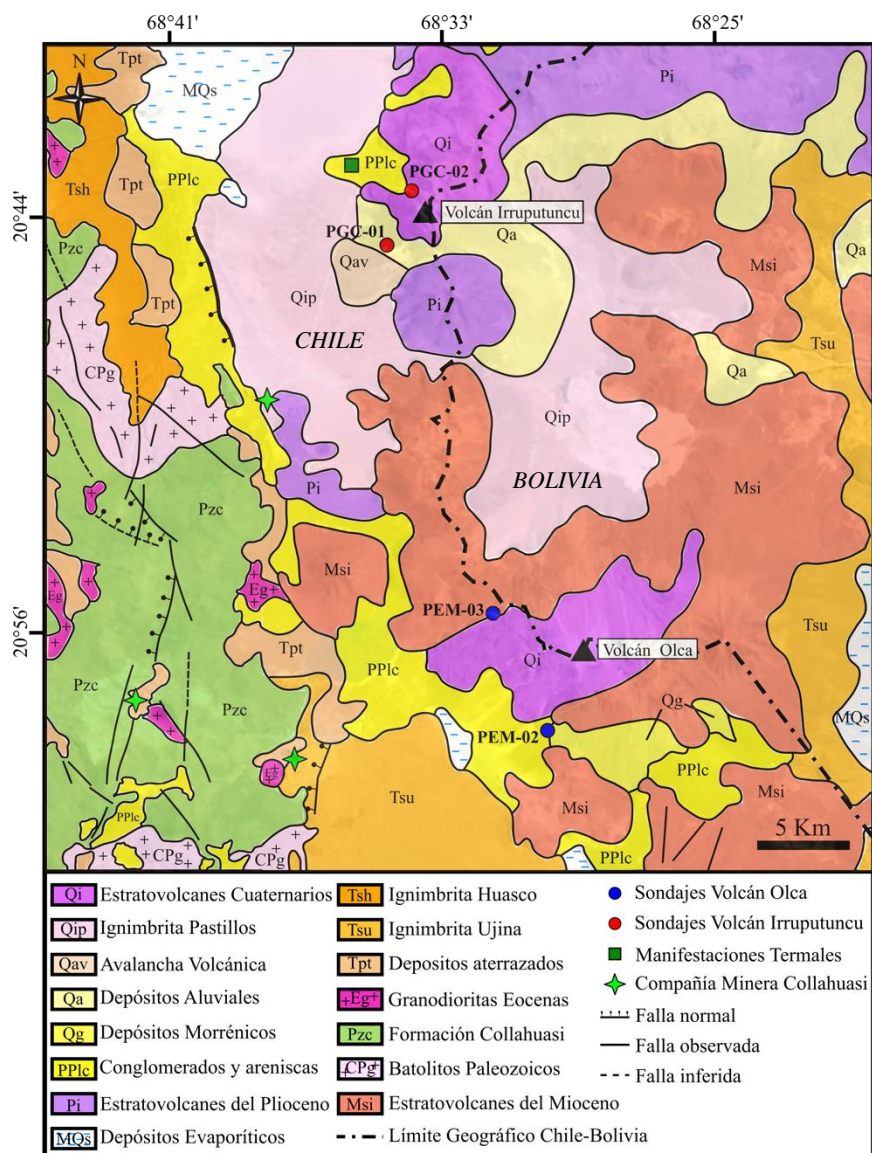


Figure 1 Geological map of the Irruputuncu and Olca volcanoes with the four exploratory wells (after Vergara and Thomas, 1984)

The exploratory slim well PGC1 was drilled in the south-western flank of the Irruputuncu volcano by Doña Inés de Collahuasi Mining Company (CMDIC) in the framework of an exploration of geothermal resources in the proximity of its copper mining (Reyes et al., 2011). The well reached ~800m MD (Measured Depth) and the temperature profile indicates a conductive regime with a temperature of ~150°C at 700m (i.e 3350 m a.s.l; Reyes et al., 2011). The rocks encountered in the well are mostly pyroclastic or sedimentary (Betancourt et al., 2020).

The upper part of the well is composed by crystalline tuffs with fragments of andesitic and dacitic lavas (Figure 2) (Betancourt et al., 2020). The andesitic fragments present mostly plagioclase followed by biotite and hornblende phenocrysts immersed in an microlithic groundmass, whereas the dacitic fragments mostly display plagioclase as well as primary quartz and alkali feldspar phenocrysts in lower amount in a felsitic groundmass. In general, minerals crystals comprise around 40-60% of the samples, with the rest of it being the ash matrix and lithic fragments. The size of the andesitic and dacitic fragments vary from 1mm to ~15 cm and their quantity varies greatly between sample, but usually is less than 20%. Most of the samples show a pyroclastic texture and the ones from 58 to 244m MD which display some spherulitic and axiolitic textures resulting from glass devitrification. Other common textures that can be seen in most of the samples are minerals zoning, which are usually seen in plagioclase and quartz respectively. The texture of samples from 244 to 271m cannot be observed because these samples are unconsolidated. In the deepest part of the well below 387m MD, the drill hole crosscuts sedimentary rocks intercalated with andesitic rocks from 411 to 420m MD. The sedimentary intercalations mainly consist of sandstones and conglomerates (Vergara and Thomas, 1984). These rocks are composed mainly by quartz and plagioclase and alkaline feldspar, with a varying amount of andesitic fragments (10-25%) (Betancourt et al., 2020).

Some veins were observed along the length of the well. They do not only vary in terms of mineralogy fillings, but also in their orientations. A special attention will also be paid in this paper on the clay alteration in order to identify hydrothermal events that occurred in the well.

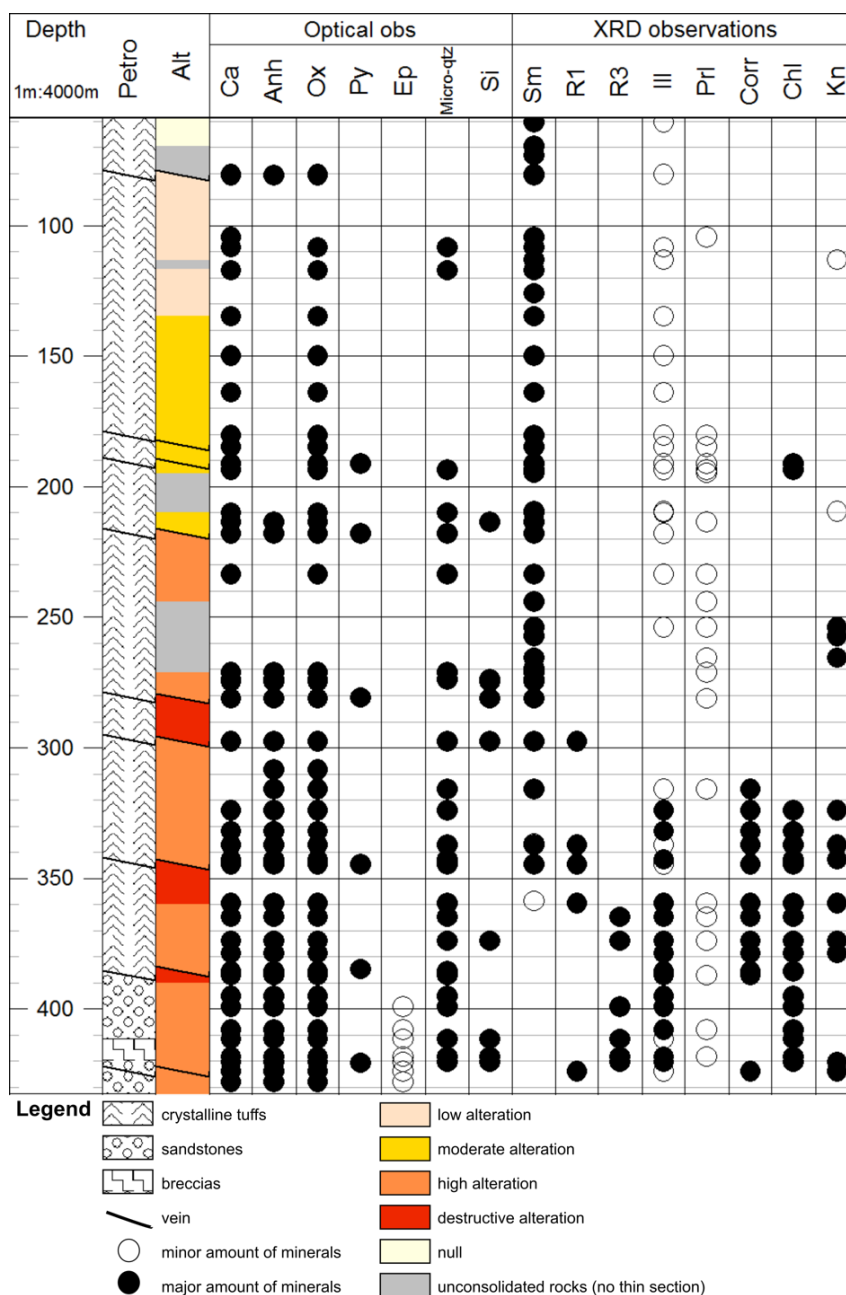


Figure 2 Petrographical log of the well PGC1 with the alteration and occurrences of minerals with depth. Anh = anhydrite, Ca = calcite, Chl = chlorite, Corr = corrensite, Ep = epidote, Ill = illite, Kn = kaolinite, Ox = oxides, Ptl = pyrophyllite, Py = pyrite, Sm = smectite (+R0 I/S ml), Qtz = quartz, R1 & R3 = illitic-smectite mixed layers, Si indicates the different form of chalcedony or opal

3. ANALYTICAL METHODS AND SAMPLES PREPARATION

In total, 55 rock samples were collected in PGC1 from 58 to 428m MD. Polished thin sections were made in order to further study their lithology and mineralogical compositions. A description of the samples including mineralogy, texture, the style and intensity of the alteration as well as any particular features was made using a petrographic microscope.

Some observations were also carried out with a scanning electron microscope JEOL JSM-IT500 SEM equipped with a BRUKER linxeye Energy dispersive spectrometer EDS associated with SPIRIT software at the IC2MP laboratory at the University of Poitiers. Preliminary chemical compositions were acquired in order to make a first order identification of secondary minerals developed in the groundmass or as vein filling.

X-Ray diffraction (XRD) analysis were conducted on the clay fraction of 52 samples. Samples were crushed with a large iron mortar. The fraction $<2\mu\text{m}$ was separated by sedimentation and then deposited onto glass slides. XRD data were acquired with a Bruker D8 Advanced diffractometer with Cu-K α radiation with a Bragg–Brentano geometry at the Department of Physics in the Faculty of Sciences and Engineering of the University of Chile. For 23 samples containing expandable phases, the clay fraction was Ca-saturated (CaCl₂, 1 N), in order to minimize the hydration heterogeneity of smectite interlayers and then analyzed with a Bruker D8 Advance diffractometer (CuK α radiation, 40 kV, 40 mA) at the University of Poitiers. Because all the XRD patterns were not acquired with the same diffractometer, the microstructural properties of the clays cannot be compared (FWHM, area...).

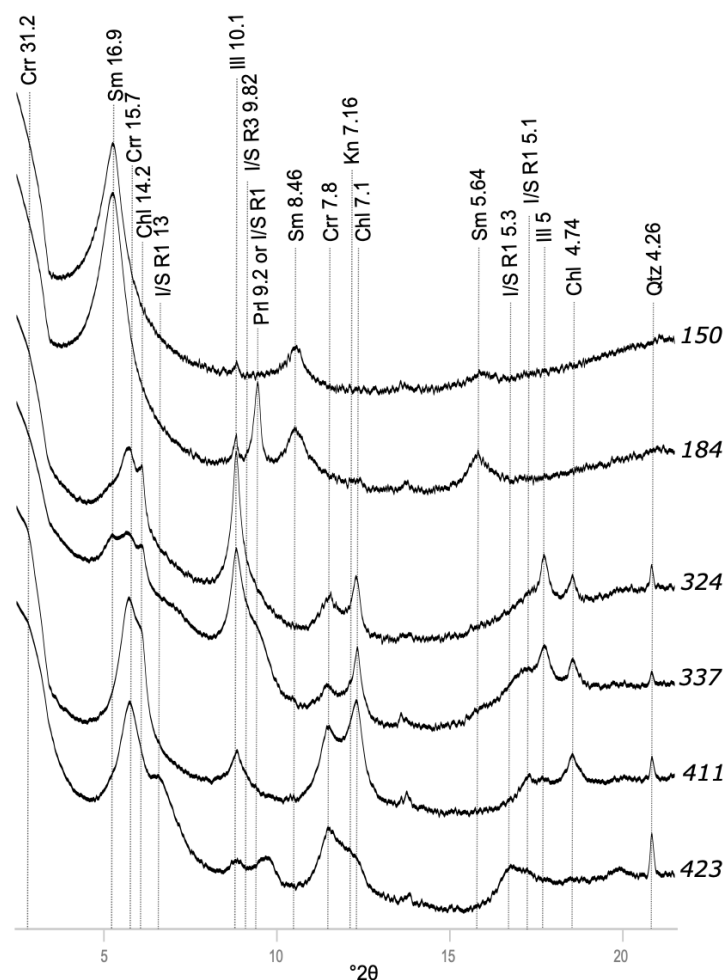


Figure 3 X-Ray diffractograms of the clay fraction in the well PGC1 at 150m, 184m, 324m, 337m, 411m and 423m MD. Ethylene-glycol saturated samples. Chl = chlorite, Corr = corrensite., Ill = illite, Kn = kaolinite, Prl = pyrophyllite, Sm = smectite, Qtz = quartz, R1 & R3 I/S = illitic-smectite mixed layers

XRD data were analyzed using the *Match! Software* (Crystal Impact). Illite was identified with the typical (00 l) reflections at 10 Å and 5 Å; the chlorite at 14.2 Å, 7.10 Å and 4.74 Å; the kaolinite at 7.16 Å and 3.58 Å; the pyrophyllite at 9.2 Å; the smectite at 16.9 Å, 8.46 Å and 5.64 Å on ethylene-glycol saturated oriented preparation (Brindley and Brown, 1980). Illite-smectite mixed layers (I/S ml) and corrensite have been determined comparing the air-dried (AD) and ethylene glycol (EG) treated oriented specimens. Illite proportion and the ordering of I-S mixed layers was usually determined by the position of the (001) and (002) reflection in EG specimen (Brindley and Brown, 1980). The R0 I/S ml are associated to smectite and equally called smectite in this study (Figure 2). Corrensite was identified based on a typical superstructure reflection at 31.2 Å and its typical harmonic reflections (Beaufort et al., 1997; Brindley and Brown, 1980).

4. RESULTS

The intensity of the alteration was determined based on Gifkins et al. (2005) (Figure 2). XRD patterns indicate an evolution of clay minerals with depth (Figure 3). At shallow depth, smectite dominate from 60 to 275m MD with locally chlorite and kaolinite (Figure 2). The deepest part, from 275 to 425m MD, is a more complex clay zone suggesting a superimposition of several alteration events.

4.1. The shallow zone dominated by smectite (60-275m MD)

In this zone, samples do not look heavily altered, preserving most of their original textures and mineral components. The alteration increases gradually towards greater depth from null to high (Figure 2). The alteration is dominated by smectite and affects predominantly the vitreous matrix of the samples and, in a lesser degree, the mafic minerals. Sometimes, smectite is associated with calcite in replacement of biotite and hornblende. Smectite is also observed in veins (Figure 4a, b & c). The preliminary chemical results indicate significant amount of magnesium suggesting a predominance of montmorillonite. Minor amount of illite and pyrophyllite were observed in XRD patterns but not microscopically. Locally, some chlorite and kaolinite are identified by XRD. Kaolinite is observed in XRD patterns but not microscopically on thin sections because they are located in unconsolidated formations. Chlorite was observed as large crystallites in the edges of the vein at 191m MD. These large crystallites of chlorite as well as pyrite in the center of the vein seem slowly replaced by later smectite (Figure 4a). The vein that intersects the sample at 191m MD also presents anhydrite under several habitus that are locally replaced by smectite (Figure 4b). Another vein at 218m MD indicates pyrite and quartz, locally replaced by anhydrite and finally, smectite (Figure 4c). This vein is the interface between moderate and high alteration. Besides of veins of pyrite and anhydrite, veins of calcite associated with oxides and a late crystallization of anhydrite were observed at 80m MD as well as blade shaped calcite that are characteristic of boiling zones (Simmons and Christenson, n.d.; Tulloch, 1982).

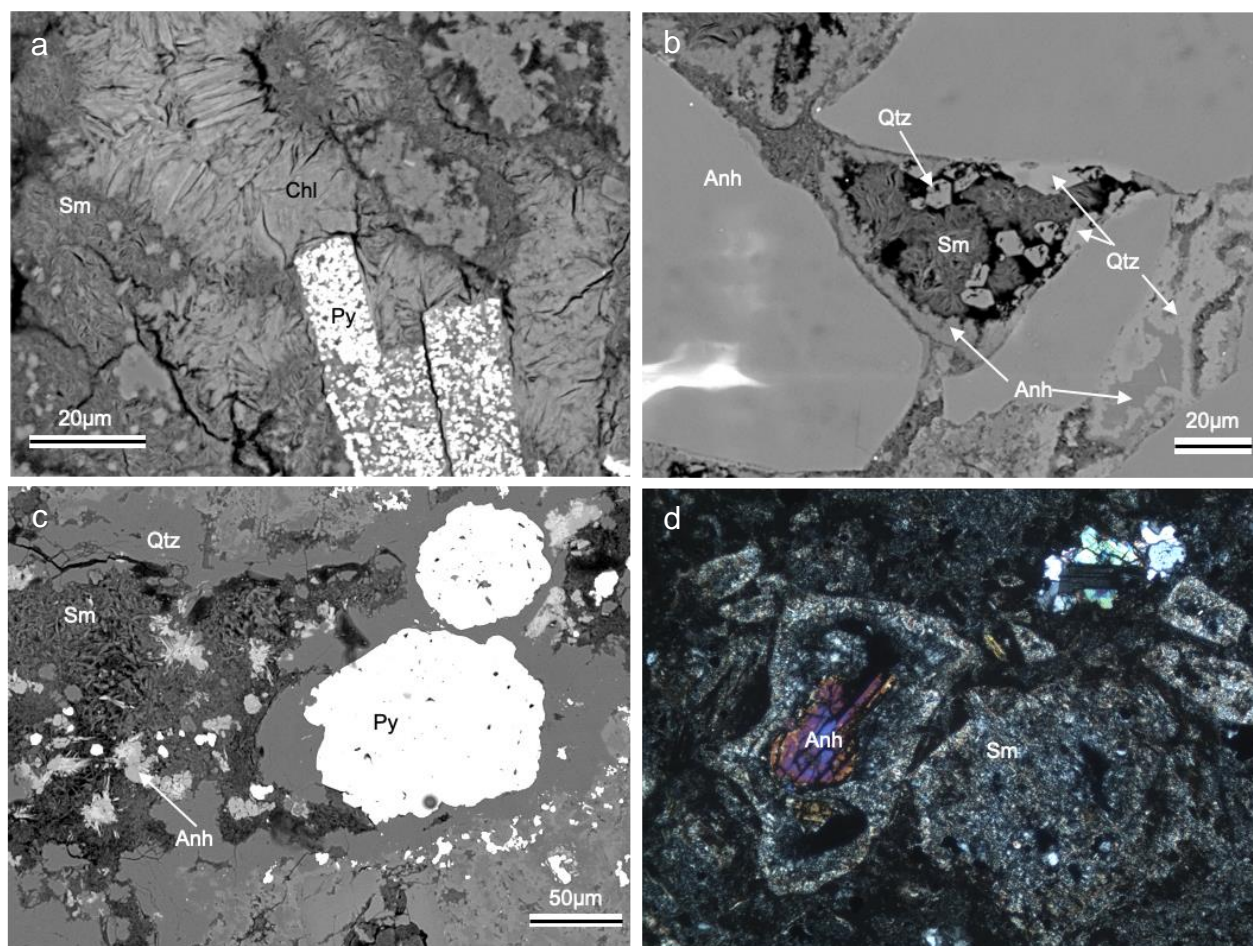


Figure 4 Microscopic observations of thin sections (a) of the edges of the vein at 191m MD dominated by smectite and chlorite (BSED), (b) of the different habitus of the anhydrite and occurrences of smectite in the vein at 191m MD (BSED) (c) of the vein composed of pyrite and quartz and locally replaced by smectite and anhydrite at 218m MD (BSED), (d) of a destructively altered sample at 281m MD with primary minerals and vitreous matrix totally replaced by smectite and anhydrite (x20, crossed polarized light). Anh = anhydrite, Py = pyrite, Sm = smectite, Qtz = quartz

4.2. The deep complex clay zone (275–425m MD)

This zone is affected by a high alteration and locally a destructive one always associated with occurrences of veins (Figure 2). Destructive alteration makes primary minerals, as well as the textures, hard to recognize; only plagioclases retain most of their integrity (Figure 4d). XRD patterns of the clay fraction indicate major amounts of illite, chlorite, corrensite and locally smectite, $R \geq 1$ I/S ml and kaolinite (Figure 2). Pyrophyllite is observed in small amount as in the previous zone. Illite and R3 I/S ml are observed in replacement of the vitreous matrix and selective or total replacement of primary minerals (Figure 5e). Chlorite and corrensite were observed in replacement of the vitreous matrix as well as in vein replacing anhydrite at 385m MD (Figure 5d).

When observed, smectite is in replacement of vitreous matrix and primary minerals and as late crystallization in veins as in the previous zone (Figure 5a). The preliminary chemical results indicate an Al-rich octahedral layers typical from beidellite in replacement of matrix and primary minerals at 281m MD. Measurements at 297m MD indicate a significant amount of magnesium suggesting a predominance of montmorillonite in replacement of the matrix and in the vein. These results should be deepened and extended to other samples of the zone. R1 I/S ml are also observed in replacement of vitreous matrix and primary minerals as well as late crystallization in veins (Figure 5a, c & f).

Kaolinite associated to secondary quartz with epitaxial growth and opale are observed in the matrix and in replacement of primary biotite (Figure 5b). These forms of silice as well as chalcedony are observed in several samples, sometimes even in veinlets and associated with pyrite.

Observations from veins indicate that anhydrite seems to replace quartz and pyrite, sometimes still observed in the veins and in the edges and a late stage of crystallization of smectite and R1 I/S ml observed in replacement inside the veins and in the edges (Figure 5a, c, d & f). The veins intersect primary minerals that are already illitized from a previous hydrothermal events (Figure 5e).

Anhydrite is not only observed in veins but also in replacement of primary minerals (Figure 4d). As in the previous zone, calcite is present in replacement of primary minerals mainly plagioclase. Epidote is observed below 387m and in extremely small amount (Figure 2).

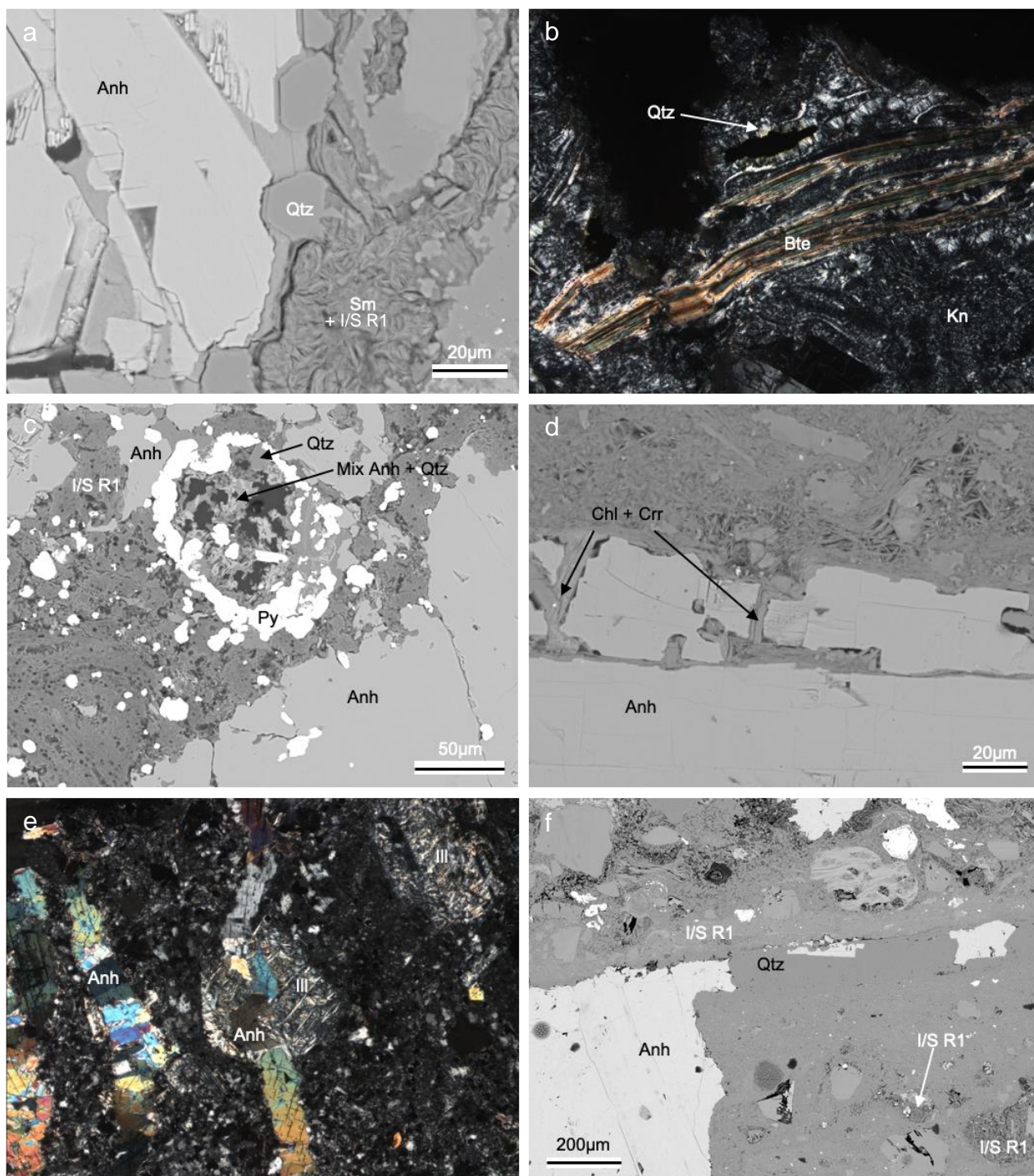


Figure 5 Microscopic observations of thin sections (a) of the edges of the vein at 297m MD dominated by smectite (BSED), (b) of the secondary quartz and kaolinite replacing biotite and vitreous matrix at 337m MD (x20, crossed polarized light) (c) of the vein composed of pyrite and quartz and locally replaced by anhydrite and R1 I/S ml at 345 MD (BSED), (d) of chlorite and corrensite replacing a vein of anhydrite at 385m MD (BSED) (e) of a vein of anhydrite replacing primary minerals entirely illitized at 385m MD (x5, CPL) (f) of the vein composed of pyrite and quartz and locally replaced by anhydrite and R1 I/S ml at 421m MD (BSED) Anh = anhydrite, Bte = biotite, Chl = chlorite, Crr = corrensite, Ill = illite, Kn = kaolinite, Py = pyrite, Sm = smectite, Qtz = quartz, R1 I/S = illitic-smectite mixed layers.

5. DISCUSSION

Observations from 52 XRD patterns along the well PGC1 indicate two main zones:

- A shallow zone from 60 to 275m MD dominated by smectite with locally chlorite and kaolinite that are inherited from an early alteration event. Occurrences of kaolinite and opale in unconsolidated formations could testify of an aggressive and acidic alteration event (Figure 2). However, except these depth sections, this zone is generally not affected by an intense alteration. The absence of intense alteration suggests that the cap rock indicated by Reyes et al. (2011) is more related of the lithology than the abundance of smectite leading to a sealed clay cap as usually described in the literature (Bouchot et al., 2010; Maza et al., 2018). Vergara and Thomas (1984) described several rock formation in the zone of the Irruputuncu volcano that vary in term of welding. Some of them are cinerites and disaggregated pyroclastic materials whereas others are partially to totally welded tuffs that could explain the poor circulation of fluids and thus, the low alteration levels.
 - A deep zone from 275 to 425m MD presenting a complex clay superposition with illite, chlorite, corrensite and locally smectite, $R\geq 1$ I/S ml and kaolinite (Figure 2). At first sight, this zone could be interpreted as the transition zone from smectite to pure illite with an increasing temperature gradient observed in several active systems (Harvey and Browne, 2000; Mas et al., 2006; Maza et al., 2018; Vazquez et al., 2016, 2014). However, the petrographic observations suggest a more complex history with several mineral parageneses superimposed.
- 1) Early hot stages of alteration ($>150^{\circ}\text{C}$)
 - a) Quartz + Pyrite + Illite + R3 I/S ml + Chlorite + Corrensite \pm Anhydrite
 - b) Kaolinite + Opale/chalcedony/secondary quartz crystallizing locally under acidic conditions
 - c) Anhydrite \pm Quartz

These parageneses can be crystallized in the same time.

- 2) Late stages of alteration under subactual temperature conditions ($\approx 150^{\circ}\text{C}$)
Smectite + R1 I/S ml

The vertical distribution of clays from XRD patterns are not sufficient to conclude on an hydrothermal history because the preliminary microscopic observations reveals a complex scenario and encourage to deepen the study of the petrography and minerals relation (Figure 4 & 5). The opening of the vein is associated to boiling indicators such blade-shaped calcite and silica under hotter temperature than the actual one. The several habitus of anhydrite observed in samples suggest polygenetic origins. Besides veins of anhydrite that intersect illitized primary minerals can not be the same generation than veins of anhydrite that is intersected by veins of chlorite and corrensite (Figure 5d & e). Its presence could be explained by magmatic origin, as well as by a meteoric recharge influenced by the presence of the Coposa Salt Flat in the zone (Figure 1). Ongoing fluid inclusions study will clarify its origin. Anhydrite usually replaces pyrite indicating a change of the fluid chemistry. Finally, the smectite and R1 I/S ml in the edges or in replacement of the previous minerals inside veins suggest a late crystallization in equilibrium with the actual temperature of the reservoir (Figure 4 & 5).

In the active part of the reservoir such as in the unconsolidated shallow formations, occurrences of kaolinite correlating opale and others silicic forms are coherent with the hot and acidic condensates that aggressively altered the formations (Figure 2).

The very low but constant amounts of pyrophyllite along the well depth and the absence of microscopic observations in thin sections suggest that they could be relicts of the primary minerals from lithic fragments.

Occurrences of epidote in the deepest part of the well confirm that temperature was hotter in the past (Figure 2).

6. CONCLUDING REMARKS AND PERSPECTIVES

In this study, the XRD results of the clay fraction from core samples along the well PGC1 well indicate, two zones: a shallow one dominated by smectite and a deep one more complex in term of occurrences of clay minerals (illite, chlorite, corrensite, kaolinite, smectite, $R\geq 1$ I/S ml). The shallow zone is associated to a gradual gradient of alteration increasing from null to high with depth whereas the deepest one corresponds to the active zone of the reservoir, with a high alteration that increases notoriously in the vicinities of veins that intersect the well. This vertical distribution might suggest that the deep part is a transition zone towards a pure illite zone usually observed in active geothermal system. However, petrographic observations at microscopic scale reveals mineral parageneses and mineralogical relation inside vein fillings indicating a complex hydrothermal history.

Illite + R3 I/S ml, chlorite, corrensite are inherited from hotter hydrothermal events than the actual temperature of the well ($>150^{\circ}\text{C}$). If illitic minerals are only observed in replacement of vitreous matrix and primary minerals, chloritic minerals are also observed in veins. They belongs to different events because illitized primary minerals are intersected by vein of anhydrite whereas chloritic minerals destabilize anhydrite inside vein fillings. These clay minerals are not only associated with anhydrite but also quartz and pyrite that seem to be prior to the anhydrite. Kaolinite observed more locally and associated with silica are also relicts of an hotter and acidic episode of alteration that was probably very aggressive for the rock formations. The only clay minerals consistent with the actual temperature of the reservoir ($\approx 150^{\circ}\text{C}$) are the smectite and the R1 I/S ml associated to late events that recrystallized the vitreous matrix, the primary minerals but also existing minerals inside vein fillings. Kaolinite observed in vein and the active part of the reservoir can also by crystallized under these actual temperatures.

The varying alteration parageneses and intensities observed in the samples PGC1 seem to be controlled by several factor, such as temperature, fluid composition and properties, lithology... The coexistence of the same parageneses inside all the veins of the well suggests a pulsed system of circulations with physico-chemical changes of the fluids through the hydrothermal history. The superimposition of intense fluid circulations probably lead to a sealing of the veins as permeability indicators were not noticed in the well. The preliminary petrographic results evidenced in veins bring promising results in order to understand this complex history of

the geothermal field where XRD pattern are not sufficient. This petrographic investigation should be deepened in order to clarify the scenario of alteration in the well. Further chemical studies of the clay minerals are ongoing in order to better identify types of smectite and their distribution in the well.

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REFERENCES

- Beaufort, D., Baronnet, A., Lanson, B., Meunier, A., 1997. Corrensite; A single phase or a mixed-layer phyllosilicate in saponite-to-chlorite conversion series? A case study of Sancerre-Couy deep drill hole (France). *Am. Mineral.* 82, 109–124. <https://doi.org/10.2138/am-1997-1-213>
- Beaufort, D., Papapanagiotou, P., Patrier Mas, P., Fouillac, A.M., Traineau, H., 1996. I/S and C/S mixed layers, some indicators of recent physical-chemical changes in active geothermal systems: The case study of Chipilapa (El Salvador), in: *Proceedings of Seventeenth Workshop on Geothermal Reservoir Engineering*. Stanford University, California, USA.
- Beaufort, D., Patrier, P., Meunier, A., Ottaviani, M.M., 1992. Chemical variations in assemblages including epidote and/or chlorite in the fossil hydrothermal system of Saint Martin (Lesser Antilles). *J. Volcanol. Geotherm. Res.* 51, 95–114. [https://doi.org/10.1016/0377-0273\(92\)90062-I](https://doi.org/10.1016/0377-0273(92)90062-I)
- Betancourt, C., Vidal, J., Morata, D., Maza, S., 2020. Hydrothermal alteration in the geothermal system of the Irruputuncu Volcano, Northern Chile, in: *Proceedings of World Geothermal Congress 2020*. Reykjavik, Island.
- Bouchot, V., Traineau, H., Thinon, I., Baltassat, J.-M., Fabriol, H., Bourgeois, B., Lasne, E., 2010. Assessment of the Bouillante Geothermal Field (Guadeloupe, French West Indies): Toward a Conceptual Model of the High Temperature Geothermal System., in: *Proceedings of World Geothermal Congress 2010*.
- Brindley, G.W., Brown, G., 1980. X-ray Diffraction procedures for clay mineral identification, in: *Crystal Structures of Clay Minerals and Their X-Ray Identification*. Brindley G.W. and Brown G., London, Great Britain, pp. 305–360.
- de Silva, S.L., Francis, P.W., 1991. *Volcanoes of the central Andes*. Springer-Verlag, Heidelberg.
- Gifkins, C., Herrmann, W., Large, R., 2005. Describing Altered Volcanic Rocks, in: *Altered Volcanic Rocks : A Guide to Description and Interpretation*. University of Tasmania, Australia.
- Harvey, C.C., Browne, P.R.L., 2000. Studies of mixed-layer clays in geothermal systems. A review of the developments and their effectiveness as mineral geothermometers., in: *Proceeding of the World Geothermal Congress 2000*. Kyushu - Tohoku, Japan.
- Harvey, C.C., Browne, P.R.L., 1991. Mixed-layer clay geothermometry in the Wairakei geothermal field, New Zealand. *Clays Clay Miner.* 39, 614–621. <https://doi.org/10.1346/ccmn.1991.0390607>
- Inoue, A., Kitagawa, R., 1994. Morphological characteristics of illitic clay minerals from a hydrothermal system. *Am. Mineral.* 79, 700–711.
- Inoue, A., Utada, M., 1983. Further investigations of a conversion series of dioctahedral mica/smectites in the Shinzan hydrothermal alteration area, Northeast Japan. *Clays Clay Miner.* 31, 401–411.
- Ji, J., Browne, P.R.L., 2000. Relationship between illite crystallinity and temperature in active geothermal systems of New Zealand. *Clays Clay Miner.* 48, 139–144.
- Lonker, S.W., FitzGerald, J.D., Hedenquist, J.W., Walshe, J.L., 1990. Mineral-fluid interactions in the Broadlands-Ohaaki geothermal system, New Zealand. *Am. J. Sci.* 290, 995–1068. <https://doi.org/10.2475/ajs.290.9.995>
- Mas, A., Guisseau, D., Patrier Mas, P., Beaufort, D., Genter, A., Sanjuan, B., Girard, J.P., 2006. Clay minerals related to the hydrothermal activity of the Bouillante geothermal field (Guadeloupe). *J. Volcanol. Geotherm. Res.* 158, 380–400. <https://doi.org/10.1016/j.jvolgeores.2006.07.010>
- Maza, S.N., Collo, G., Morata, D., Lizana, C., Camus, E., Taussi, M., Renzulli, A., Mattioli, M., Godoy, B., Alvear, B., Pizarro, M., Ramírez, C., Rivera, G., 2018. Clay mineral associations in the clay cap from the Cerro Pabellón blind geothermal system, Andean Cordillera, Northern Chile. S.N. Maza et al. Clay mineral associations in the Cerro Pabellón geothermal system, N. Chile. *Clay Miner.* 53, 117–141. <https://doi.org/10.1180/clm.2018.9>
- McDowell, S.D., Elders, W.A., 1980. Authigenic layer silicate minerals in borehole Elmore 1, Salton Sea Geothermal Field, California, USA. *Contrib. Mineral. Petrol.* 74, 293–310. <https://doi.org/10.1007/BF00371699>
- Patrier, P., Papapanagiotou, P., Beaufort, D., Traineau, H., Bril, H., Rojas, J., 1996. Role of permeability versus temperature in the distribution of the fine (< 0.2 µm) clay fraction in the Chipilapa geothermal system (El Salvador, Central America). *J. Volcanol. Geotherm. Res.* 72, 101–120. [https://doi.org/10.1016/0377-0273\(95\)00078-X](https://doi.org/10.1016/0377-0273(95)00078-X)
- Reyes, N., Vidal, A., Ramirez, E., Arnason, K., Richter, B., Steingrimsdottir, B., Acosta, O., Camacho, J., 2011. Geothermal exploration at Irruputuncu and Olca volcanoes: pursuing a sustainable mining development in Chile, in: *GRC Transactions*.

- Roberson, H.E., Lahann, R.W., 1981. Smectite to Illite Conversion Rates: Effects of Solution Chemistry. *Clays Clay Miner.* 29, 129–135. <https://doi.org/10.1346/CCMN.1981.0290207>
- Rodríguez, I., Roche, O., Moune, S., Aguilera, F., Campos, E., Pizarro, M., 2015. Evolution of Irruputuncu volcano, Central Andes, northern Chile. *J. South Am. Earth Sci.* 63, 385–399. <https://doi.org/10.1016/j.jsames.2015.08.012>
- Simmons, S.F., Browne, P.R.L., 1998. Illite, illite–smectite and smectite occurrences in the Broadlands–Ohaaki geothermal system and their implications for clay mineral geothermometry, in: *Proceedings of Water Rock Interaction-9*. Arehart, G.B., Hulston, J.R. (Eds), Balkema Rotterdam, pp. 691–694.
- Simmons, S.F., Christenson, B.W., n.d. Origins of calcite in a boiling geothermal system. *Am. J. Sci.* 294, 361–400.
- Tassi, F., Aguilera, F., Vaselli, O., Darrah, T., Medina, E., 2011. Gas discharges from four remote volcanoes in northern Chile (Putana, Olca, Irruputuncu and Alitar): a geochemical survey. *Ann. Geophys.* 54. <https://doi.org/10.4401/ag-5173>
- Tulloch, A.J., 1982. Mineralogical observation on carbonates scaling in geothermal wells at Kawerau and Broadlands, in: *Proceedings of New Zealand Geothermal Workshop*, Auckland, pp. 131–134.
- Vazquez, M., Bauluz, B., Nieto, F., Morata, D., 2016. Illitization sequence controlled by temperature in volcanic geothermal systems: The Tinguiririca geothermal field, Andean Cordillera, Central Chile. *Appl. Clay Sci.*, Clay mineral indices in palaeo-geothermal and hydrothermal studies 134, 221–234. <https://doi.org/10.1016/j.clay.2016.04.011>
- Vazquez, M., Nieto, F., Morata, D., Droguett, B., Carrillo-Rosua, F.J., Morales, S., 2014. Evolution of clay mineral assemblages in the Tinguiririca geothermal field, Andean Cordillera of central Chile: an XRD and HRTEM-AEM study. *J. Volcanol. Geotherm. Res.* 282, 43–59. <https://doi.org/10.1016/j.jvolgeores.2014.05.022>
- Vergara, H., Thomas, A., 1984. Hoja Collagua: región de Tarapacá, n°59, p. 79.
- Vidal, J., Patrier, P., Genter, A., Beaufort, D., Dezayes, C., Glaas, C., Lerouge, C., Sanjuan, B., 2018. Clay minerals related to the circulation of geothermal fluids in boreholes at Rittershoffen (Alsace, France). *J. Volcanol. Geotherm. Res.* 349, 192–204. <https://doi.org/10.1016/j.jvolgeores.2017.10.019>