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HR-TEM Studies in Geothermal Alteration Mineralogy: from the Nano Scale to Conceptual Models

Diego Morata[1], Mercedes Vázquez[1] and Fernando Nieto[2]

[1]Department of Geology, Fac. Ciencias Físicas y Matemáticas, Universidad de Chile and Centro de Excelencia en Geotermia de los Andes (CEGA), Santiago, Chile

[2]Department of Mineralogy and Petrology, Universidad de Granada, Granada, España

dmorata@ing.uchile.cl

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ABSTRACT

High-resolution transmission electron microscopy (HR-TEM) allows observation at the nano scale of geothermal alteration minerals. It is particularly relevant for the case of clay minerals, where interlayering is mostly controlled by temperature. Some of these clay minerals are typically used as a proxy to temperature determination. Currently this information is obtained from XRD determinations or punctual chemical (EDX or WDS) analyses. Nevertheless, careful and detailed observations of clay minerals by HR-TEM allow the discrimination of different clay mineral generation, and even the precise determination of chemical composition by EDX analyses. In this work we present our advances in clay mineral studies in the Tinguiririca geothermal field (Andean Cordillera, central Chile) based on HR-TEM. Reaction progress and chemical evolution of these alteration minerals could be precisely determined. Moreover, different clay mineral generation is possible to identify allowing diverse interpretation for the alteration processes (and timing). These nano scale studies have major consequences because precise temperature conditions on core drill samples could be obtained and compared with present day direct temperature measurements. Concordance and/or discrepancies between measured and calculated temperatures could be related with regional evolution of the geothermal field and must be considered for the global conceptual model proposed.

1. INTRODUCTION

Clay minerals are widespread alteration products in most active and fossil geothermal systems, as they are excellent tracers of hydrothermal history (Robinson and Santana de Zamora, 1999; Robinson et al., 2002; Mas et al., 2003, 2006; Vázquez-Vílchez et al., 2014 and references therein). Many studies have considered both the sequential distribution from smectites to non-expandable di- or trioctahedral phyllosilicates and the chemical variations of the non-expandable clay phases (i.e., chlorite and/or illite) as a function of past or present thermal conditions (e.g. Cathelineau and Nieva, 1985; Ji and Browne, 2000). However, properties of clay minerals and mineralogical transformations are not only affected by temperature but also by rock and fluid chemistry, time, fluid/rock ratio, the nature of the precursor material, tectonic stress and/or mechanisms of crystal growth (e.g. Essene and Peacor, 1995; López Munguira et al., 2002). The above factors affect the crystal parameters of clays: structure (coherent domain size in the *c*-direction, polytypism, mixed-layering), composition (cation site occupancy), texture (particle size, morphology) as well as temperature. Moreover, during low-temperature conditions typical of geothermal alteration processes, thermodynamic equilibrium is not attained by the paragenesis of clay minerals (Merriman et al., 1995; Árkai et al., 1996, 2000; Warr and Nieto, 1998; Abad et al., 2001, 2003a, b; Robinson et al., 2002). Consequently, the crystal-chemical parameters of phylloslilicates cannot be used alone for geothermometric determinations as previously proposed (e.g. Cathelineau and Nieva, 1985). Careful studies and chemical considerations need to be present when we use these minerals for temperature estimations (see Essene and Peacor, 1995 for a review). Moreover, the clay mineral reactions are normally governed by the Ostwald Step Rule (Morse and Casey, 1988), which states that the clay mineral paragenesis evolves through the formation of successive metastable phyllosilicates that progress towards the state of stable chemical and textural equilibrium (eg. Nieto et al. 1996; Robinson et al., 2002). This equilibrium condition could be reached during greenschist-facies (Abad et al., 2006), but it is difficult to achieve under geothermal alteration conditions as evidenced by Robinson and Santana de Zamora (1999) and Robinson et al. (2002), among others.

However, the characteristics of clay minerals are qualitative indicators of the reaction progress, or in other words, the stage phyllosilicates have reached through a series of metastable mineral reactions (Merriman and Peacor, 1999; Robinson et al., 2002). Consequently, the conditions at which these minerals crystallized in the active and fossil geothermal fields would be more properly approached by an integrated study of all the crystal parameters of clay minerals together with neoformed CaAl-silicates (e.g. zeolites, epidote, prehnite) at the field scale.

Alteration mineralogy in geothermal fields is normally studied using petrographic analyses coupled with X-ray diffraction (XRD). In some cases, more detailed scanning electron microscopy (SEM) coupled with electron microprobe analyses has been done to better characterize alteration paragenesis and mineral chemistry (e.g. Reyes, 1990; Robinson and Santana de Zamora, 1999; Robinson et al., 2002; Mas et al., 2003, 2006; Libbey et al., 2013). However, the resolution scale of these two techniques limits mineral transformations and mineral reactions at the nano-scale, missing in some cases key information that could be of major interest in geothermal exploration. Smectite-illite and smectite-chlorite are the two main clay mineral processes normally observed in low-temperature geothermal systems. Smectite-illite reaction is mostly controlled by temperature (see Libbey et al., 2013 and Vázquez-Vílchez et al., 2014 for a detailed discussion) but also whole-rock composition or local microdomain composition could control this reaction progress. The other common reaction (smectite to chlorite) is also temperature dependent, and different reaction mechanisms have been proposed. Robinson et al (2002) proposed that the reaction progress mechanism from smectite to chlorite in two geothermal fields is controlled by three contrasting reaction pathways, which are kinetically controlled and linked to variations in fluid/rock ratios and/or contrasting between advective or diffusive fluid transport rather than differences in thermal gradients or clay grain size.

Nevertheless, when moved to nano scale observation by means of high-resolution transmission microscopy (HR-TEM), more detailed analyses can be performed, revealing a new way to help understand the alteration mineralogy and reaction progress in geothermal systems (e.g. Inoue et al., 2004; Murakami et al., 2005; Vázquez-Víchez et al., 2014). In the present study, we analyze the clay mineral evolution in an active geothermal field using High Resolution Transmission Electron Microscopy (HR-TEM) together with Analytical Electron Microscopy (AEM). Our results suggest that classical identification of clay minerals using whole-rock X-Ray Diffraction (XRD) could not be enough to precisely characterize and identify the clay mineral assemblage. Moreover, XRD data lost any spatial relationship observed with clay minerals. Lynne *et al* (2013) have recently shown how Scanning Electron Microscopy (SEM) research can help to understand major, regional scale, processes related with geothermal development. Schiffman et al (2014) also showed how detailed mineral composition using electron microprobe analyses could aid in better understanding of the conceptual model of active geothermal field. In this work we will apply HR-TEM survey to the Tinguiririca geothermal field (central Chile), showing how this high resolution technique could be, in some cases, the only one available to a correct identification of clay minerals. We will also discuss subsequent implications in order to understand the evolution of this geothermal system, which will lead to correct management and modelling.

2. THE TINGUIRIRICA GEOTHERMAL FIELD AS A CASE STUDY: GEOLOGICAL SETTING, SAMPLING AND METHODOLOGY

The Tinguiririca Geothermal field (*c*. 150 km SW Santiago, in the Andean Cordillera of central Chile), is developed on the Pleistocene-Holocene Tinguiririca volcano (Clavero et al., 2011). Geothermal manifestations in this volcanic field comprise steam vents, bubbling mud pools and flowing hot springs; these are associated with steam-heated, acid sulfate and near neutral pH bicarbonate waters (Clavero et al., 2011). Water and gas geochemistry along with He isotope ratios suggest equilibrium temperatures between 230° to 300°C with He a clear magmatic source, possibly related to basaltic systems (Clavero et al., 2011). A first exploration well with a total depth of 815 m and complete core (Pte-1 borehole) was drilled by the Energia Andina (EASA) company on the southwestern flank of the volcanic complex. The well lithology, dominated by Pliocene basaltic andesite lava flows and minor intercalated volcaniclastic layers, is summarized in Figure. 1. According to geological, geochemical and geophysical data, the geothermal reservoir could be hosted in the Oligo-Miocene volcanic and volcaniclastic units (not drilled in Pte-1 borehole) over which the Tinguiririca volcano was built, and also in the lower part of the Pliocene volcanic sequences (Clavero et al., 2011). Alteration mineralogy was determined by Droguet et al. (2012) using petrography, XRD, fluid inclusions and SEM-EDX analyses. A summary of the alteration mineralogy pattern is also indicated in Fig. 1. A more detailed XRD and XR-TEM study was done by Vázquez-Vílchez et al (2014), showing the main characteristics of the clay mineral evolution along the drilled borehole.

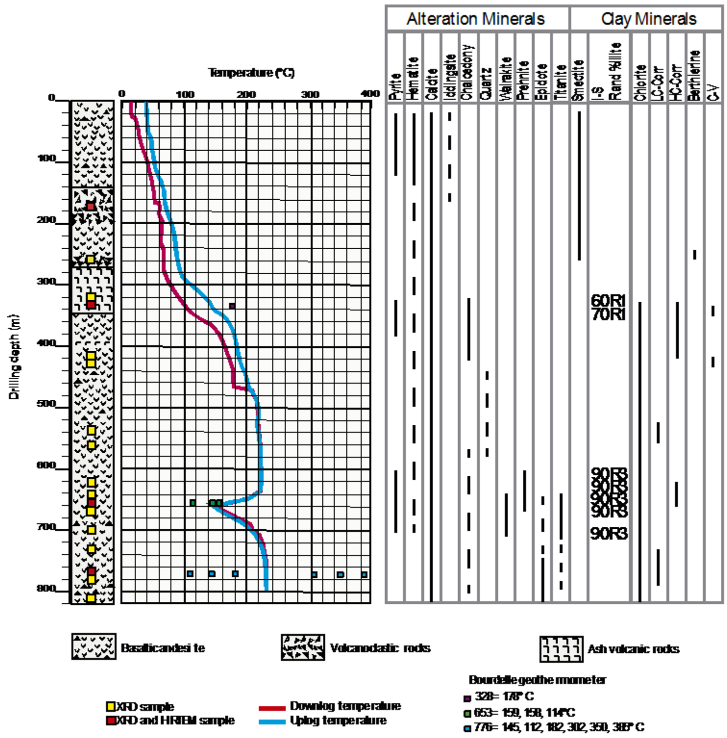

Figure 1: Lithology and distribution of secondary minerals in PTe-1 (Tinguiririca geothermal field, central Chile) from Vázquez-Vílchez et al. (2014). Clay mineral distribution is also plotted according to their sampling depth. The values of temperature calculated by Bourdelle et al. (2013) geothermometer, using chlorite composition are shown. I-S: Illite-smectite minerals; R= I-S Ordering; HC-Corr: High-charge corrensite; LC-Corr: Low-charge corrensite; C-V: chlorite-vermiculite mixed layers.

For the present work, we have selected some representative samples from the bottom of the PTe-1 in which detailed HR-TEM studies have been necessary to better understand the alteration mineralogy and the different reaction mechanism involved during alteration. After detailed petrographic study, samples were selected for XRD analyses, obtaining the main mineralogy as shown in Fig. 1. Clay mineral fraction < 2 μ was analyzed after air-dried and 300º C heating procedures were conducted, allowing the identification of the main clay mineral phases and polytypes (Fig. 2). The HRTEM studies were then performed using two high resolution microscopes at the Universidad de Granada (Spain). Quantitative chemical analyses of clay minerals were made in STEM mode with an EDAX microanalysis system (see more details for HR-TEM analytical procedures in Vázquez-Vílchez et al., 2014). The new Bourdelle et al (2013) chlorite geothermometer (based on internally consistent thermodynamic database) was applied to pure chlorite layers, identified and analyzed by HR-TEM as a way to be sure that smectite layers would not be involved in the microanalysis. This constraint is critical when applying this new geothermometer calibration, because in the absence of smectite layers, the chlorite composition would really be controlled by temperature and not by the amount of other interlayering phases. Results of chlorite composition are also indicated in Figure 2.

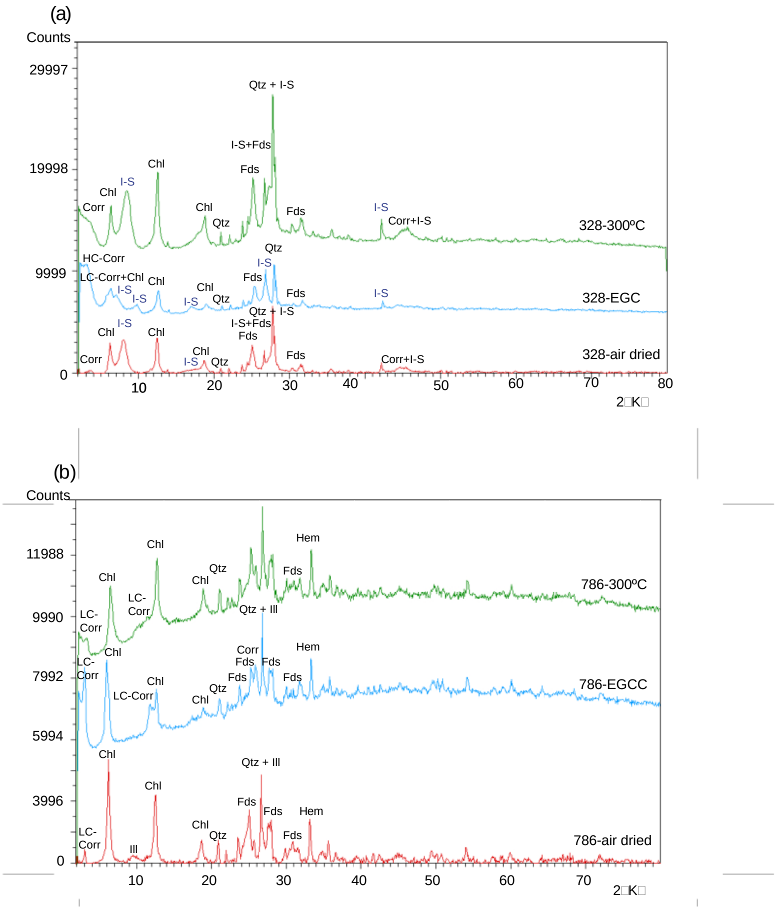

Figure 2: XRD patterns of selected samples along the PTe-1 drill core from the Tinguiririca geothermal field from Vázquez-Vílchez et al (2014). (a) Illite-Smectite (I-S) with 70% of illite and R1 ordering and low-charge corrensite in sample 328. (b) Low-charge corrensite and chlorite in sample 786. In both diagrams, diffractograms were obtained in air dried, EG solvated and after 300ºC heating.

3. RESULTS AND DISCUSSIONS

The continuous slim hole drilled to a total depth of 815 m in the Tinguiririca geothermal field in the Andean Cordillera of central Chile offers an excellent case study of clay mineral evolution in an active geothermal system. In both the smectite-illite and smectite-chlorite systems, various kinds of mixed layers are present; these can be correlated with present day temperatures directly measured in the borehole (Fig. 1), and contrasted if the observed secondary mineralogy is consistent with in situ measured temperatures.

The alteration mineralogy profile, defined using classical petrography and XRD analyses, is consistent with typical geothermal patterns evolving from a clay-rich domain in the upper alteration zone to a propylitic alteration zone, with the presence of epidote and other Ca-aluminium silicates (wairakite, prehnite, and titanite). The distribution of the clay minerals along the borehole shows a zonation according to the depth (Fig 1), allowing the definition of four main clay mineral alteration zones: (1) alteration zone I (from 0 to 300 m) dominated by smectite, (2) alteration zone II (from 300 to 410 m) dominated by R1 I-S mixed layers, chlorite and high-charge corrensite ; (3) alteration zone III (from 410 to 700 m) dominated by R3 I-S mixed layers, chlorite and high-charge corrensite; (4) alteration zone IV dominated by low-charge corrensite and chlorite (Vázquez-Vílchez et al., 2014). Temperatures obtained using the new geothermometric calibration from Bourdelle et al (2013) are consistent with present day directly measured temperatures in the borehole as shown in Figure 1.

However, detailed HR-TEM observations at the nano scale allow us to better characterize the mineralogy, textural relationships and chemical composition of clay minerals along the borehole and also better understand the different mechanisms implied in the formation of secondary minerals. Clay minerals replace plagioclase, volcanic glass and groundmass and show curved, lens-shaped morphology with no preferred orientation. Smectite, showing a ribbon-like morphology, normally appears to fill pores inside plagioclase crystals at 158m of depth (Fig. 3a). I-S mixed layers can be recognized at the HAADF image of sample 328, showing a similar texture to smectite (Fig. 3b), with curved and lens-shaped morphology and no preferred orientation. Volcanic glass is easy to identify by its composition and completely amorphous character (absence of diffraction spots in SAED). It was possible to observe a genetic relationship between glass and the process of dissolution-precipitation, which occurred during the crystallization of I-S mixed layers (Fig. 3c). Low-charge corrensite appears to fill irregular cavities of plagioclase, providing direct evidence for neocrystallization from hydrothermal fluids. It is also possible to identify the presence of clay minerals filling open spaces like veinlets (Fig. 3d). Chlorite is usually intergrown and/or interstratified with 10Å and 7Å layers (Fig. 4). In some cases small packets (20 nm thick) of pure chlorite may be recognized. The presence of 10 Å layers is coherent with the XRD results, which showed chlorite and corrensite co-existing in the same sample (Fig. 1 & 2).

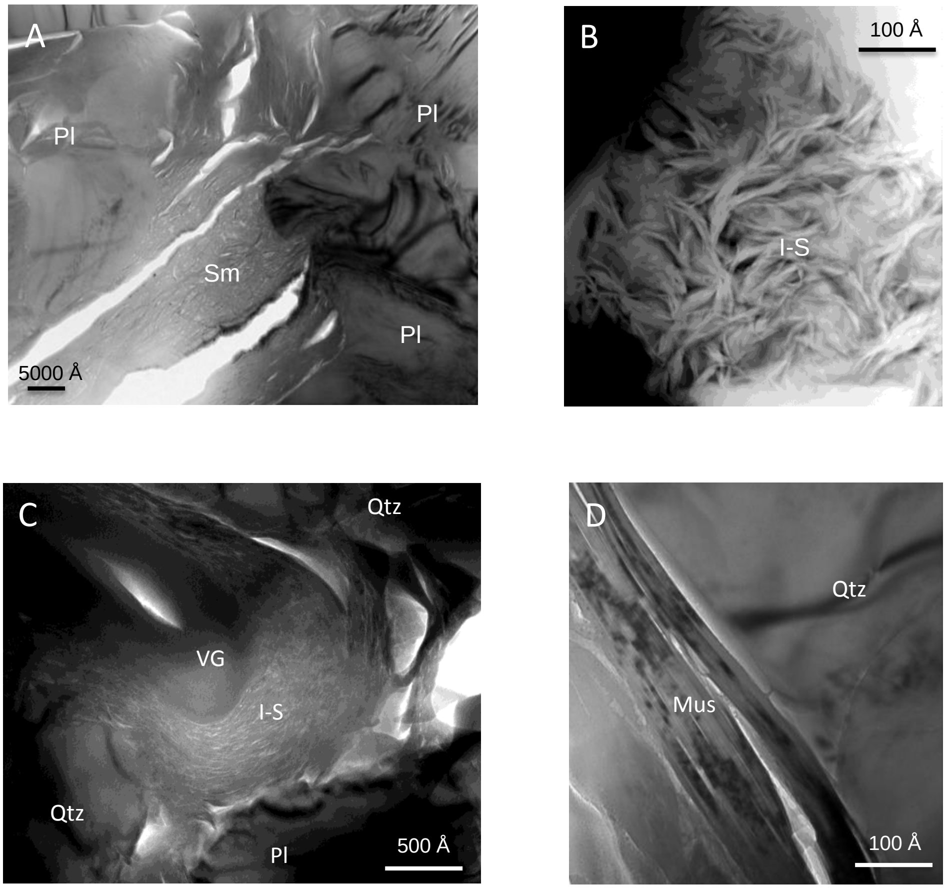

Figure 3: Textural images of dioctahedral clay minerals. (a) Smectite (Sm) filling voids of plagioclase (Pl) in sample 158. (b) HAADF image of I-S mixed layers showing curved and lens-shaped morphology and no preferred orientation in sample 328. (c) Volcanic glass (VG) transformed to I-S mixed layers, quartz (Qtz) and plagioclase in sample 328. (d) Mature mica filling vein. Figures (a), (b) and (c) from Vázquez-Vílchez et al. (2014).

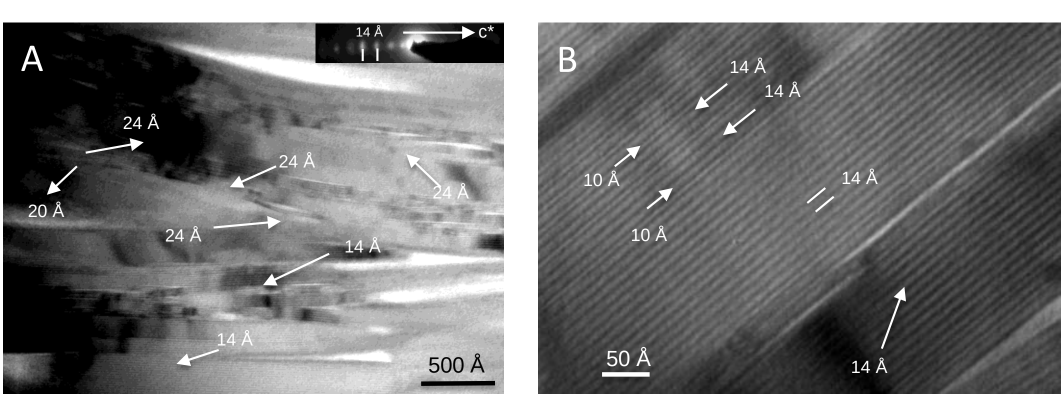

Figure 4: Chlorite and low-charge corrensite in sample 776 (from Vázque-Víchet et al., 2014). (A) Layers to 24 Å corresponding to corrensite, are the result of an ordered sum of one chlorite layer (14 Å) and one contracted smectite layer (10 Å). They are intergrowth with 14 Å chlorite layers and 20 Å of illite layers (2M polytype). (B) Layers to 14Å with minor 10Å layers showing chlorite intergrowth and/or interstratified with corrensite.

The textural evidence of clay minerals under TEM along with classical petrographic observations indicate that primary minerals were in part dissolved by hydrolytic reactions, and that the smectite and I-S mixed layers precipitated in situ from the altering solutions. The typical defective characteristics of smectite, with layer terminations, dislocations and contrast changes were also observed in the I-S mixed layers, indicating that these phases are involved in the prograde reaction. This reaction was detected from 325 to 408 m, where fine (ash size) to medium pyroclastic levels were penetrated by the borehole. It is known that solutions reacting with vitric materials at a given temperature might increase in pH and dissolved solids, enriching the solution with Mg, Ca and Na as well as SiO_2. The resulting high pH and Na solution favors the formation of smectite (eg. Inoue et al., 2004). Due to a higher temperature in the 325 –408 m intervals, the hydrolytic reaction forms aluminous I-S minerals instead of montmorillonite by incorporating K ions into the structure from ambient solutions. To the bottom of the drill core, the increase in chlorite content is also related with an increase in temperature. Corrensite occurs between 100 and 200ºC (Inoue and Utada, 1991). The complete change of corrensite to discrete chlorite is completed above 240º C (eg. Keith and Bargar, 1988 and references therein). High chlorite content can also be related to high fluid/rock ratio or mineral alterations, which provide the Al needed to form chlorite (Shau and Peacor, 1992; Schmidt and Robinson, 1997).

Many authors have focused their studies on establishing the temperatures of the transformations in the system smectite-I-S-illite. Generally, the temperatures where I-S mixed layers R1 with approximately 50-60 % of illite layers appears in diagenetic environments in the range of 75 to 120º C (e.g. Abid et al., 2004 and references therein). Libbey et al. (2013) also showed a positive correlation between the proportion of illite in the I-S interlayer and downhole temperature in the Te Mihi area, Wairakei geothermal field (New Zealand), even suggesting a local I-S geothermometer based on the illite proportion. In the Tinguiririca borehole the last smectite sample corresponds to a temperature of 80ºC and the first to be replaced by the R1 I-S to 120ºC. Therefore, a temperature around 100ºC, perfectly compatible with the previous range defined in the literature, may be considered as a valid reference for this first step of the transformation from smectite to illite. Finally, it is highlighted that the transformation into pure illite has not been completed at the bottom of the borehole, with some minor residual smectitic layers even at temperatures as high as 220ºC. The difficulty of the completeness of the reaction based only on thermal effects, without tectonically induced strain as a driving force for the reaction, is a widely accepted fact in the incipient metamorphism literature (Merriman and Peacor, 1999).

Finally, concerning chlorite, additional information using HR-TEM analyses could be obtained. Discrete chlorite displays a wide range of non-stoichiometric compositional variations depending on bulk rock composition and physicochemical conditions prevalent at the formation. Therefore, the variation of chemical composition in chlorite is useful in obtaining information on the physicochemical conditions of the formation, such as the temperature. Most of the chlorite “geothermometers” have been calibrated based on empirical relationships between some chemical parameters and measured temperatures in geothermal areas (e.g. Los Azufres, Mexico, Cathelineau and Nieva, 1985), but there was concern that they were widely affected by small scale interstratifications and intergrowths and were not based on chemical equilibrium (Essene and Peacor, 1995). Recent efforts have been conducted in order to introduce thermodynamic constraints to the temperature control on the chlorite composition. The most recent calibration has been published by Bourdelle et al. (2013). According to these authors, this calibration must be used in chlorites free of 10 Å layers. Thanks to the high-resolution images obtained from transmission electron microscopy, we can apply this calibration to pure chlorite layers, obtaining temperature values that could be controlled by temperature and no other interlayering phases. As showed in Fig. 1, some differences have been observed between the empirical temperatures calculated using chlorite chemical composition and the present day measured temperatures. However, major differences were obtained in sample 776 (bottom of the drill core). In fact, in this sample we can identify two well defined groups of temperatures, which are clearly different to the 233ºC of the measured temperature of the borehole at this depth. One group has an average temperature of 139º C and the other 346 ºC. These two groups of temperatures are also the consequence of two well defined groups of chlorites in the sample with very different morphology and compositions (Fig. 5). The existence of these two groups of chlorites would have been impossible to be determined using XRD (Fig. 2) or petrographic studies due to the small grain size. Only by means of HR-TEM analyses was it possible to identify such chlorite generation that could have been related to at least two distinct alteration events in the history of the Tinguiririca geothermal field. Because low temperature chlorite cannot be in equilibrium with Ca-silicates present in the same samples (epidote, prehnite, wairakite), this low-T chlorite group could be related to the cooling of the system by cold water influx, as reflected by the present day measured temperature (Fig. 1). In any case, the persistence of two morphologically and chemically contrasted chlorite families indicates disequilibrium conditions and must be related with the kinetics of the alteration processes in geothermal systems, as also previously indicated by Inoue et al (2004).

4. CONCLUSIONS

Different physical controls, together with temperature, would be involved in the formation of clay minerals during geothermal alteration processes. A lithological control seems to be evident when different rock types, each with different primary permeability/porosity and composition are affected. This fact is more evident when clay minerals formed in ash-rich layers, contrasting with massive basaltic andesite lava flows. Also, using high-resolution imaging, it is possible to identify how clay minerals form and from which phase they crystallize. This information is critical for a better understanding of the secondary permeability induced in geothermal field by processes of dissolution/precipitation from previous and neoformed minerals. Lynne et al (2013) have recently shown the importance of detailed (SEM scale) mineralogical studies to understand dissolution/precipitation processes and how these processes control subsurface processes, leading to subsidence at Tauhara Geothermal Field in New Zealand where weakening rocks have modified original geotechnical behavior. More detailed information is obtained using HR-TEM studies as showed in the Tinguiririca geothermal field. This additional information allows a better understanding of the geothermal field and the different processes related to alteration and even the existence of different alteration events affecting host volcanic rocks. Finally, the ability to obtain temperature values of pure chlorite layers aides the global understanding of the geothermal history of the field, and allows one to better constrain the conceptual model, final management and modelling of the geothermal field.

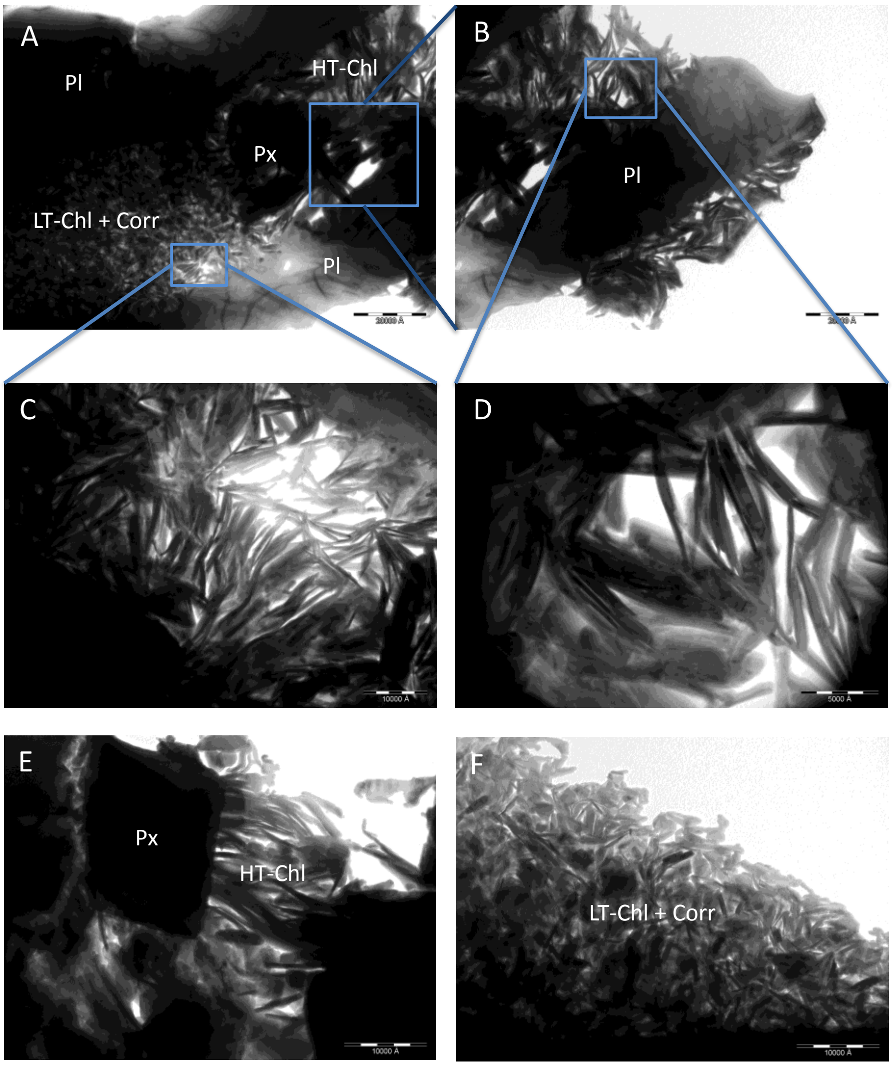

Figure 5: TEM textural image of sample 786. A) Chlorite and low-charge corrensite filling irregular cavities of plagioclase. B) Detail image of chlorite of high temperature. C) Detail image of chlorite of low temperature. D) Detail image of chlorite of high temperature. E) Chlorite of high temperature growing throughout primary pyroxene crystals. F) Chlorite of low temperature and low-charge corrensite filling open spaces. .

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