UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY

Escuela de Ciencias de la Tierra Energía y Ambiente

TÍTULO: XRD ANALYSIS PROCEDURE FOR CLAY MINERALS – APPLICATION TO CHACHIMBIRO GEOTHERMAL SYSTEM

Trabajo de integración curricular presentado como requisito para la obtención de título de Geólogo

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Urcuquí, febrero 2020

Urcuquí, 26 de febrero de 2020

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CARRERA DE GEOLOGÍA
ACTA DE DEFENSA No. UITEY-GEO-2020-00001-AD

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Dedication

To my wonderful family for all their sustenance and unconditional love.
Especially to Doris, Stefany, Ricardo and Guillermo, my reason in life.

Doménicca Guillén

Acknowledgments

Choosing Geology as my career has been the most accurate decision I have ever taken. It gave me other point of view and also, opportunities I have never though I can reach. I am so grateful to all people that have encourage me in this difficult but amazing process. I want to express a deep admiration to Yaniel, Luke, Elisa, Uwe, Jorge that specially challenged my capacities and make me believed in myself. I will keep their example always inside.

I want to recognize the great labor of Celine Mandon being my advisor. Working with her has been inspiring and honestly one of the most beautiful experiences of Yachay Tech. She has supported me not only academically but also emotionally; her words of motivation have helping me to finish this thesis with new knowledge and feeling proud of my work.

I thank CELEC and IIGE, for providing me the cutting samples of Chachimbiro geothermal well and all the laboratory equipment where I can do the experimentation of this research.

My deepest appreciation to Diani and Lai who were my roommates and become into my sisters. Thank you for your energy and love transmitted me, you made my live beautiful every day. Finally, to Luis who graduated before me, is my inspiration and my favorite partner.

Doménicca Guillén

Resumen

Esta investigación estudia sistemas geotérmicos, su clasificación, exploración y explotación con énfasis en su aplicación dentro de Ecuador. También, trabaja conceptos de alteración hidrotermal para explicar el rol de minerales arcillosos como evaluadores descriptivos. Dada la carencia de investigaciones en esta área a nivel nacional, este estudio elabora un manual de laboratorio para análisis de arcillas por DRX. Este fue elaborado comparando metodologías ya existentes y añadiendo conclusiones empíricas obtenidas durante la experimentación en el Instituto de Investigación Geológico y Energético. La aplicabilidad del procedimiento desarrollado fue comprobada con la identificación de cinco tipos de arcilla en el pozo geotérmico PEC1 de Chachimbiro. Asumiendo que las arcillas se formaron dentro de un régimen térmico estable, se presentan dos conclusiones importantes. Primero, existe un proceso de ilitización que garantiza un elevado incremento de temperatura con profundidad y sugiere alteración argílica en toda su extensión. Esto implica que la capa sello podría extenderse más que 340 metros, que es la profundidad que otros autores sostienen. Segundo, de acuerdo al perfil de temperatura obtenido, se propone una temperatura máxima de 170°C a 310 metros de profundidad y un rango de temperatura de 240 °C a 260°C a una profundidad mayor a 700 metros.

Palabras clave: Sistemas geotérmicos, alteración hidrotermal, pozo geotérmico de Chachimbiro, arcillas, ilitización, DRX.

Doménicca Guillén

Abstract

This study comprises concepts about geothermal systems, their classification, exploration and exploitation with emphasis in Ecuador advance. Also, it involves principles about hydrothermal alteration and clays as descriptive clue. Besides, with the purpose to contribute to national knowledge, this research composes a laboratory procedure for clay mineral preparation to XRD analysis. It was structured by contrasting stablished methodologies but also based on conclusions empirically obtained during the experimentation in the Instituto de Investigación Geológico y Energético. The applicability of this newly procedure was remarked with the identification of five different clays in PEC1 geothermal well of Chachimbiro. Assuming they were on a stablish regime, we present two considerable advances. First, there is an illitization processes which guarantees a high increase of temperature with depth and implies the existence of argillic alteration. It allows us to suggest that the clay cap of Chachimbiro geothermal field is thicker than 340 m as other authors hold. Second, according to the temperature profile we propose a maximum temperature of 170°C until 310 meters depth and 240°C to 260°C, at greater depths than 700 meters.

Key words: Geothermal systems, hydrothermal alteration, Chachimbiro geothermal well, clays, illitization, XRD.

Doménicca Guillén

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Problem Statement

Ecuador has a lot of potential for geothermal energy production. However, after more than 40 years, we are still in the pre-feasibility phase, with only exploratory wells in Chiles and Chachimbiro. This is in part related to the lack of technical and analytical capabilities within Ecuador. In fact, the drilling of the first exploratory well at Chachimbiro in 2017 was performed thanks to the economic and technical support of JICA. All the analyses were performed in Japan, with restricted access to the data until 2022. This project arose from a demand of CELEC and IIGE to develop an efficient methodology for clay sample preparation and analysis by XRD. In fact, because of their special properties, clays need special procedure for XRD analysis. Many studies have been published detailing such procedures. However, they all diverge in the techniques used. The demand was thus to compare the existing methodologies in order to establish a manual for clay sample preparation and analysis with XRD as efficient as possible and in line with the means of CELEC and IIGE laboratories.

General Objectives

The type of clay minerals and their distribution within a geothermally active area provide key information for exploration, such as temperature and composition of the fluid, duration of fluid-rock interaction, permeability of the system. Being able to perform these analyses is thus crucial for a country like Ecuador, with geothermal prospection likely to increase in the near future.
The objectives of this research are as follows:

- To establish a procedure manual for clay sample preparation and analysis with XRD by comparing existing methodologies for the chemistry lab of the Insitituto de Investigación Geológica y Energética (IIGE)

- To apply this newly established methodology to the identification of clay minerals in the Chachimbiro geothermal well to contribute to a better interpretation of the geothermal system

General Structure of the thesis

Chapter 1: Introduction of the study. First, background of some general concepts about geothermal systems and the underlying hydrothermal alterations which the rock may be subjected to. Then some key information about mineral alteration and clays particularly.

Chapter 2: Introduction to the study area describing the geological setting and its evolution with time, and giving a summary of the present knowledge of the geothermal system, past geochemical and geophysical studies, contrasting authors' interpretation. A geological description of the 2017 geothermal well, object of this study, is also given.

Chapter 3: This is the most important chapter of this investigation, describing the experimental work done for the development of the manual procedure for clay samples preparation and analysis by XRD. This chapter includes some concepts of XRD functioning, and the parameters set up for this research. Mostly, it presents a meticulous description about how the procedure for clay analysis was developed, describing how methods were contrasted and evaluated and which instruments were employed.

Chapter 4: This section describes the results of clay analysis from the 2017 geothermal well at Chachimbiro, obtained using the newly developed method for clay sample preparation and analysis by XRD. It also includes a discussion of the implications these results bring to the interpretation of Chachimbiro's geothermal system. It tries to relate geological setting, chemical analysis and some other previous studies with the results obtained.

Conclusions: This chapter summarizes the findings of this investigations, including recommendations for future investigations.

CHAPTER 1.
INTRODUCTION

1.1. Geothermal systems

The cooling of the Earth through heat emission at the surface has various types of manifestations, volcanoes, hot springs, fumaroles and geysers being some common examples. This heat, accumulated during accretion of the Earth and subsequently by radioactive decay, is transferred mainly by convection in the mantle and conduction in the lithosphere. The increase in temperature with depth is what we call the geothermal gradient. The average geothermal gradient in the crust is about 25-30 °C/km (Brown, 2002), however, there are locations subject to higher gradients, which are advantageous for the development of geothermal systems.

Geothermal systems are regions where large mass and energy flows are transferred from depth to shallow surface. The main components of geothermal systems are: a heat source commonly associated with magmatic intrusions, a permeable reservoir and water to carry heat and solutes (Figure 1.1). The reservoir is overlying a magmatic chamber heating up rocks, from which the circulating fluids extract heat. The reservoir is within a permeable layer that is overlain by an impermeable cap rock, and connected to surficial recharge zone (Dickson and Fanelli, 2013). The presence of a well-developed fracture network within the geothermal system is also of importance, since it facilitates the circulation of hydrothermal fluids. Fractures and faults thus serve as an excellent path way until they are filled out by mineral precipitation (Figure 1.2) (Lagat, 2014).

Classifying geothermal systems is rather complex. Each of them is unique and has its particular geological, geophysical, geochemical and hydrological context. Moreover, no standard international terminology has been established yet. This represents a problem because it hinders mutual comprehension among the geothermal community. Various classifications exist, based on different parameters such as temperature, geological settings, reservoir equilibrium and conceptual models (see Table 1.1). Despite similarities among them, none offers a complete classification useful in all cases.

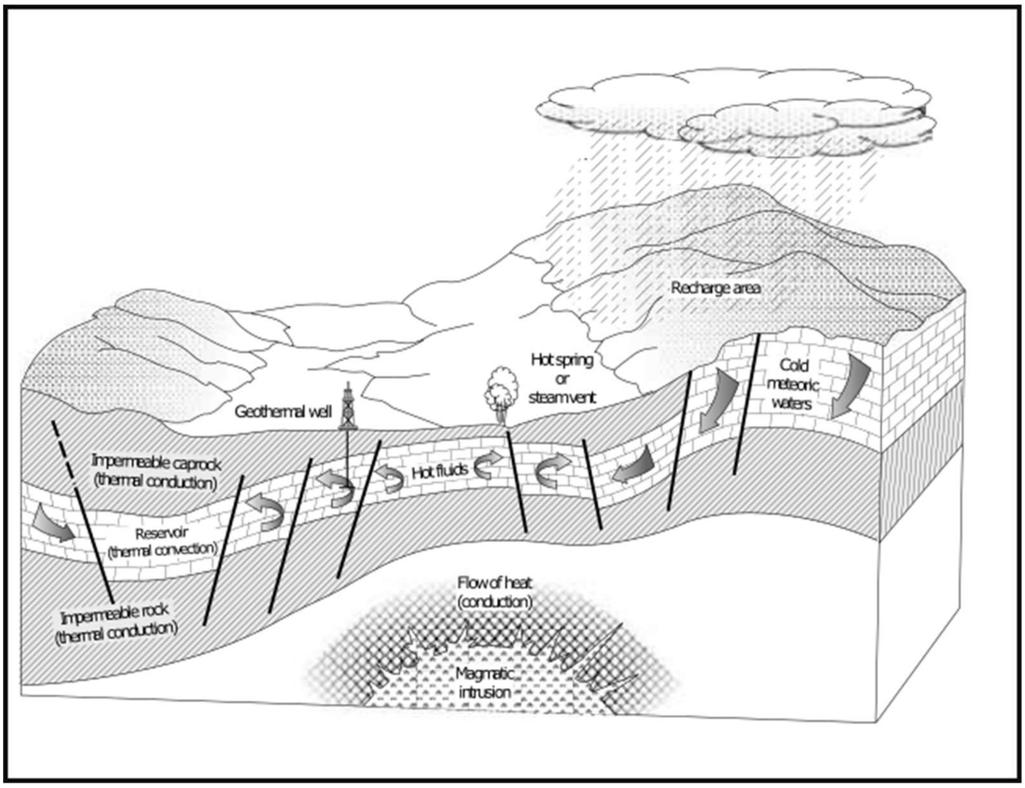

Figure 1.1 Main components of a geothermal system (Francisco, 2013)

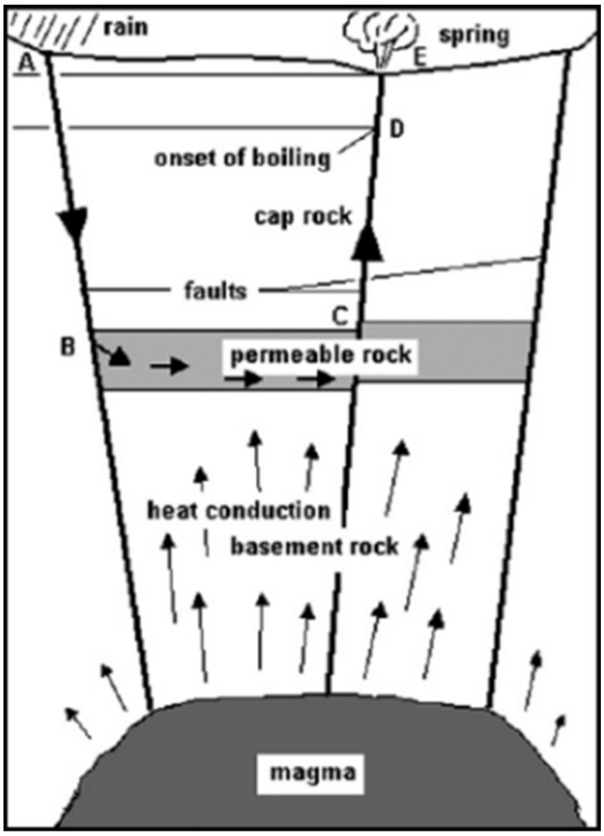

Figure 1.2 Ideal scheme of a geothermal system (Francisco, 2013)

Table 1.1: Some of the existing classifications for geothermal systems based on different parameters.

Classification based on	**Categories**					**References**
Temperature	**Low enthalpy <** 100 °C	**Intermediate enthalpy** 100-200 °C		**High enthalpy** >200 °C		(Benderitter and Cormy, 1990)
Geological Context	**Extensional**			**Compressional**	**Translational**	(Speight, 2015)
	Spreading Centers	Back-arc basins	Intracontinental rift zones			
Reservoir equilibrium State	**Dynamic system (convective)** Reservoir is continually recharged by water that is heated and then discharged from the reservoir.			**Static system (conductive)** Only minor or no recharge to the reservoir. They are found in deep sedimentary basin.		(Nicholson, 2012)
	Low temperature < 150 °C	High Temperature >150°C		Low temperature ~70°Cat depth of 2-4 km	Geopressurised ~ 150 °C at depth of 3-7 km	
		Liquid Dominated	Vapor Dominated			
Conceptual Models	**Young igneous model** Associated with Quaternary volcanism and shallow (< 6 km) magmatic intrusions. T= 220-350 °C.		**Tectonic model** Extensional environment results in basins formation.	**Vapor-Dominated System** Liquid water is continuous pressure-controlling fluid phase.	**Liquid Dominated System** Vapor as pressure-continuous controlling phase.	(Scarpati, 2019)

1.1.1. Geothermal Systems as a clean source of energy

Geothermal energy is a renewable type of energy that takes advantage of the Earth’s heat for producing electricity. Its use thus contributes to decrease greenhouse gas emissions and therefore to address the current environmental crisis. Moreover, it limits the increase in the global temperature and the effects of global warming by diminishing reliance in fossil fuels (Moya et al., 2018). Compare to some other renewable energies, geothermal has the advantage of being independent of climate conditions, being continuous and having a global distribution. The use of the Earth’s internal heat to benefit society is not a new discovery. In fact, the first geothermal power plant installed in the world was in Larderello, Italy in 1904 (Dickson and Fanelli, 2013).

However, geothermal energy is far from being the biggest source of electrical power nowadays. The unused global potential of geothermal energy is 119 423 million tons of oil equivalent (Mtoe), seven times larger than the global energy supply at the end of 2017 and five times larger than the global energy supply predicted for 2050 (Moya et al., 2018). All of the aforementioned suggests that the use of geothermal energy in both developed and developing countries will give us a chance to generate a sustainable alternative for future energy challenges that does not compromise nature and climate.

1.1.2. Geothermal resource assessment

The presence of a geothermal reservoir at depth is not always evident from the surface. So, in order to exploit this resource, it is necessary to complete a procedure composed of several phases (Table 1.2)

Table 1.2: Phases of geothermal resource assessment (from McNutt et al., 2015 and Glassley, 2010).

Phase	Characteristics	Results
1. Surface exploration	Cheapest stage Geological studies Geochemical, geophysical surveys Hydrological balance	Selection of priority areas Definition of the research area
2. Prefeasibility study	Volcanological studies Geothermal test boreholes Geophysical surveys: Gravity, magnetics, seismic, electromagnetic, geoelectrical profiles.	Preliminary estimate of geothermal potential Definition of exploration projects
2. Exploration drilling	Expensive stage First direct data obtained about the reservoir: Temperature, permeability, fluid composition, thermal output	Location of a promising production well field
3. Feasibility study Appraisal drilling	Recover the needed amount of fluid for the production	To quantify the production characteristics
4. Feasibility study and preliminary plant design	Fluid measurement Environmental studies Economic study Reservoir physics	Predict the generating capacity and longevity of the well field Evaluation of resources/reserves
5. Development and exploitation	Plant commissioning management and maintenance	

1.1.3. Ecuador geothermal historical development

Even though Ecuador started geothermal preliminary studies in 1979, only two prospects have reached the prefeasibility stage with an exploratory well perforation, Tufiño-Chiles in 2009 and Chachimbiro in 2017. Unfortunately, the prospect of Tufiño-Chiles was shut down in 2014 (Beate and Urquizo, 2015), while Chachimbiro project is on standby at the time of writing, waiting for further financing. Ecuador had an episodic geothermal development over the last 40 years, with two marked periods of reconnaissance and prefeasibility studies in which organizations both national (INECEL[1], MEER[2], CONELEC[3], ELECTROGUAYAS, CELEC EP[4], INER[5], INIGEMM[6], SENACYT[7]) and international (OLADE[8], AQUATER, BRGM[9], IAEA[10], JICA[11]) participated. The main reconnaissance study took place between 1979 and 1981 and comprised preliminary activities such as field surveys/field observations, aerial photos, geochemical analyses of rock and water samples. From these, potential locations where identified (Figure 1.3), with the most prominent divided in two groups: high-temperature systems: Tufiño, Chachimbiro and Chalupas, and low temperature systems: Ilaló, Chimborazo and Cuenca (Beate and Salgado, 2005; Lloret, 2014).

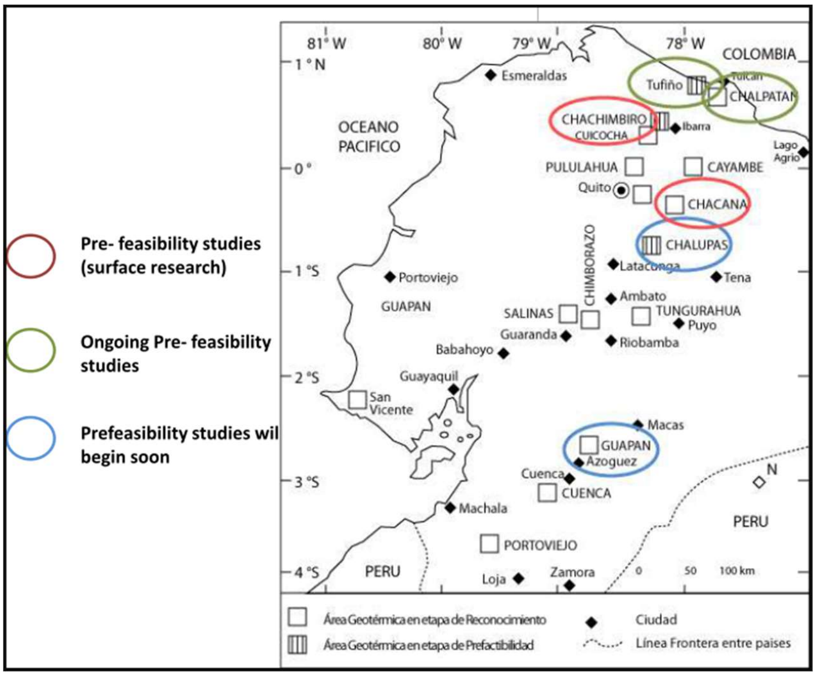

Figure 1.3 Areas of interest. By the 2014, some location where in different phases of prefeasibility studies. Modified from (Aguilera, 1998).

An extensive prospection took place for the most promising locations This stage lased for about 22 years, from 1981 to 1993 and from 2007 to 2017 and provided notable advances that are summarized in Table 1.3.

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[1] Instituto Ecuatoriano de Electrificación

[2] Ministerio de Electricidad y Energía Renovable

[3] Consejo Nacional de Electricidad

[4] Corporación Eléctrica del Ecuador

[5] Instituto Nacional de Eficiencia Energética y Energías Renovables

[6] Instituto Nacional de investigación Geológico Minero Metalúrgico

[7] Secretaria Nacional de Ciencia Tecnología e Información.

[8] Organización Latinoamericana de Energía

[9] Bureau de Recherches Géologiques et Minières

[10] International Atomic Energy Agency

[11] Japan International Cooperation Agency

Table 1.3: Prominent results from prefeasibility surveys in Ecuador

Geothermal Prospect	Water Samples		Gas geothermometers Reservoir Temperature	Surveys	Project Status	Estimated Potential	Application	References
	Sample temperature	Type						
Tufiño-Chiles	55 °C	Bicarbonate	230 °C	Resistivity Magnetotellurics	Final prefeasibility study. First drilled hole reached depth of 554 m	138 MWe	Electricity generation Direct uses	2 4 5
Chachimbiro	40-55 °C	Neutral Chloride-Bicarbonate Neutral alkali-chloride	200 °C-260 °C	Magnetotellurics Time domain electromagnetic Gravity Magnetic Active microearthquakes Risk assessment	Feasibility study. Drilling exploratory stage reached depth of 1500 m	81 MWe	Electricity generation Direct uses	2 4 5
Chacana (Cachiyacu, Jamanco, Chimbaurcu, Plaza de armas)	1.63-2.72 °C	Neutral alkali-chloride	Three models predicted with different reservoir temperatures: **I)** High-temperature GS 150-240 °C **II)** GS in a cooling stage 110-120 °C **III)** Immature GS	Magnetotellurics Time domain electromagnetic Gravity Magnetic Active microearthquakes Risk assessment	Prefeasibility study	156 MWe	Electricity generation Direct uses	1 4 5
Chalpatán	26-36 °C	Na-Ca bicarbonate	74-137 °C	**---**	Prefeasibility study	---	Direct uses	2 5
Cuenca	75 °C	Alkali-chloride-bicarbonate	100-140 °C	**---**	Prefeasibility study	**---**	Direct uses	1 3 4
Chalupas	30-40 °C	---	---	**---**	Prefeasibility study (insufficient data)	283 MWe	Electricity / Direct uses	1 5

References: 1: Beate and Salgado, 2005 ; 2: Beate and Urquizo, 2015 ; 3: Lloret, 2014 ; 4: Panichi et al., 1992 ;5: Moya et al., 2018

1.2. Hydrothermal alteration in geothermal systems

Alteration in a rock refers to the change in its mineralogy, chemistry and texture. Primary minerals of a rock are replaced by secondary minerals as a consequence of a thermodynamic instability. It is produced by the change in the prevailing conditions of the rock. Hence, hydrothermal alteration is the change in mineralogy and chemistry due to interaction of the rock with hot fluids. Such hydrothermal fluids passing through the rocks induce changes in their composition by adding, removing or redistributing components (Lagat, 2014). Hydrothermal alteration occurs so that a new equilibrium between the rocks and the circulating solution is approached (Inoue, 1995).

The grade of alteration within a geothermal system is governed by multiple factors that vary from field to field. Active geothermal systems are places where reactions are occurring now, so, they are considered as large-scale, uncontrolled, open-end natural experiments that are not completely understood yet. Factors affecting hydrothermal alteration are: temperature, pressure, rock type, permeability, fluid composition and duration of the activity. Each of these factors is strictly related with hydrothermal mineral formation and its influence should be studied individually. For example, studies confirmed the important effect of temperature in the formation of hydrothermal mineral assemblages, but also demonstrated the critical role of permeability (Browne, 1978).

Likewise, there is an intimate relationship between fluid composition and mineral deposition from a geochemical point of view. Fluid compositions are extremely variable. Usually of meteoric origin, they also comprise several types of dissolved gases and ions. Metals are common constituents, brought into solution by leaching out the host rock and carried as different ionic complexes. As previously said, hydrothermal fluids are mainly of meteoric origin. However, there can be addition of magmatic fluids exsolved from the cooling magma in volcanic context. Metamorphic fluids, formed by dehydration reactions during metamorphic events, can also add up (Lagat, 2014). Addition of these fluids result in the variety of hydrothermal fluids encountered at the surface of the Earth, bringing a distinct geochemical signature.

Nicholson (2012) describes the types of geothermal fluids based on their dominant anion. The three principal types of fluids are alkali-chloride, acid-sulphate and bicarbonate waters. Each of them is associated with a type of hydrothermal alteration and a determined mineral assemblage.
Alkali-chloride waters have the greatest Cl concentration, typical of the deep geothermal fluid in most high-temperature systems. Sodium and potassium often are the principal cations with important concentration of silica and boron. The main dissolved gas is carbon dioxide with low percentage of hydrogen sulfide. The pH of these waters can vary between slightly acidic to slightly alkaline. The characteristic minerals with these fluids are silica, albite, adularia, illite, chlorite, epidote, zeolites, calcite and pyrite (Nicholson, 2012). Silica sinter is a classical feature at the zone of discharge of these fluids at the surface, often indicating a subsurface temperature in excess of ~200 °C (Nicholson, 2012).

Acid-sulphate waters are formed by the condensation of geothermal gases such as H_2S in the shallow subsurface. The volatiles, originally dissolved in deep fluids, were separated by boiling during depressurization. As they rise towards the surface, these gases condensate into surficial waters, bringing sulfate ions and acidity. The pH can be as low as 2.8, so these waters are highly reactive and corrosive and the characteristic minerals are kaolin, montmorillonite, mordenite, halloysite, cristobalite and alunite (Nicholson, 2012). Since most of the reactions are taking place in the near-surface, we cannot infer the conditions of the reservoir from this type of fluids. Bicarbonate waters are the product of steam and gas condensation into poorly-oxygenated sub-surface groundwaters. They have a near-neutral pH with bicarbonate and sodium as the principal constituents (Nicholson, 2012). Deposits of travertine ($CaCO_3$) are common at the discharge areas and indicates subsurface fluid temperatures below ~150 °C.

Hydrothermal alteration can be classified depending on the characteristic mineral assemblage: argillic, propylitic, potassic and phyllic, but also, by temperature and activity ratio of aqueous cation species in hydrothermal solution. Utada (1980) defines three types of hydrothermal alteration, an acid-type at low cation/hydrogen ratio, an intermediate one at medium cation/hydrogen ratio, and an alkaline alteration at high cation/hydrogen ratio (Figure 1.4). Each alteration type comprises several mineral zones corresponding to different temperature conditions.

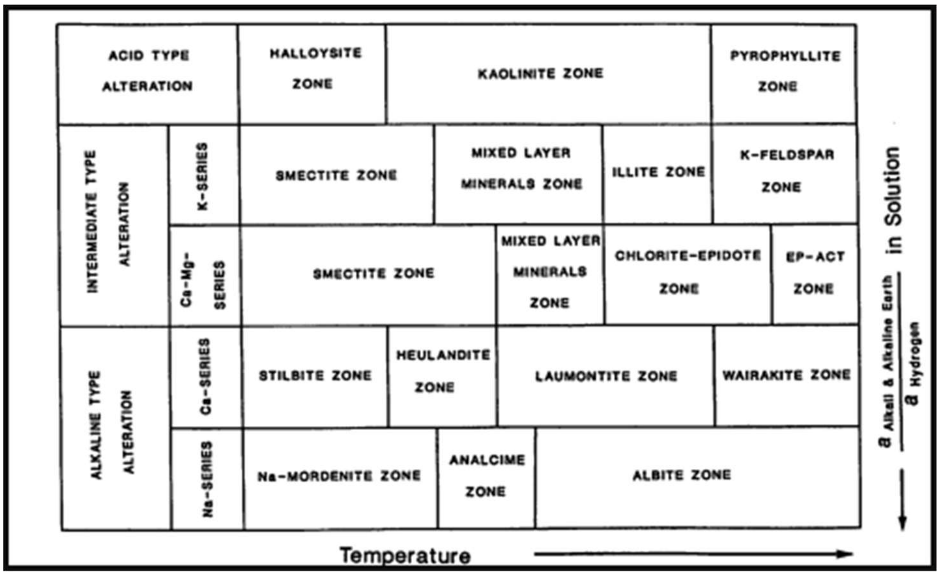

Figure 1.4 Division of the three types of hydrothermal alteration following Utada (1980).

The acid-type alteration is characterized by minerals containing Al_2O_3, SiO_2 and H_2O, such as kaolin, pyrophyllite, andalusite, corundum, and Al-hydroxides. If saturation of SiO_2 occurs, there is a sequential appearance of clay minerals with increasing temperature, which will be detailed in the coming paragraphs. If there is no SiO_2 saturation, aluminum hydroxides such as gibbsite, boehmite, and diaspore occur characteristically (Figure 1.5). The intermediate and the alkaline types of alteration have considerable amount of alkali and alkaline earth elements present in solution. These two types are subdivided into four series which are distinguished by the predominant cation species in solution (Figure 1.6) (Inoue, 1995).

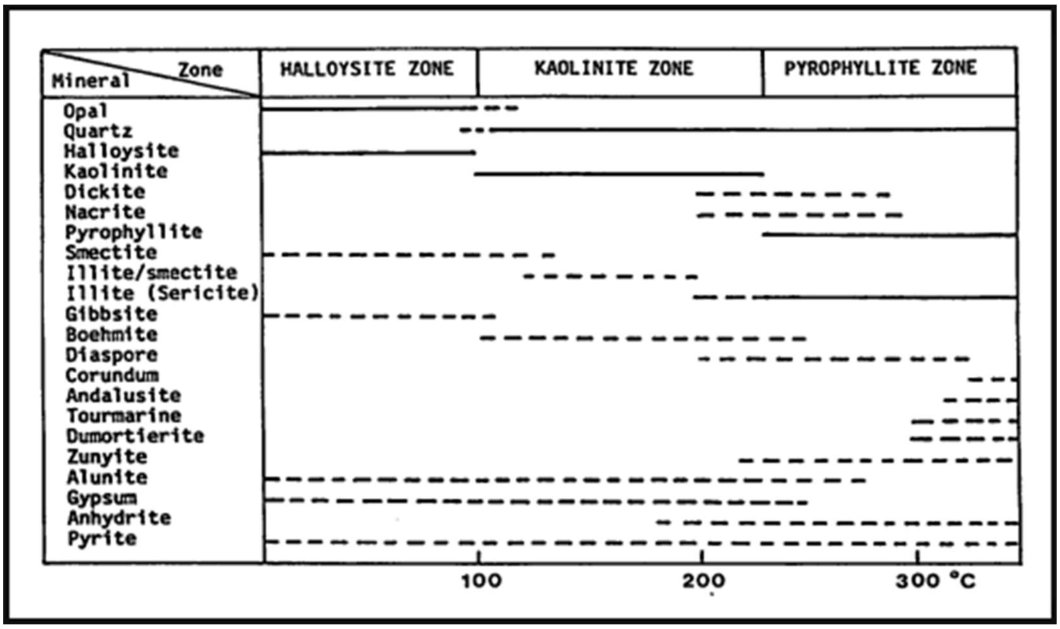

Figure 1.5 Mineral assemblages observed in the acid type alteration in function of the approximate temperature (Utada, 1980).

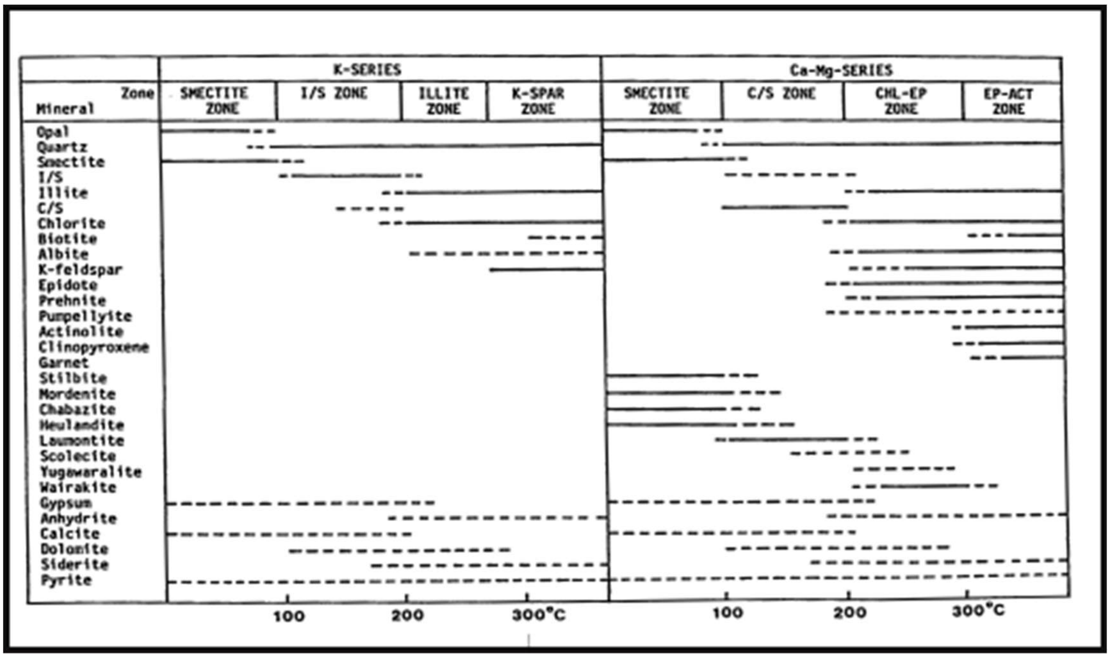

Figure 1.6 Mineral assemblages observed in the intermediate and alkaline types alteration in function of the approximate temperature (Utada, 1980).

1.2.1. The importance of clay minerals in hydrothermal alteration

A characteristic of the acid alteration type is the formation of clay minerals in a sequential order. Specific clay assemblages develop close to the heat source, while different assemblages form in the colder zones of the host rock, away from the heat. Therefore, clay minerals can be used as geothermometers (Brigatti et al., 2006). Furthermore, we can use clays as indicators of the fluid/rock ratio, the duration of fluid/rock interaction and the nature and composition of the original rock, allowing us to reconstruct the thermal evolution of the geothermal system (Brigatti et al., 2006).

Due to their particular importance and useful information, they should be identified by X ray diffraction. However, it is necessary to go deeply into their characteristics and behavior to understand why clays need an extra processing before can use XRD on them.

1.2.2. General structure of clays

Clay minerals are phyllosilicates with a complex molecular structure. They are formed by two units: a sheet of corner-linked tetrahedra and a sheet of edge-linked octahedra (Moore and Reynolds, 1989). Tetrahedral sheets are composed of individual tetrahedrons, usually with Si^{4+} and Al^{3+} as the cation T, and occasionally Fe^{3+}. This cation bonds with four atoms of oxygen, three of them are basal while one is apical. The basal oxygens link two adjacent tetrahedra and construct a bidimensional pattern (Figure 1.7) (Brigatti et al., 2006). The octahedral sheets are modeled as two planes of closest-packed oxygen ions with cations placed on the final octahedral space between the two planes (Moore and Reynolds, 1989). The cations are usually Al^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+} and other transition elements. The free oxygens within the octahedron are oriented towards a common position, allowing the link with a tetrahedral sheet and the construction of a common plane between the two sheets (Figure 1.8) (Brigatti et al., 2006).

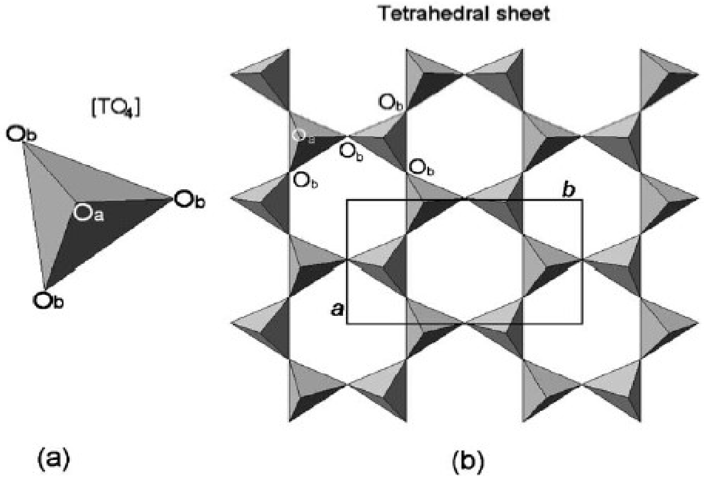

Figure 1.7 Molecular structure of a tetrahedral sheet. (a) Individual tetrahedra [TO4]; (b) Tetrahedral sheet configuration. Ob) Basal oxygens, Oa) Apical oxygen, (a-b) unit cell (Brigatti et al., 2006).

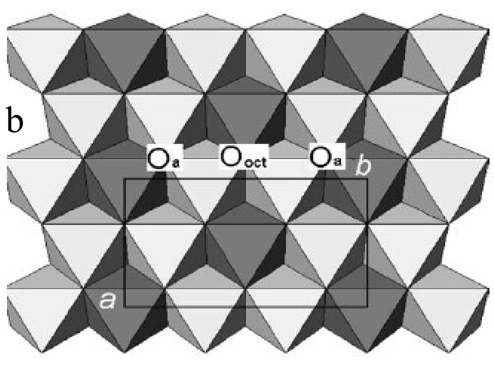

Figure 1.8 Molecular structure of an octahedral sheet. (a) Part of a sheet of edge-linked octahedra b) octahedral sheet. Oct) Basal oxygen, Oa) Apical oxygen, (a-b) unit cell (Brigatti et al., 2006).

Clays present two types of structures. The structure of sheets 1:1 or TO consists on the repetition of a tetrahedral sheet with an octahedral sheet. Meanwhile, the structure of sheets 2:1 or TOT are constructed of an octahedral sheet comprised between two tetrahedral sheets (Figure 1.9). The structure 1:1 has six octahedral and four tetrahedral sites in their unitary cell, while structure 2:1 has six octahedral and eight tetrahedral sites in their unitary cell.

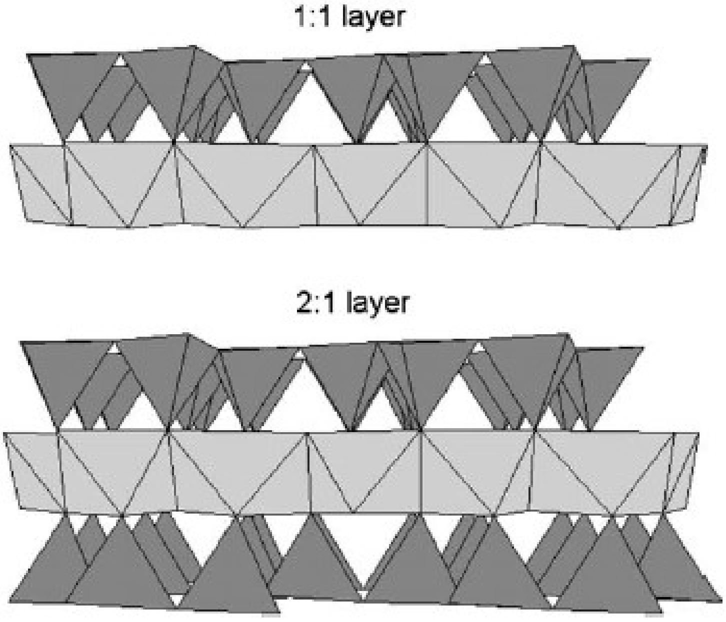

Figure 1.9 Molecular structure of a TO or 1:1 layer and a TOT or 2:1 layer (Brigatti et al., 2006).

1.2.3. Properties and behavior

Exchangeable ions or Cation-Exchange capacity

The charges on clay surface determine ion-exchange capacities. These can be negative or neutral. Electrical negative charge happens when there is a substitution of a cation of lower valence. For example, when Al^{3+} is substituted for Si^{4+} in the tetrahedral sheet or Mg^{2+} is substituted for Al^{3+} in a dioctahedral sheet. Neutral charge is obtained by having individual ions or ionic groups in the interlayer space. The most common interlayer cations are K, Na and Ca (Moore and Reynolds, 1989).

The surface charge of clay minerals compared to their volume is extremely large. The majority of this charge remains on the [001] crystallographic plane and only few percentages on the edges. This induces that cations are more attracted to the [001] plane and anions to the edges which enforces cation exchange. Law of mass action governs this process, however also depends on temperature and pH. Then, the sequence of cation exchange for a montmorillonite series would be:

$$Li^+ < Na^+ < K^+ < Cs^+ < Rb^+$$

This example shows cations with the same charge but important to remark that cations with different charges can also be exchanged.

Electric double layer

The surface of clays attracts cations these cations will attract anions and these anions would attract more cation and so on, when particles approach one another to a short enough distance, Van der Waals forces can bind them into a larger compound. These agglomerates become so large than the Brownian movement cannot longer keep them in suspension and flocculation takes place (Moore and Reynolds, 1989).

In order to avoid this to happen, the negative charge of the clay surface has to be neutralized by univalent cations. These will form an immobile layer around the clays that will keep them away from one another making more difficult Van der Waals effectiveness. On the contrary, if there are divalent or trivalent cations around, the immobile layer cannot be formed causing in consequence flocculation.

Interaction of water

Only some clay minerals have the property of expand themselves in contact with water. When it occurs, the swelling or expansion is exclusively along the [001] plane, so crystallographic integrity is maintained. This property is controlled by mainly two aspects: (1) the polar nature of the water molecule, (2) the size and charge of cation in the interlayer space. (Moore and Reynolds, 1989). Swell- clay minerals are carrying water that during burial, sedimentation, compactation processes can be released. It is thus the principal controlling factors of diagenesis or alteration in rocks.

Interaction with organic compound

When organic compounds are located in the interlayer space of clay minerals, they cannot polymerize in the same manner as silica. In order to conserve the tetrahedral bonding angle, four hydrogens must be dropped from a carbon and then shared by another carbon(Moore and Reynolds, 1989). The resultant structure has a plane that may be parallel or perpendicular to the [001] plane. When aliphatic complexes such as ethylene glycol are introduced into the interlayer space, some clay minerals form a perpendicular chain to the [001] plane which causes a mineral expansion. This feature is important for identification of clay mineral species.

1.2.4. Classification of clay minerals

Clays are classified depending on their type of layer, TO or TOT, with further groups and subgroups depending on other characteristics. Table 4.3 presents a classification modified from (Moore and Reynolds, 1989).

Table 4.3 Classification of clay minerals.

Layer type	Group	Subgroup	Species
1:1	Serpentine-kaolin	Serpentines (2:1)	Chrysotile, antigorite, lizardite, berthierine, odinite
		Kaolin (1:1)	Kaolinite, dickite, nacrite, halloysite
2:1	Talc-pyrophyllite	Talc (2:1)	
		Pyrophyllite (1:1)	
	Smectites	(2:1) smectites	Saponite, hectorite
		(1:1) smectites	Montmorillonite, beidellite, nontronite
	Vermiculites	(2:1) vermiculites	
		(2:1) vermiculites	
	Illite	(2:1) illites	
		(1:1) illites	Illite, glauconite
	Micas	(2:1) micas	Biotite, phlogopite, lepidolite
		(2:1) micas	Muscovite, paragonite
	Brittle mica	(2:1) brittle micas	Margarite
	Chlorite	(2:1) chlorites	
		(1:1) chlorites	Donbassite
		(2:1) (1:1) chlorites	Sudoite, cookeite
		(2:1) (1:1) chlorites	
2:1	Sepiolite-palygorskite		

1.2.5.Key examples of clay minerals

Illite

Compositionally, illite is straightly related to muscovite and smectite. Illite is specially known to have more Si, Mg and H_2O but less tetrahedral Al and less interlayer K than muscovite (Bailey, 1980) (Figure 1.10). This is the most abundant clay mineral in sedimentary rocks, formed by the alteration of feldspars and the degradation of muscovite (Poppe, 2001). It can also form through hydrothermal alteration and metamorphism. Further alteration provokes changes in the illite structure to become a fully expendable clay. Illite is formed by the opposite process during burial, replacing smectite (Moore and Reynolds, 1989).

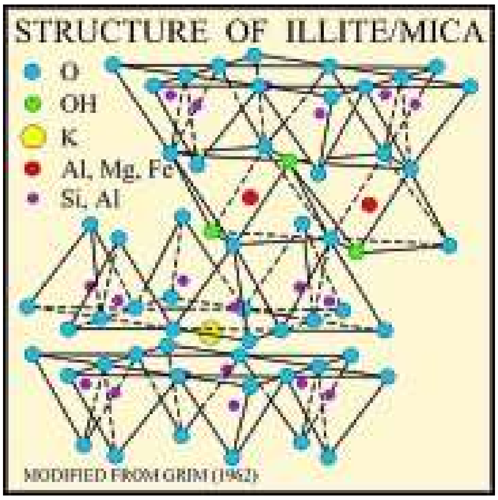

Figure 1.10 Structure of Illite taken from Poope (2001)

Smectites

Smectites have the property to expand and contract their structures, keeping two-dimensional crystallographic integrity (Figure 1.10). Expansion happens as water or some polar organic compound, like ethylene glycol, interacts with the interlayer space (Moore and Reynolds, 1989). Smectites are frequently produced during weathering of basic rocks, or in terranes poorly drained and mildly alkaline having high Si and Mg contents (Poppe, 2001).

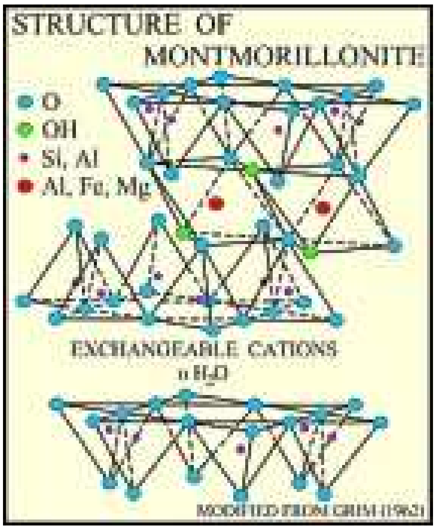

Figure 1.11 Structure of Smectite taken from Poope (2001).

1.2.6. Mixed layered illite/smectite

Illite is more stable than smectites at higher temperature and pressure and in different chemical environments than those generally found at the surface of the Earth (more acidic for example). That is why interstratified clays are commonly found in burial environments, generally basins. They form as follows:

Kfeldspar + smectite→ illite + chlorite + quartz

However, geothermal areas and hydrothermally altered zones also present this transition series (I-S). Geothermal implication are huge, these are related with temperature but also, permeability, chemistry of fluids, composition with mother rock. (Moore and Reynolds, 1989).

CHAPTER 2.
GEOLOGICAL FRAMEWORK

2.1. Ecuador Geological Setting

The Andes mountain range were created by the continuous subductions of oceanic lithosphere since the Jurassic (Eguez and Aspden, 1993). The Ecuadorian Andes are part of the Northern Volcanic Zone (NVZ) of the Andean Cordillera and comprise two parallel NNE mountain chains, the Cordillera Real to the east and the Cordillera Occidental to the west, divided by the Inter-Andean Valley (Aguilera, 1998). Volcanism in the NVZ is the result of Nazca plate and Carnegie Ridge subduction under South American margin since early Miocene (Guillier et al., 2001; Gutscher et al., 1999).

The Cordillera Real is formed by sub-linear belts of rocks of Paleozoic to early Mesozoic age mostly, intruded by granitoids of early Mesozoic age. The Cordillera Occidental, in turn, consists of basalts and volcaniclastic rocks belonging to allochthonous oceanic terrains of late Mesozoic age (Hughes and Pilatasig, 2002). The Inter-Andean Valley is a sedimentary basin filled with volcaniclastic and epiclastic rocks of Tertiary age, currently surrounded by active inverse faults, the Pujilí-Calacalí suture to the west and the Peltetec suture to the east (Beate, 2010).

The extensive volcanism of Ecuador has been controlled by processes of convergence, which has also generated regional uplift and crustal failure and deformation (Lonsdale, 1978). Northern Ecuador is characterized by an active volcanic arc which extends toward Colombia. It has calc-alkaline affinity linked to contemporary subduction (Barberi et al., 1988; Hall and Beate, 1991). Within this area (Figure 2.1), Ecuador counts more than 30 active volcanoes that favor the presence of positive thermal anomalies to feed geothermal systems (Beate, 2010).

2.2. Study area

Chachimbiro volcanic complex is located at the northern part of Ecuador, in the Imbabura province. Its geology is composed by the following formations: the Pallatanga Formation, which are mainly Cretaceous volcanic rocks that constitutes the basement of the Western Cordillera (Vallejo Cruz, 2007). Over this unit is the Rio Cala Group, which comprises massive basaltic to andesitic lavas and volcanic breccias. The outcrops of this unit are exposed on the Southeastern flank of the volcanic complex (Granda, 2011). The Natividad Formation comprised in Rio Cala Group, is composed by sedimentary rocks forming the dominant Cretaceous lithology covering the southern and eastern slopes of Chachimbiro volcanic complex (Granda, 2011). Silante Formation is clearly exposed on western and northern flanks of the volcanic complex and include channelized conglomerates, breccias, red mudstones and shales of Paleocene ages (Granda, 2011). The Pugaran volcanic unit occurs both southeast and northwest of the Chachimbiro complex. It is formed by deposits of andesitic lava flows and hornblende dacite tuffs and breccias, deposited during the Tertiary (Granda, 2011).

The long lasting evolution of the Chachimbiro Volcanic Complex contains three successive phases called Huanguillaro, Tumbatú and Hugá (Pilicita, 2017). Phase 1 is composed of andesite lava flows that formed the andesitic stratovolcano known as Huanguillaro (Bellver-Baca et al., 2019). A collapse occurred after phase 1, forming a horseshoe that opened to the east. Phase 2 comprises Tumbatú or Chachimbiro volcano, consisting of a dacitic dome that suffered a landslide to the east forming a scar which formed a second horseshoe (Bernard et al., 2014). Phase 3 is the most recent period of dome building. These dacitic domes occupy the center of the crater and include the large domes of Cerro Hugá and Cerro Albují.

Three faults systems are believed to play important roles in the origin of the volcano and the potential location and circulation fluids in the geothermal systems. The NE-SW striking Florida fault systems forms the contact between the Natividad and Silante units (CELEC and SYR, 2012). This fault complex underlies the eruptive centers of Huanguillaro volcano and the Hugá-Albuji domes (CELEC and SYR, 2012). The Azufral fault system also trends NE-SW, and is interpreted as being a right lateral strike slip fault system. This fault zone may represent the transition of the Natividad to the Rio Cala formation, bringing the Rio Cala unit into contact with the Quaternary volcanic unit (Pilicita, 2017). The Pijumbí fault is a segment parallel to the Azufral fault. Finally, the third important fault zone that extends E-W through the eastern part of Chachimbiro, is called the Chachimbiro Fault and controls the hydrothermal alteration and hot springs found along the trace of this fault zone (CELEC and SYR, 2012; Pilicita, 2017). Figure 2.1 shows a map of the principal fault systems and the alterations zones that seem to be related with these faults

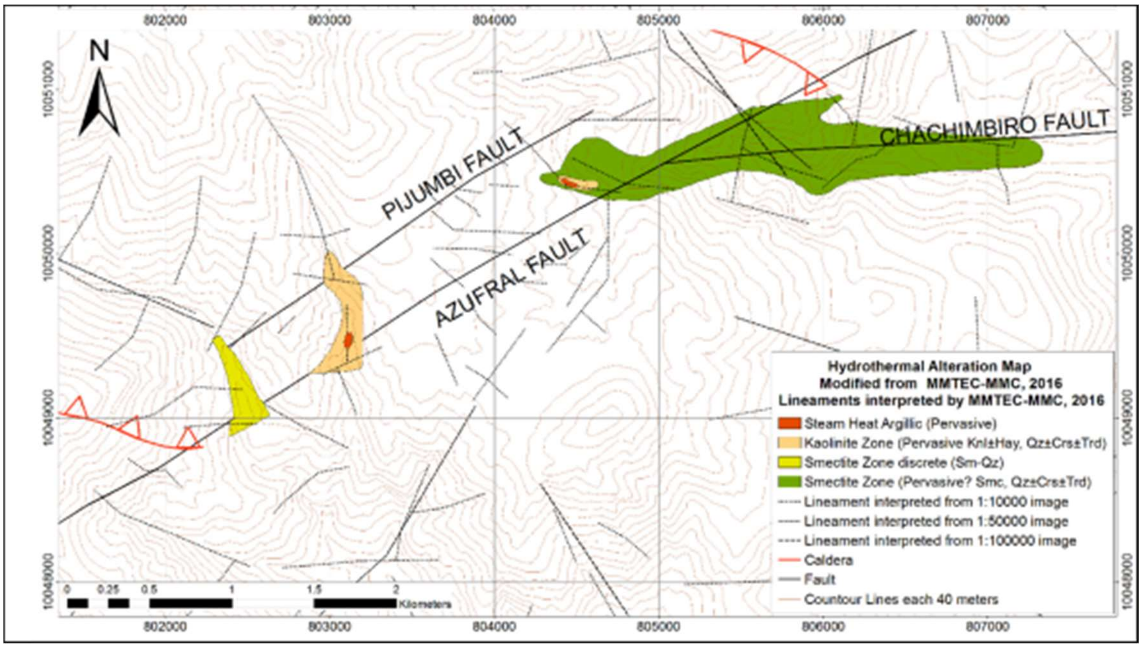

Figure 2.1 Topographic map of Chachimbiro geothermal area with the principal fault systems and hydrothermal alteration zoning (CELEC and SYR, 2012; Pilicita, 2017).

There have been various studies of surface waters from Chachimbiro geothermal field. Aguilera et al. (2005) analyzed waters of alkali-chloride to bicarbonate type (Figure 2.2a) with a corresponding reservoir temperature from cation geothermometry between 225 °C and 260 °C (Figure 2.2b). Beate (2010) showed that the reservoir was liquid-dominated and proposed the model for Chachimbiro geothermal system presented in Figure 2.3.

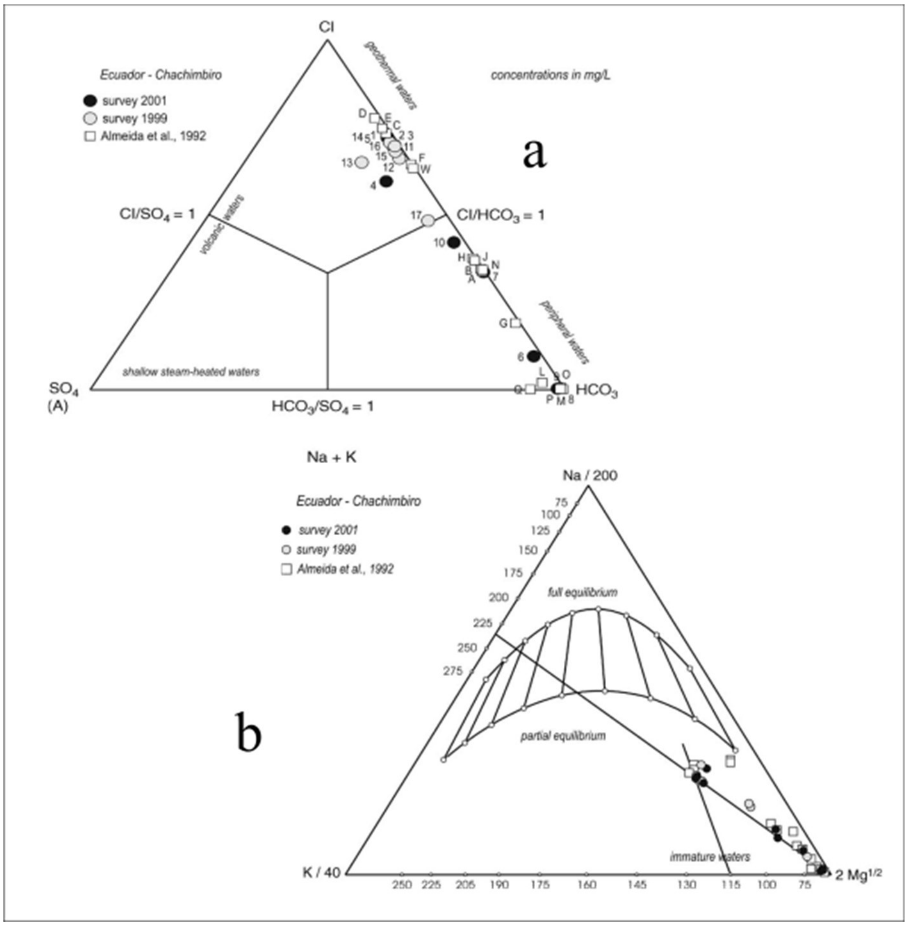

Figure 2.2: Ternary diagrams of Chachimbiro geothermal waters. a) Geothermal fluid type from hotsprings sampling. b) Geothermometry based and modified from Giggenbach model (Aguilera et al., 2005).

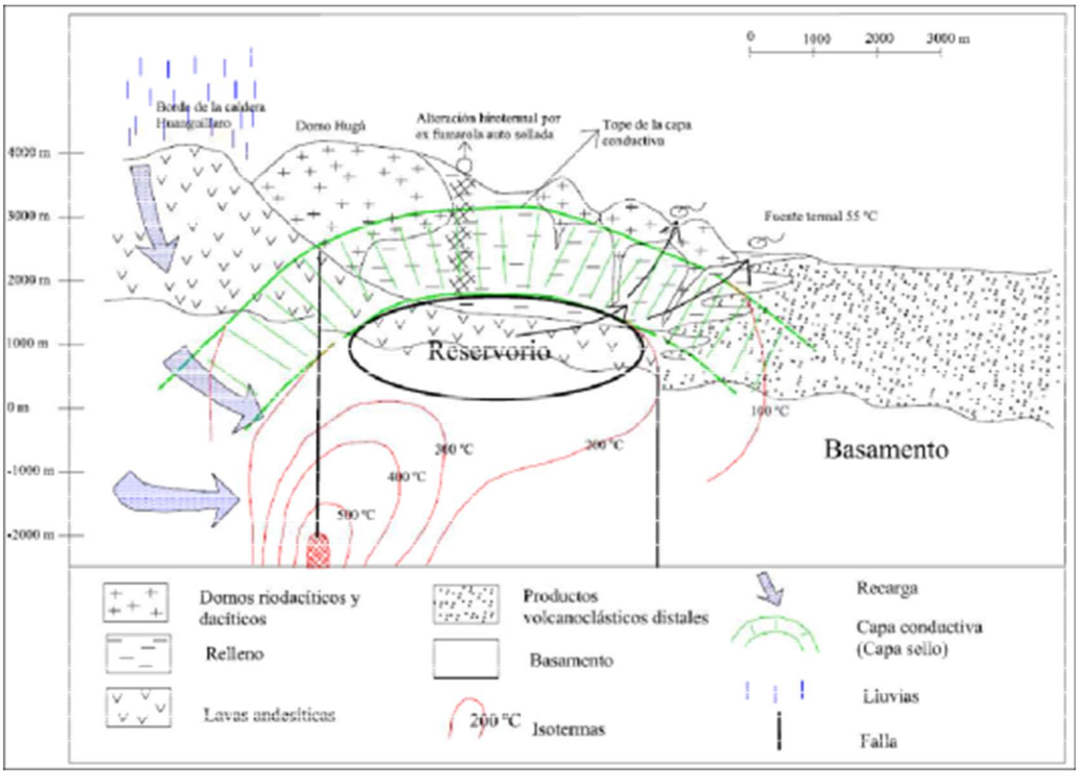

Figure 2.3: Preliminary model of the Chachimbiro geothermal system (Beate, 2010).

CELEC & SYR also performed geophysical surveys, included in their 2012 report. Among them, 70 magnetotelluric and 35 time-domain electromagnetic stations. They suggested an extensive, low-resistivity, clay alteration zone covering the reservoir which can be associated with the cap rock. They also mentioned a potential high-resistivity cap below the clay cap, suggesting a loss of reservoir permeability. Moreover, Pilicita (2017) describes a similar cap rock <10 Ω by magnetotelluric surveys and calculated its area corresponding to 11 km^2 and a thickness of 340 m. It suggested smectite as the clay forming the cap rock. Pilicita (2017) performed a 3D model based on geochemical results and the trend of faults systems trending, using PETREL software, presented in Figure 2.4.

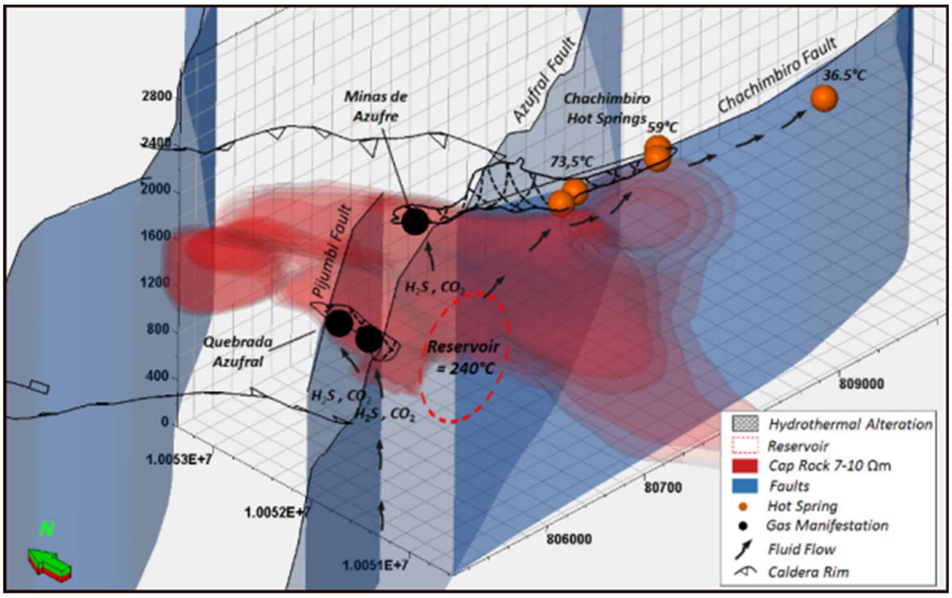

Figure 2.4 3D model of Chachimbiro geothermal system exemplifying the cap rock extent and the fluid flow directions (Pilicita, 2017).

There are multiple hydrological models proposed for Chachimbiro, however none of them includes all the chemical and physical parameters already discovered. Some examples are summarized in Beate & Urquizo (2015). One model depicts a small to medium size geothermal reservoir hosting moderate to high temperature geothermal fluid and controlled by a fault. A second model proposes a cooling system that has already reached its high temperature peak. And a third model assumes an immature system that failed to reach chemical equilibrium, implying that there is no commercial potential for Chachimbiro.

With the purpose of having a better understanding of Chachimbiro geothermal system, an exploration drilling was carried out in Novemeber 2017, following the pre-feasability study for the Chachimbiro geothermal system, driven by CELEC EP and sponsored by the Japan International Cooperation Agency (JICA). Some of the analyses of the material from the exploration well PEC1 were carried out in Japan and are under a 5 year embargo. As part of Ecuador's development towards renewable energy, CELEC is making effort into improving their skills to be able to do some of the analysis within the country. This thesis is part of this effort, through the development of a method for clay analysis by X-Ray Diffraction (XRD), fundamental to locate the reservoir and estimate fluid temperature through alteration assemblages.

CHAPTER 3.

DEVELOPMENT OF A PROCEDURE MANUAL FOR CLAY ANALYSIS BY XRD

3.1. XRD theory

X-rays are high-energy electromagnetic radiations with a wavelength ranging from 0.01 to 10 nanometers. The energy of an electromagnetic beam interacting with a medium is partially transmitted, partially refracted/dispersed and partially absorbed by this medium. The energy packages can transmit momentum which is an exclusive property of a discrete particle. But also, they can diffract through a grid and have a measurable wavelength which are both special properties of a wave. Max von Loue, physicist from Germany won a Nobel Prize in 1914 by noticing that the spaces within a crystalline structure were similar as a grid. So, by knowing the diffractogram pattern, it was possible to infer the crystal's structure, giving rise to X-ray crystallography studies (Moore and Reynolds, 1989).

In order to understand the diffraction phenomena, consider that an electron within an electromagnetic field oscillates with the same frequency as the field. When an X-ray beam impacts an atom, the surrounding electrons start to oscillate with the same frequency as the incident beam. Interferences are created from the combination of these frequencies, some being destructive and others constructive. A destructive interference is the combination of waves out of phase so that there is no resultant energy leaving the solid phase. On the opposite case, a constructive interference is the combination of waves in phase that complies with the Bragg's law, so that there is energy leaving the solid phase as a diffracted beam (Scintag, 1999).
Bragg's law tells that two or more beams diffracted by parallel crystalline planes construct positive interferences if the optic length covered by those beams (MN segment in Figure 3.1) is an integer multiple (n) of the wave length (λ) of the incident radiation (Waseda et al., 2011).

$$\boldsymbol{2d \sin(\theta) = n\lambda}$$

Where d is the interplanar distance of the crystal and θ the diffraction angle (Figure 3.1). Following Bragg's conditions, each plane of the crystal forms a peak of diffraction, also called constructive interference. The interference pattern, i.e. all the peaks, is unique for each crystal and is called diffractogram. From it, we can infer the geometry of the unit cell, the crystalline system and the internal structure of a crystal.

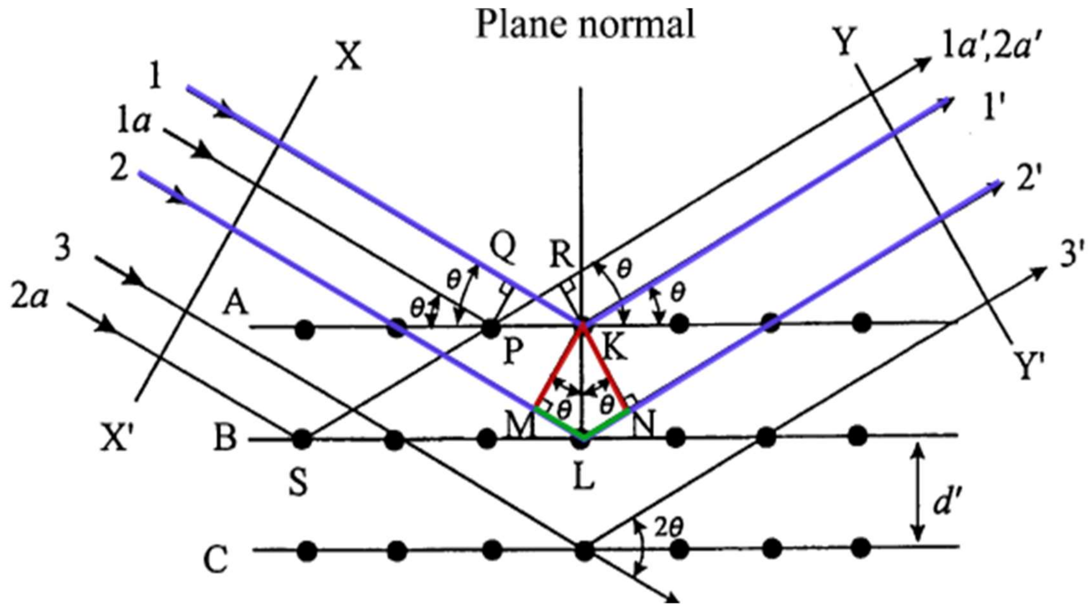

Figure 3.1 Scheme of X-ray diffraction of a crystal under Bragg's conditions. Blue beams are in phase, while green segments represent the optic length. Red segments are the interplanar distance. Figure taken from (Waseda et al., 2011).

3.2. XRD instrument characteristics

The diffractometer used in this analysis was a BRUKER ADVANCE 08 (CuKα radiation, 40 kV, 40 mA). It has a potency of 230 V, 50 Hz, 6.5 kVa. It was set up to collect data from 2° to 30° at intervals of 0.02° for a time of one second. All the data was processed through EVA X-ray diffraction analysis software.

3.3. Sample preparation procedure for XRD clay analysis

There are various ways to prepare clay samples for XRD analysis. The preparation techniques depend on laboratory supplies and available equipment, but mostly on the habits of the researcher. The sample characteristics, such as the carbonate and organic material contents, the grain size and the nature of the sample, heterolithic versus monolithic, also influence preparation procedures.
Currently, there is an extensive literature of clay sample preparation methods in Moore and Reynolds (1989). Also, Hauff et al. (1984) and more recently Poppe (2001), both published by the United States Geological Survey, contributed to XRD clay analysis development. Various methods are used in South America also, FAINGENIERON, which is a Peruvian mineralogical consulting company, and CELEC presented a manual for clay mineral identification and analysis (Farinango, 2017; Yparraguirre, 2018), each of them applied respectively in their laboratories.

This thesis aim was to establish a sample preparation procedure for clay analysis by XRD at the Instituto de Investigation Geológico y Energético (IIGE) of Ecuador. This procedure was elaborated considering IIGE's laboratory supplies and needs by applying a comparison of existing methodology. The methodologies cited in the previous paragraph were used for this comparison. For a known sample, I used the preparation procedure of each of these methods and evaluated the most efficient steps.

The rocks used for this comparison were from IIGE’S rock sample collection. They were chosen based on field notes and infrared light spectrum analysis data. We wanted rocks that contained clays in order to have a reference before our XRD analysis. Finally, four rock samples were chosen. Three of them were from Azuay and Cañar provinces and one was from Manabí province. These were experimentation samples that served only for defining an efficient preparation procedure. We will thus not include the interpretation of their mineralogy in this thesis.

With the purpose of being systematic, we established three phases for sample preparation 1) rock crushing, 2) clay mineral separation, 3) crystal orientation. And two phases after the first XRD analysis to distinguish among clay species: 4) thermal treatment, and 5) ethylene glycol saturation. In the following paragraphs, I will explain the importance of each phase, the methods that were compared and how they were evaluated.

3.3.1. Rock crushing

The objective of this phase is to separate the rock in all the grains or minerals that form it. Poppe (2001) suggested that the grain size of the sample has to be much finer than 67 µm, however, it does not specify which instruments are suitable to reach that size. Moore & Reynolds (1989) are explicit in saying that the rock must be powdered, not ground, so they recommend to avoid the use of grinder, ball mix and shatter box. Nevertheless, they do not specify the final grain size. CELEC and FAINGENIERON procedure manuals are slightly similar in the sense that both proposed first crushing of the rock to reach a grain size of 67 µm, then sieving using a #400 sieve to get grains of approximately 38 µm. The difference between them is that CELEC’s procedure describes that crushing must be done with a shatter box and water for screening. The FAINGENIERON’s procedure, however, does not advocate any instrument for crushing nor does use water to sieve.

Figure 3.2: Hammer and a metal rectangular base.

First, in the attempt to replicate what Moore & Reynolds (1989) suggested, a hammer was used for crushing the rocks. The skill required for this process is low, however it is necessary to have the adequate space and instruments as the rock pieces tend to sprinkle at every hit. The base should also be resistant and clean to avoid contamination. It is very time-consuming method. For obtaining 10 grams of material, I spent 40 min (Figure 3.2).

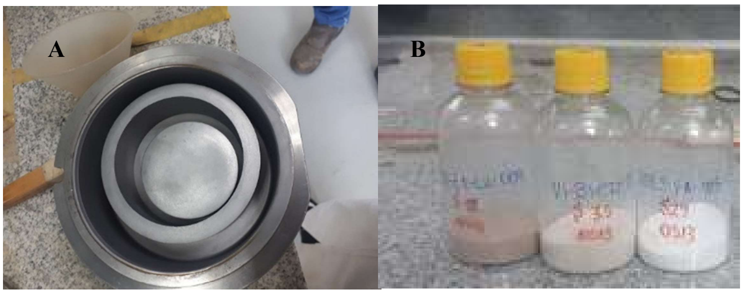

Figure 3.3: Poope (2001) procedure. A) Shutter box B) Obtained powder.

As a comparison, we used a shatter box to crush the sample to quickly obtain the 67 µm material advised by Poppe (2001) (Figure 3.3). Crushing 50g of sample took about 3 minutes.

Figure 3.4: CELEC's procedure. A) Water for screening B) Material after heating at 60°C.

In the case of CELEC and FAINGENIERON, screening is performed after crushing. The use of water for screening following CELEC's procedure made it easy and fast (Figure 3.4). However, we had to put the samples in a stove at 60 °C during 14 hours to evaporate all the liquid after screening. FAINGENIERON advocates sieving the sample without water, which makes the process longer and more tenuous (Figure 3.5). An agate mortar and a fine bristle brush were used to pass grains trough the #400 sieve (38 µm). It took about 40 minutes to sieve 8 grams of material.

As a summary, the figure 3.6 illustrates all the methods contrasted at this stage.

Figure 3.5: Sieving of the material without water, only using a brush and agate mortar.

As time of execution is an important factor in the evaluation among these methods, we may consider Moore & Reynolds (1989) and FAINGENIERON's procedures, as candidates to dismiss and CELEC or Pope's as favorites. However, it is necessary to highlight the following. Contrasting diffractograms, the samples sieved with water reflect bad shaped peaks (Figure 3.7). While the samples sieved without water show many peaks of non-clay minerals (e.g. quartz, albite, anorthite) interfering with clay peaks (Figure 3.8). In the first case, the samples processed with water may be atrophied by the heat required for evaporating the liquid. It can explain the lack of peaks in the diffractogram. We can thus say that CELEC's and FAINGENIERON's procedures are not optimum procedures.

The worst diffractogram was obtained by applying the method of Moore & Reynolds (1989) (hammer). Peaks of clays were mostly invisible or not defined at all. This may result from not enough crushed material in which clays are not separated from other minerals at all. Finally, the best diffractograms were obtained from the samples directly crushed with the shatter box, following Poppe (2001) suggestion (Figure 3.9). Peaks are clearly defined, and despite peaks of non-clay minerals are visible, they do not interfere with clay minerals.

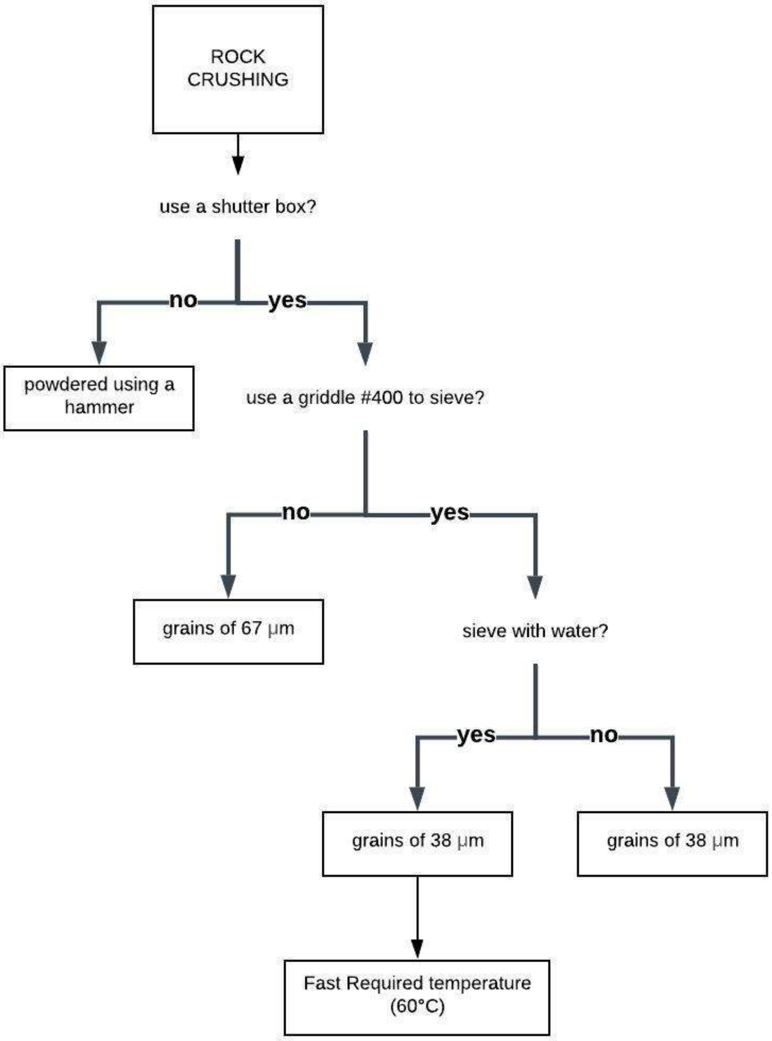

Figure 3.6 Summary of the methods contrasted in rock crushing stage

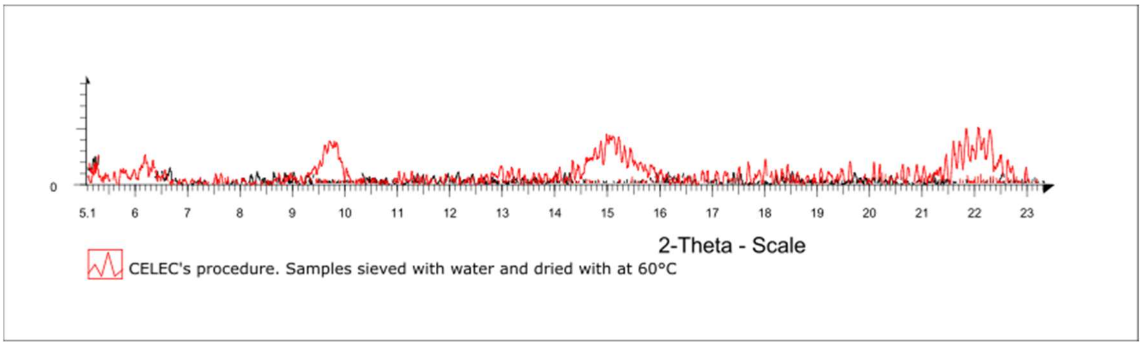

Figure 3.7 Diffractogram of a sample sieved with water.

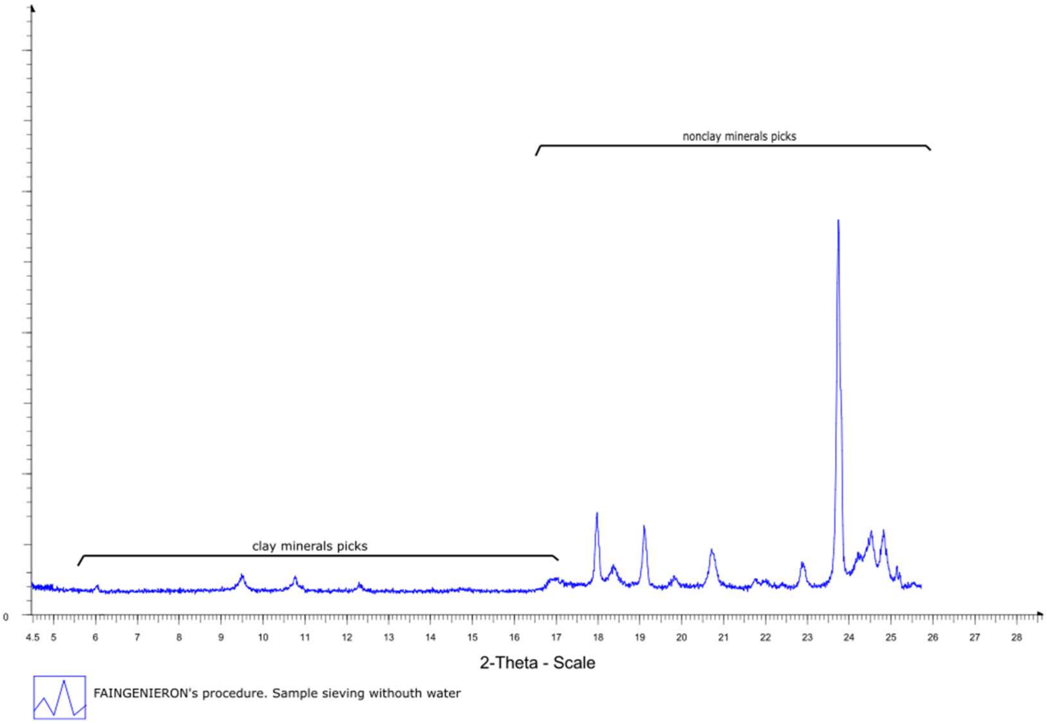

Figure 3.8 Diffractogram of a sample sieved without water.

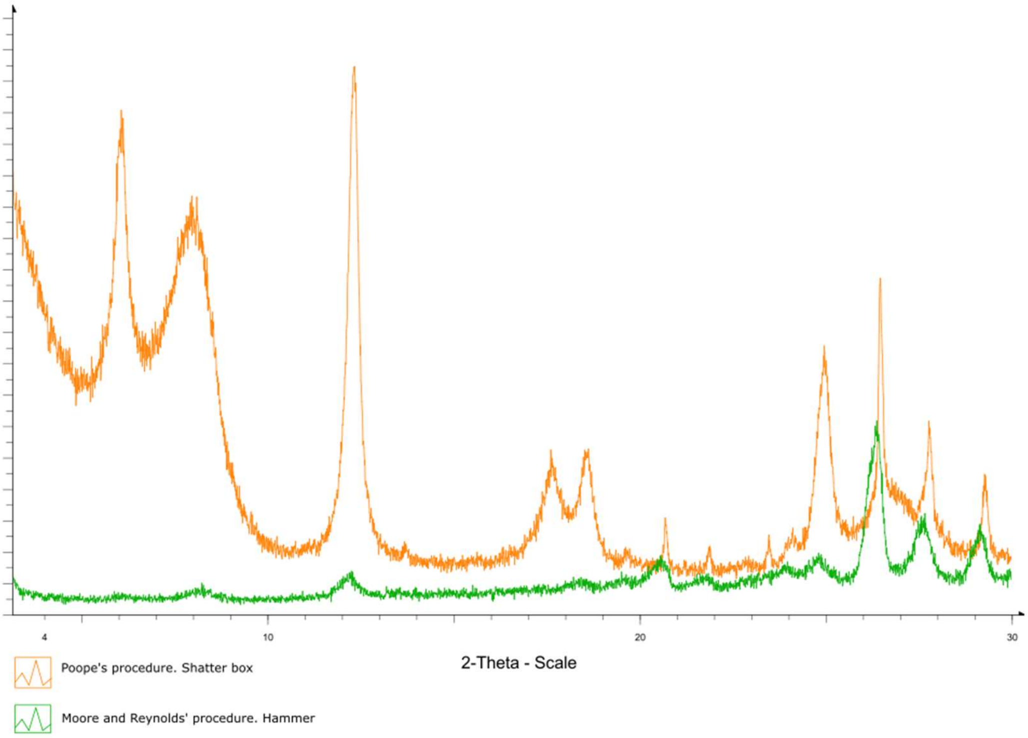

Figure 3.9 Diffractogram of the best and worst procedure.

3.3.2. Clay mineral separation

Ideally, once the rock is crushed, the particles are single crystals. It is then necessary to extract only the clay material from the sample. This arises from some minerals having big peaks that completely cover smaller clay peaks. Separation of clays for X-ray powder diffraction has been done with two different techniques: centrifugation and decantation. They both follow Stokes law, stating that if particles within a medium are subjected to a laminar flow, the coarse fractions (sand and gravel) will deposit first, while the finer fraction (silt and clay) is retained as a suspension.

CELEC's manual and Poppe (2001) suggested clay mineral separation through centrifugation (Figure 3.10), using dispersant agents, a sodium chloride solution for the former and sodium hexametaphosphate for the latter. Dispersant agents produced a buffered pH from neutral to high preventing clays from flocculating. CELEC procedure also saturated the samples of magnesium chloride, later removing the salt excess, washing them with ethyl alcohol and hydrochloric acid. The CELEC procedure thus uses many chemicals, opposite to the recommendations from Moore & Reynolds (1989) to use as little as possible to preserve the fragile phyllosilicates. In the case of Poppe (2001), we did not use hexametaphosphate as dispersant because IIGE did not have, instead added 0.25 grams of NaCl to the centrifuge tubes directly.

Figure 3.10 Separation of clays through centrifugation

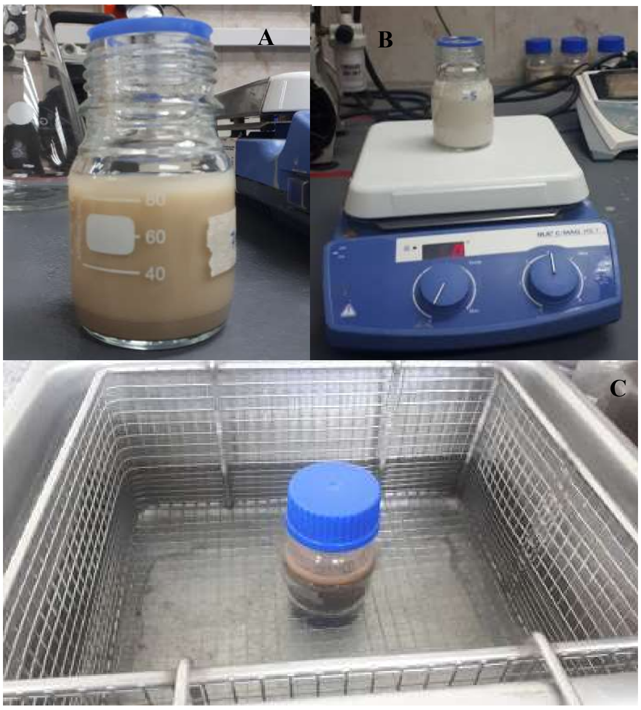

Figure 3.11 Separation of clays through decantation A) Sample leave in rest B) Magnetic stirrer C) Ultrasonic

Poppe (2001) also proposed clay mineral separation through decantation (Figure 3.11), similar to FAINGENIERON's manual. In this case, no dispersant in used following FAINGENIERON's manual, and a magnetic stirrer is used to generate a laminar flow. Poppe (2001) in turn, recommends NaCl as a dispersant, corresponding to less than 0.5% of the weight of the total material, and uses an ultrasonic bath probe for the laminar flow. As for the influence of the agitators, ultrasonic bath versus magnetic stirrer, we processed similar samples with both agitators to contrast results. As a summary, the figure 3.12 illustrates all the methods contrasted at this stage.

Centrifugation techniques were the fastest but not the most efficient. We found that centrifugation time to obtain clay in suspension varied between samples. It can be because of the composition of the sample. We found that the best dispersant is sodium chloride in solution rather than sodium chloride in powder added to the centrifuge tube (Figure 3.13). The samples that used the latter dispersant resulted in bad diffractograms with large peaks with a mountain shape, preventing identification of clays (Figure 3.13). We suggest that the amount of dispersant may have been too much, causing clay flocculation. The second point was that, even though Moore & Reynolds (1989) said that the use of chemicals should be minimal, when CELEC's treatment was applied the results were not so bad. Samples with this treatment showed clear diffractograms with clay peaks (Figure 3.14).

Decantation techniques appeared more efficient than centrifugation. This is partly because all the samples required the same treatment and therefore the same time for preparation. We only adjusted the amount of material, temperature of the medium and use an appropriate jar height in order to perform stokes law correctly. It is thus a process that can be applied to numerous samples at once, in accordance with IIGE requirements. Moreover, the use of dispersant resulted in better diffractograms. The samples subjected to the process of FAINGENIERON, without dispersant, showed disturbed diffractograms in which clay minerals were difficult to find, except for the kaolinite group which were registered in two samples. The samples without dispersant which also used ultrasonic bath as agitator gave even worse results in the diffractograms (Figure 3.15). Samples following Poppe (2001) recommendations, with the use of dispersant and ultrasonic bath as agitator, resulted in diffractograms with clay mineral peaks clear and better localized. However, some quartz peaks were also present in the diffractogram. Instead, the samples processed with a magnetic stirrer as agitator and dispersant resulted in diffractograms without these intense quartz peaks and clay peaks well defined (Figure 3.16). We therefore recommend the use of a magnetic stirrer as FAINGENIERON suggested but also the use of a dispersant as Poope's recommends.

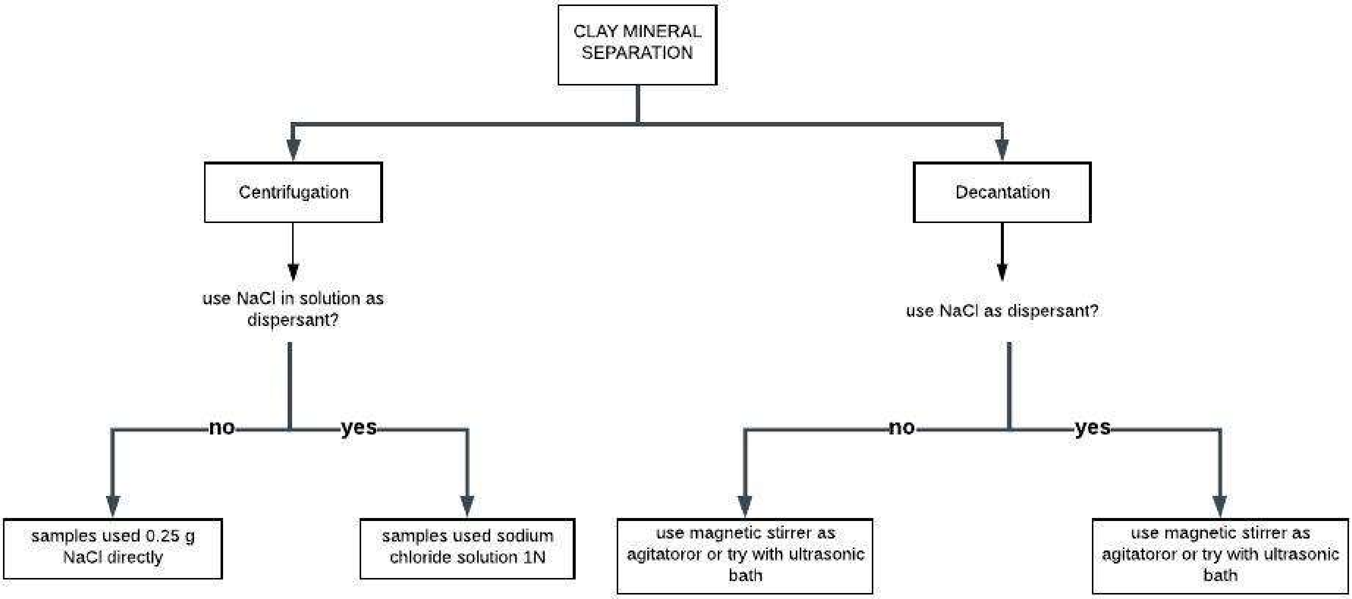

Figure 3.12 Summary of the methods contrasted in clay separation stage

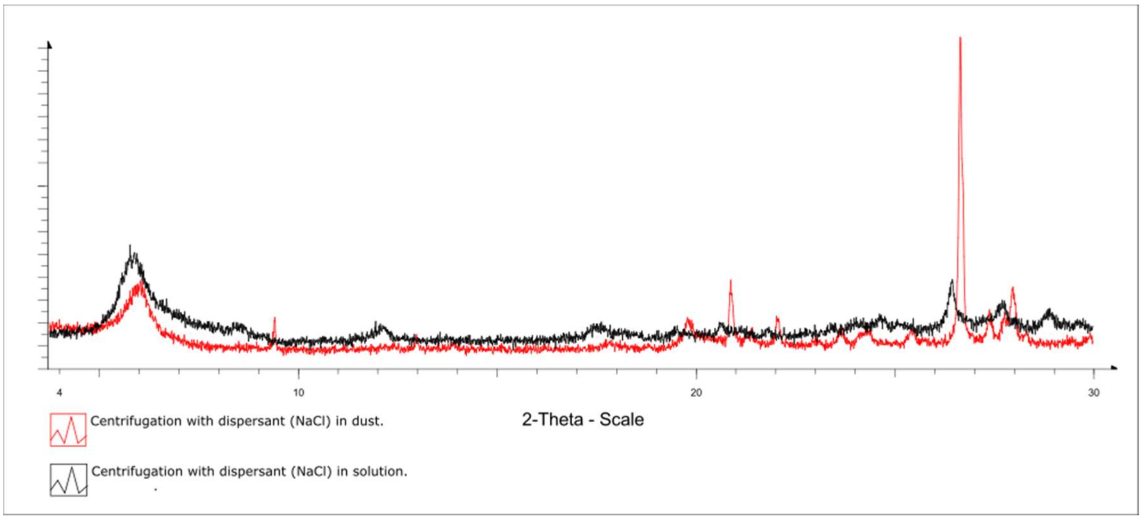

Figure 3.13 Diffractograms using dispersant in grain and in solution

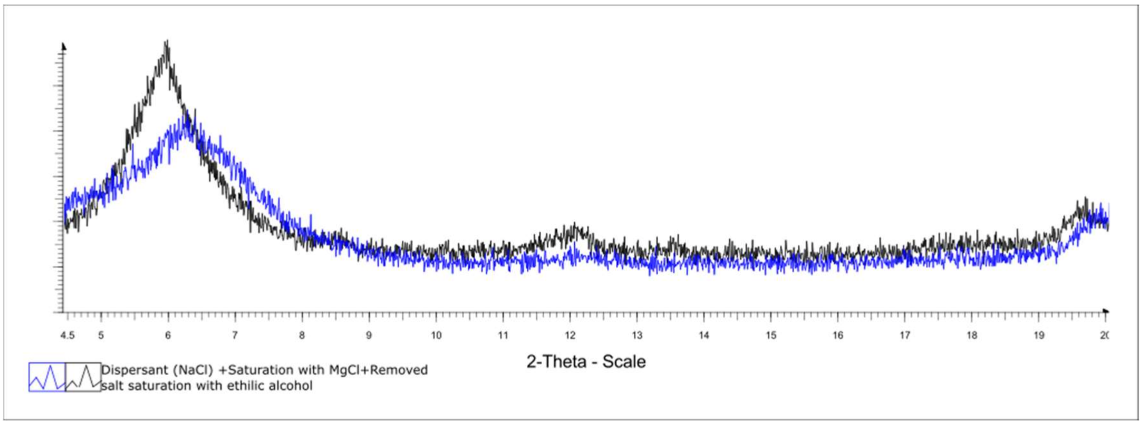

Figure 3.14 Diffractograms using dispersant ant being saturated with MgCl

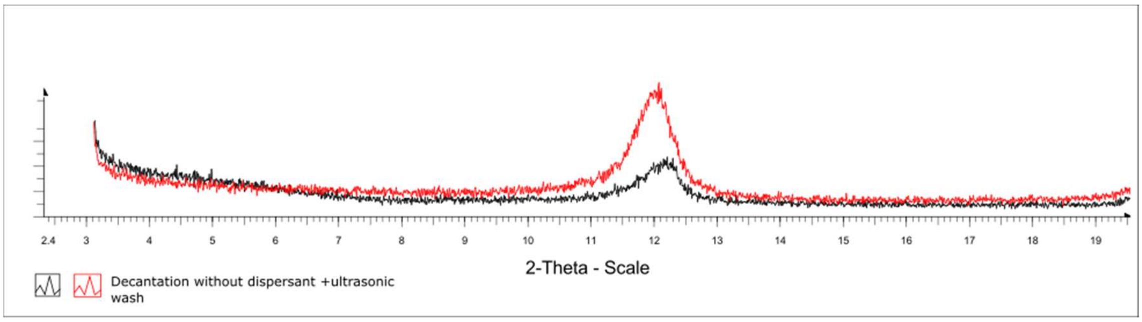

Figure 3.15 Diffractograms do not use dispersant but ultrasonic wash as agitator.

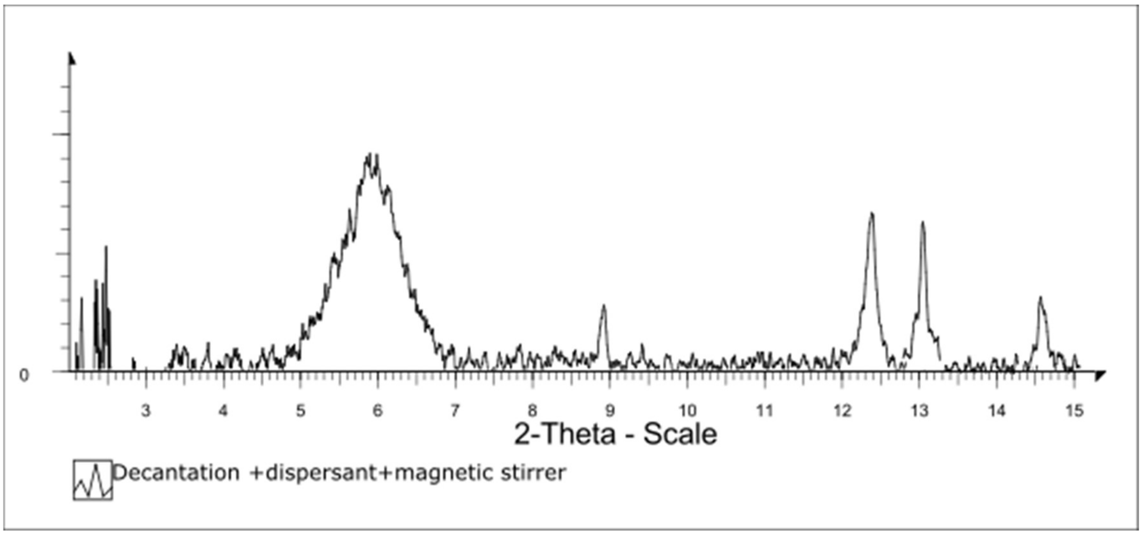

Figure 3.16 Diffractograms using dispersant and magnetic stirrer as agitator.

3.3.3. Crystal orientation

At this stage, the supernatant liquid that contains the clay-size material on suspension has been extracted. During this phase, clay aggregates or clay crystals are mounted in a sample holder and oriented in order to improve the identification of clay minerals or to quantify the amount of each clay species.

For a better characterization of clay minerals, it is strongly recommended to mount the clay particles as oriented aggregates in a sample holder. It forces the clay crystals, usually plate-shaped phyllosilicates, to lie flat, letting the incident X-ray beam impact down the z-axis of the minerals and to record the diagnostic basal fractions (Poppe, 2001). As certain clay minerals during subsequent treatments suffer changes like expansion or contraction in their interplanar distance that is notice by the picks of a diffractogram, having a sample with oriented aggregates allows to evidence these variations in clays and thus to characterize them properly.

Randomly oriented particle mounts should be used to quantify clay minerals. It ensures that the incident X-rays have an equal chance of diffracting any crystal lattice face of the minerals in the sample (Poppe, 2001). It can also work for characterizing the clay mineral species. However, it is not as good as the oriented aggregates method for characterization only. Even though the aim of this research was not to quantify clay minerals but to identify them, we performed both methods to test the difference between oriented and randomly oriented samples.

Poppe (2001) proposed a randomly oriented particle method. It uses a stove at 60°C to evaporate the supernatant liquid and obtain only the solid material. This material is separated with an agate mortar, sieved with a sifter #300 (62 µm) and placed directly in the sample holder (Figure 3.17).

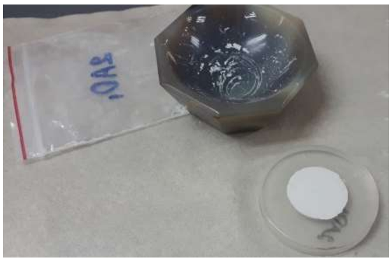

Figure 3.17 Randomly oriented particle method.

Moore & Reynolds (1989), the FAINGENIERON's manual and Hauff et al. (1984) all recommend an oriented aggregate mount made by filtering the supernatant in vacuum with a <16 µm filter (Figure 3.18). However, only Hauff et al. (1984) proposed analysis directly after the filter has settled down in the sample holder (Figure 3.19A). Conversely, Moore and Reynolds (1989) proposed the transfer method, consisting in transferring the clay material from the porous filter to a substratum such as glass slide or quartz tiles by rolling across one into another (Figure 3.19B). Finally, the last method performed, called smear method, was also taken from Moore & Reynolds (1989) but does not need vacuum filtration. It consists in centrifuging the sample until it resembles a butter-like paste. After that, using a microspatula subparallelly, spreading it uniformly flat over a substratum of glass (Figure 3.19C). All the procedures performed are comprised in the figure 3.22.


Figure 3.18 Filter the supernatant in vacuum.

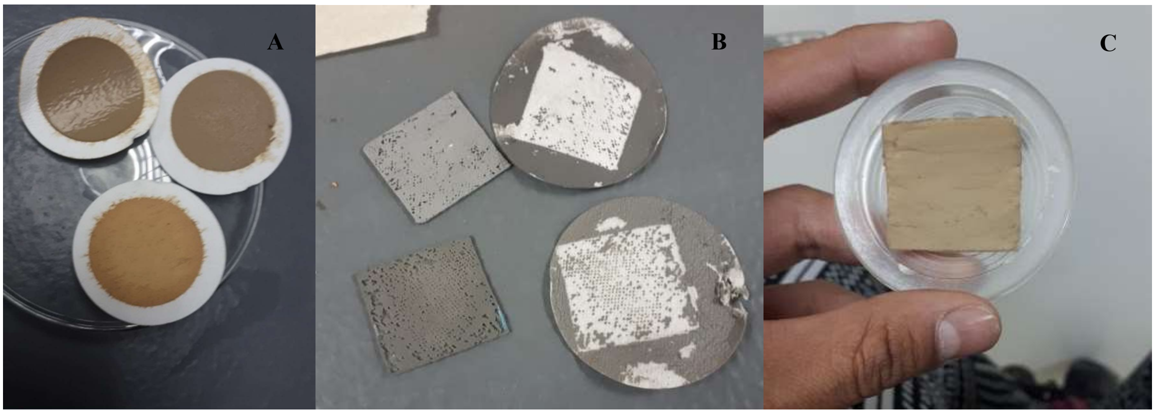

Figure 3.19 Substrates where sample where placed after vacuum filtering. A) Directly on the cellulose filter B) Transfer method C) Smear method.

The longest and least effective procedure was the randomly oriented aggregates by Poppe (2001). First, the evaporation of liquid took about 8 hours under heat exposition and the heat may have affected the structure lattice. Second, sieving the material with the sifter #300 directly over the sample holder was very difficult. IIGE does not have sifters smaller than 15 centimeters of diameter, while the sample holder has a diameter of about 2 centimeters, making it hard not to waste material. The other methods were faster but most of them required high skill level too, especially taking into account that clay material tends to be very fragile when it dries. It is therefore common to find cracks or even curls in the substratum (Figure 3.20).

Figure 3.20 Damage in the sample either cracks or curls.

The method of Hauff et al. (1984) and the transfer method of Moore & Reynolds (1989) proposed the use of filters. However, when these were applied in IIGE’s laboratory, the filters available where rough and bigger than the sample holder. Clay adopt the shape of the filter in both techniques causing undesirable results (Figure 3.21A, 3.21B). With the transfer method, the irregularity of the filter surface made the clay material crack and curl more easily, while following Hauff et al (1984) filters must be cut to fit in the sample holder. Perfectly flat surface must be required for a good analysis. In the end, the best method of oriented aggregates was the smear method (Figure 3.21C) because the spreading was simple and it avoided the formation of cracks, curls and even fractures.

Figure 3.21 Methods offered by Hauff et al (1984) and Moore & Reynolds (1989). A) Filter was cut to fit in the sample holder B) Sample adopted the roughly surface of the filter. C) Transfer method samples.

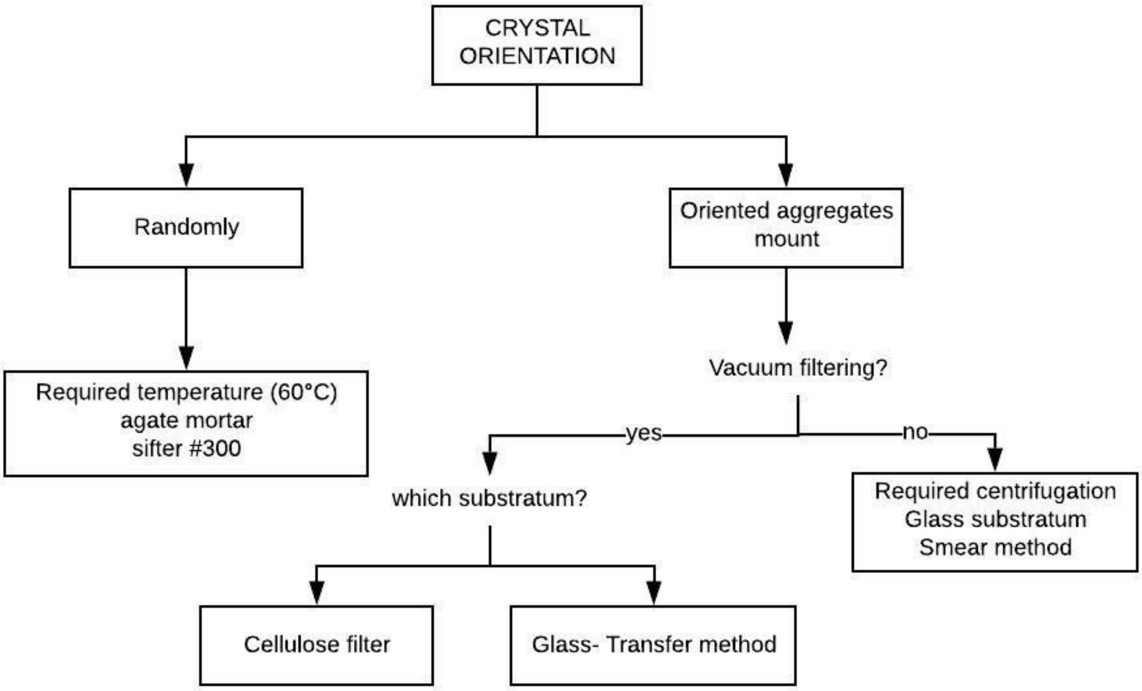

Figure 3.22 Summary of the methods contrasted in crystal orientation stage

3.3.4. Post-analysis treatments: ethylene glycol saturation and thermal treatment

These treatments were applied only for randomly oriented aggregate samples. They were used after the first XRD analysis because they induce a change, e.g. displacement, amplification and/or disappearance, of the (001) peaks (basal planes of a crystal) for certain clay minerals. Both methods were applied according to Poppe (2001) and Moore & Reynolds (1989) and they were successful in both cases. Figure 3.23 shows the change of a sample with ethylene glycol while Figure 3.24 shows the change with heat treatment.

Regarding the thermal treatment, samples have to be subjected to 550 °C for about an hour and a half, while the ethylene glycol saturation has to be done in a desiccator exposed to 60 °C for 10 hours. It is important to consider that the changes caused by these treatments are not permanent, so the XRD analysis should be done as soon as the processes end. Poppe (2001) offers a complete diagram that identifies clay minerals according to the displacement in distance ***d*** measured in Å**,** caused by thermal and ethylene glycol treatments. Figure 3.25 shows a short version of this diagram, exemplifying how clays can be identified. This chart was used in the present research to identify clay minerals from the Chachimbiro geothermal well and can be found in the website cited in the references.

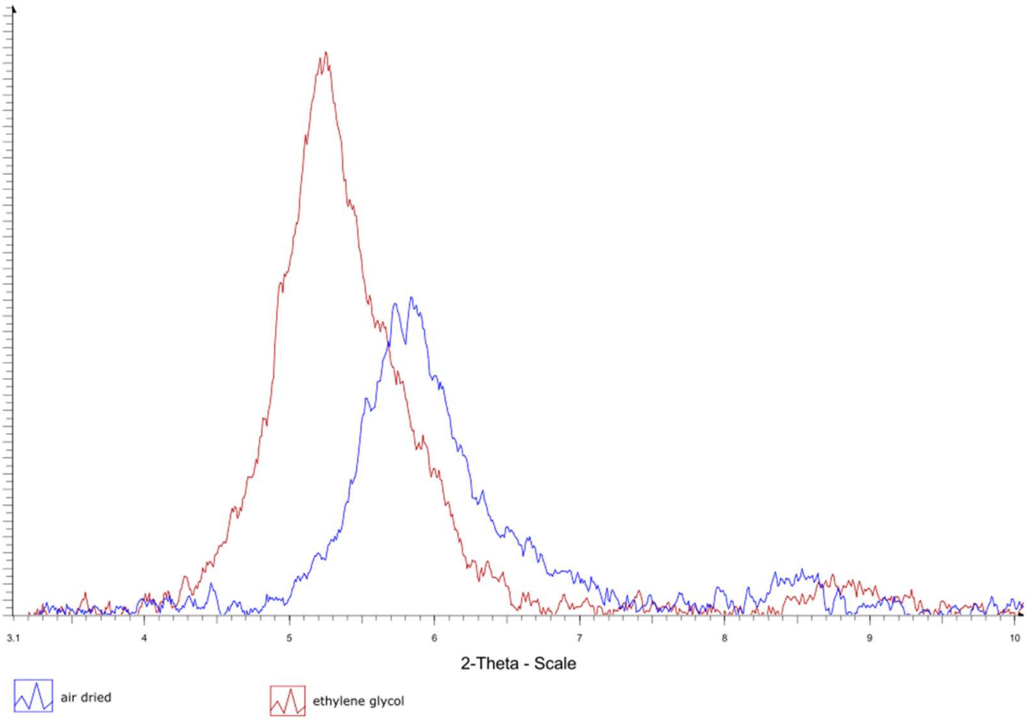

Figure 3.23 Diffractograms of a sample with and without ethylene glycol treatment showing a shift in peak position.

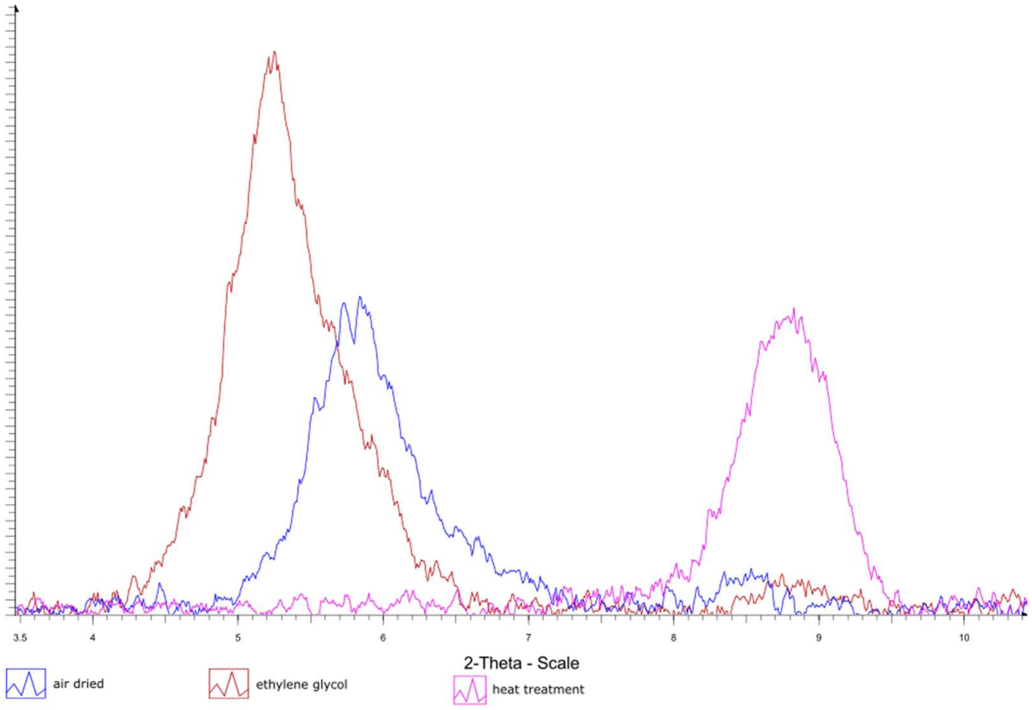

Figure 3.24 Diffractograms of a sample with ethylene glycol treatment, thermal treatment and without any post treatment showing variations in peak position and height.

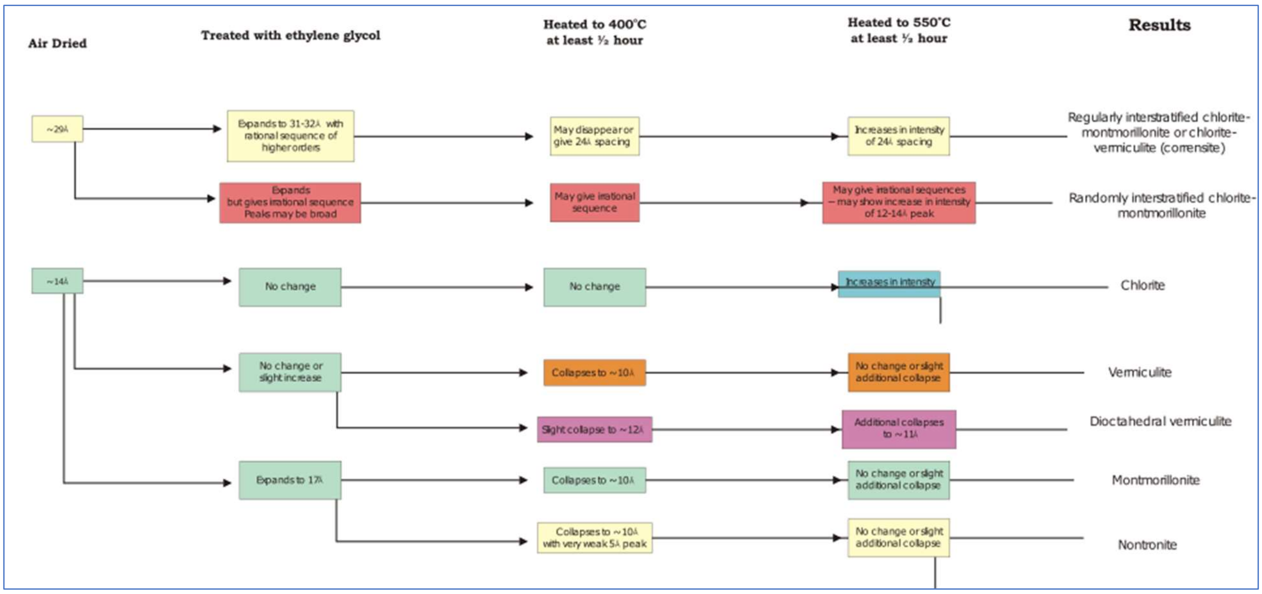

Figure 3.25 Flow diagram of Poope (2001). According the displacement of the picks with different treatments, clays can be identified. It is a short extract, the complete version is available on line.

3.3.5. Refined sample preparation procedure

After all of the experimentations detailed in the last section, it is necessary to give some conclusions and propose a procedure for clay preparation for XRD analysis to IIGE's laboratory that will be used to identify clay minerals from the Chachimbiro well cuttings.

Conclusions:

- It is not necessary to sieve the samples after pulverizing them; we can work on samples whose grain size is 67 microns.
- Sieving is not recommended for clay mineral preparation. Since, sieving with water requires heat to dry the material but also can cause a damage in the sample. Besides, sieving without water requires too much time and the use of an agate mortar that can break and force bigger minerals in the sample is not optimum.
- Samples need dispersant for better results, however, an excess cause flocculation and in consequence, all the treatment should be redone.
- The magnetic stirrer is better than ultrasonic bath.
- Clay minerals are sensible and highly susceptible to changes, so exposing them to high temperature for drying, as well as centrifuging them with reagents such as $MgCl_2$, HCl or alcohol can affect them.
- Crystal orientation is crucial and the success of the analysis depends on this. If you do not obtain a sample with flat surface in the sample holder, the diffractogram will not be good. So, avoiding cracks, curls and rough surface is crucial.
- Cellulose filter as substrate is not as favorable as glass substrate, cellulose filter has to be cut to fit within the sample holder which implies so much manipulation and a possible contamination. Besides, cellulose filter can absorb some volatiles within the desiccator while glass substrate can fit easily and it does not absorb anything.
- The procedure described next was proposed after three months of experimentation. It can however be improved. The evaluation criteria and eligibility of a technique were subjected to observation and trial and error.

Procedure for clay preparation for XRD analysis

Rock crushing

1) Crush the rock with a shatter box until it reaches 67 µm in diameter

Separation of clay minerals by decantation

2) In a wide-mouth glass jar at least eight centimeters tall with lid, mark centimeter graduations up to 5 cm, from base to top, with a permanent marker
3) Put 20 grams of crushed rock material
4) Add 0.1 grams of NaCl that will act as dispersant
5) Add distilled water until the 5-centimeter mark
6) Shake it manually for about 20 seconds
7) Shake it using a magnetic stirrer for 40 seconds, ensuring that a vortex does not form in the center
8) Let the sample rest for 4 hours and 6 minutes making sure that the solution's temperature is about 20°C
9) After this period, the supernatant liquid should be cloudy. Collect 3 mL of this liquid with a 5 mL syringe and transfer it into a 50 mL centrifuge tube. If the liquid is transparent, the clay flocculated and the procedure must be repeated. This indicates that the sample is very reactive to the dispersive agent, which quantity must be decreased for the following sample preparation. Try adding 0.07 g of NaCl instead of 0.1 g.
Note: You may notice flocculation of the clay after 40 minutes of resting

Orientation of aggregates

10) Fill the centrifuge tubes containing the clay material with distilled water up to 50 mL
11) Centrifuge all tubes for 5 minutes at 2500 revolutions per minute
12) Discard the liquid to keep the paste material only, corresponding to the clays
13) Use a microspatula to collect the material from the centrifuge tube and spread it evenly, sub-parallel onto a glass slide that must already be attached to the sample holder of the X-ray diffractometer
Note: Label the glass slide on the back with a permanent marker
14) The sample should present a flat surface, without coarse grains, cracks, fractures, or curls that would modify the relief of the slide and therefore alter the diffractogram
15) It is recommended to run the sample immediately to avoid it being damage. If the sample presents cracks or curl forms on the glass slide, the amount of material may be excessive. Repeat centrifugation by adding only 2 mL of supernatant liquid

Post-analysis treatments

16) Place the samples in a desiccator with 100 mL of ethylene glycol for 8 hours at 70 °C and analyze by XRD
17) Expose the samples to 550 °C for one hour and a half and analyze by XRD. If analysis cannot perform right away, place the samples in a desiccator to avoid rehydration during cooling.

CHAPTER 4.

APPLICATION OF THE NEWLY DEVELOPED METHOD TO CHACHIMBIRO WELL CUTTINGS

4.1. Results

The samples studied with the procedure established were from the 2017 exploration well PEC1, from Chachimbiro geothermal field. We analyzed 17 samples of cuttings drilling, ranging in depths from 190 meters to 785 meters. All the samples were subjected to ethylene glycol saturation and finally four of them were exposed to heat treatment (samples 2, 8, 13 and 17; from 225 m, 425 m, 575 m and 785 m depth respectively) (Figures 4.1, 4.2, 4,3, 4,4). The peak of the basal plane of each mineral (001) was recorded in each situation (air dried, ethylene glycol and thermal exposure). According with the change observed for each peak, a clay mineral is assigned. The results are presented in Table 4.1.

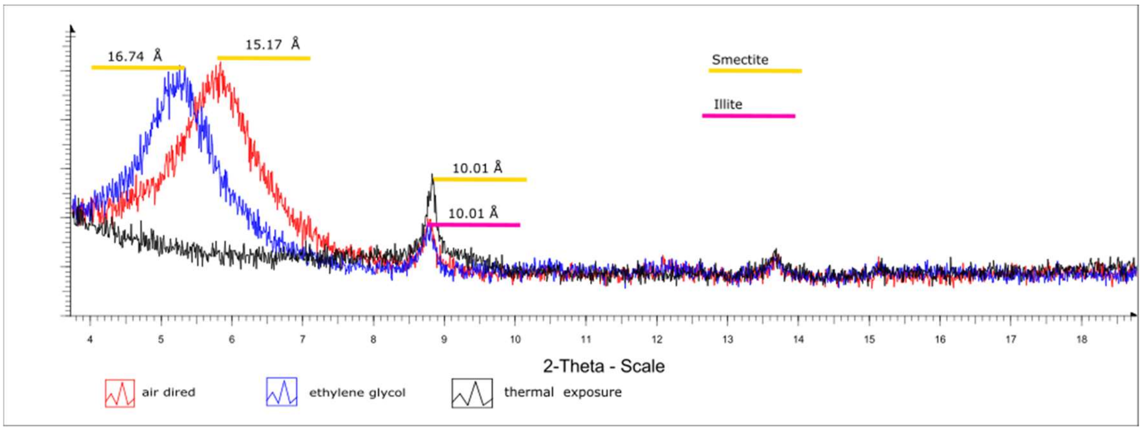

Figure 4.1 Diffractograms of sample #2 corresponding to 225 m depth showing variations in peaks position and height.

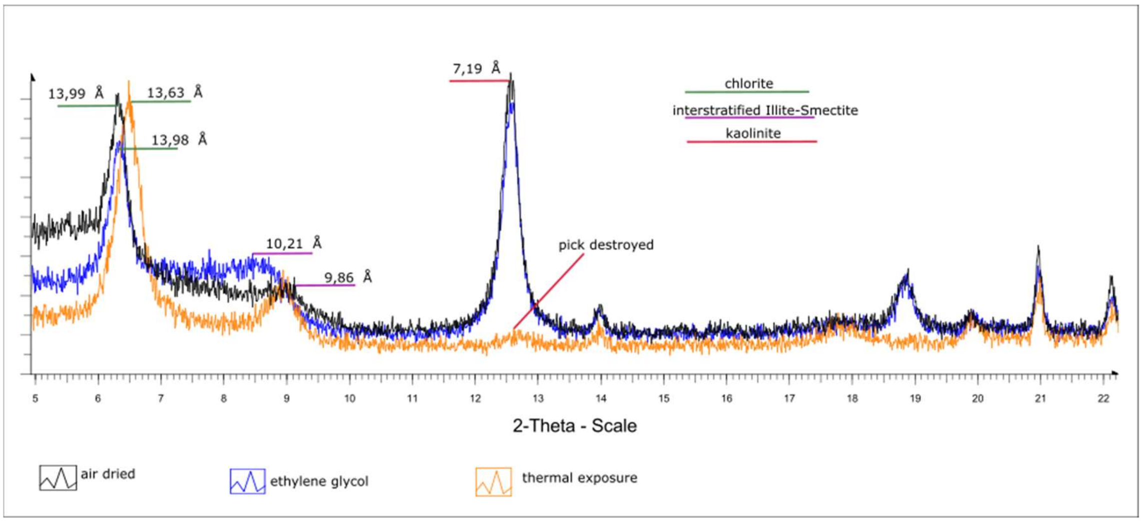

Figure 4.2 Diffractograms of sample #8 corresponding to 425 m depth showing variations in peaks position and height.

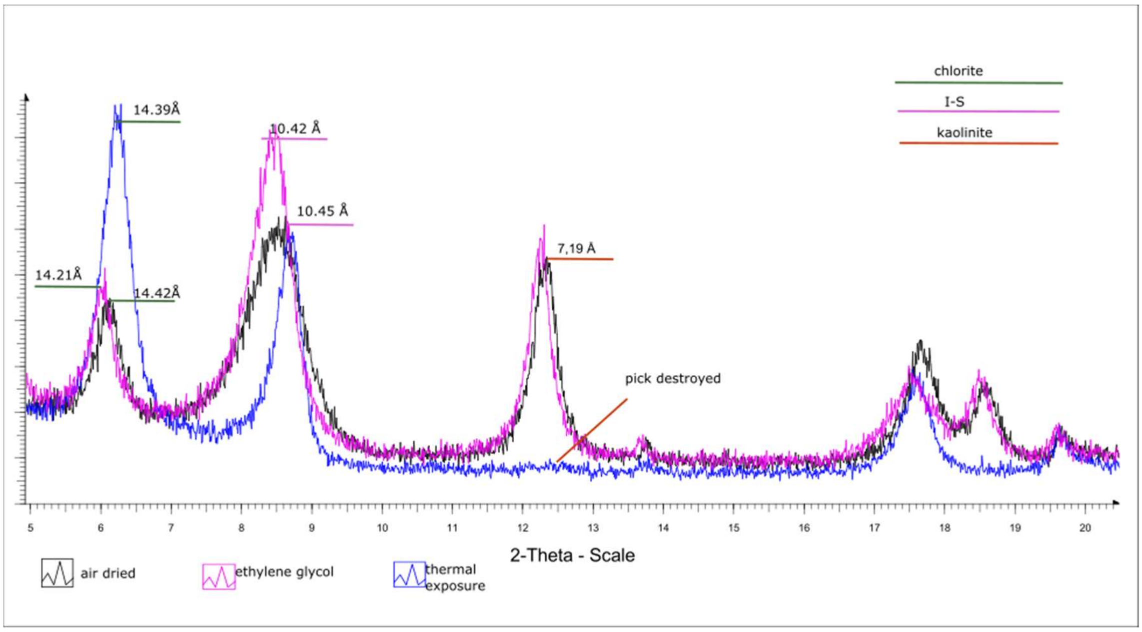

Figure 4.3 Diffractograms of sample #13 corresponding to 575 m depth showing variations in peaks position and height.

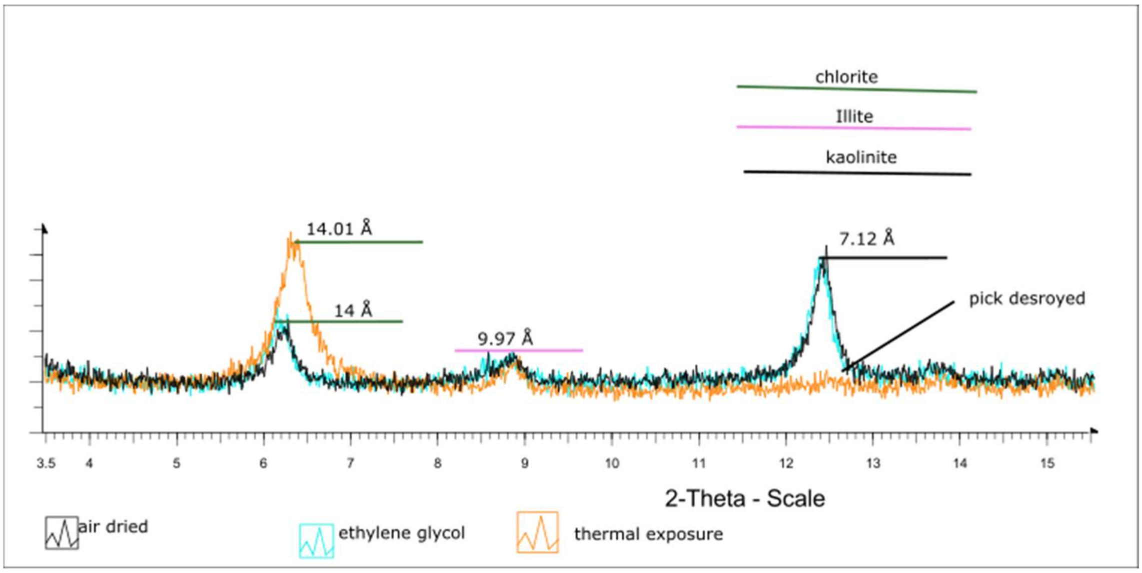

Figure 4.4 Diffractograms of sample #17 corresponding to 785 m depth showing variations in peaks position and height.

Table 4.1: XRD results for the 17 samples

SAMPLE	DEPTH m	AIR DRIED Å	ETHYLENE GLYCOL Å	THERMAL EXPOSURE Å	CLAY MINERAL
1	190	14.33	17.08		smectite
		10.02	10.02		illite
2	225	15.17	16.74	10.01	smectite
		10.01	10.01	10.01	illite
3	285	14.51	16.62		smectite
		9.90	9.90		illite
4	310	14.27	16.62		smectite
5	350	14.63	14.95		chlorite
		10.27	10.27		Illite
		7.25	7.25		kaolinite
6	380	14.59	14.59		chlorite
7	395	7.17	7.14		kaolinite
8	425	13.98	13.63	13.99	chlorite
		10.21	9.86	9.86	I-S
		7.18	7.18	destroyed	kaolinite
9	460	14.63	14.63		chlorite
10	480	14.62	14.62		chlorite
		11.02	11.02		I-S
		7.18	7.18		kaolinite
11	500	14.00	14.14		chlorite
		9.86	10.34		I-S
12	530	7.18	7.18		kaolinite
13	575	14.42	14.21	14.39	chlorite
		10.48	10.10	10.42	I-S
		7.19	7.19	COLLAPSES	kaolinite
14	605	14.71	14.71		chlorite
		10.46	10.46		Illite
		7.19	7.19		kaolinite
15	670	14.57	14.57		chlorite
		10.25	10.25		I-S
		7.19	7.19		kaolinite
16	730	7.33	7.33		kaolinite
17	785	14.01	AMPLIFIES	14.01	chlorite
		9.97	9.97	9.97	Illite
		7.12	7.12	COLLAPSES	kaolinite

Note: I-S: Interstratified Illite-Smectite clay

All the results are better visualized in Figure 4.5. It describes the range of depth that clay minerals occupied. We obtained five types of clays: smectite, illite, interstratified Illite-Smectite (I-S), chlorite and kaolinite. Smectite is localized in the shallowest part, while illite was identified at two different depths. I-S is located only in medium range while kaolinite and chlorite are the deepest, having almost the same range of occurrence.

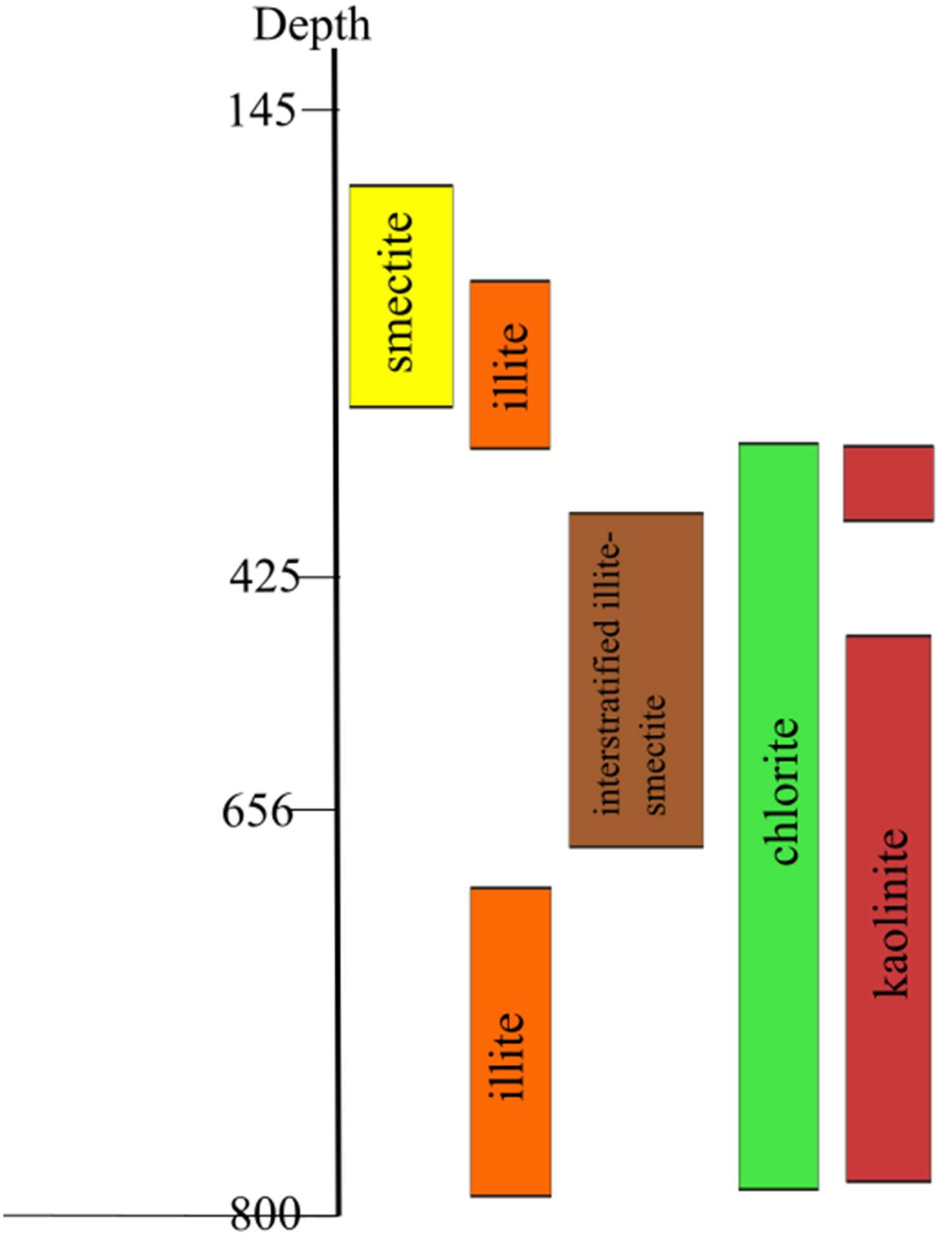

Figure 4.5 Clay minerals distribution along the Chachimbiro geothermal well.

4.2. Discussion

The results we obtained from these 17 samples will be discussed in the following part, with an emphasis on illitization process and temperature range associated with the mineral assemblages obtained. The replacement of smectite by illite with depth is known as illitization process. It has been observed and described at some geothermal fields, for example in Los Azufres geothermal system in Mexico (Pandarinath et al., 2006) or in Tinguirica geothermal system in Chile (Vazquez et al., 2016).

The thermal regime in a geothermal system is a driving factor to control the mineralization process as well as hydrothermal alteration. It is not correct thinking about the clays found in the Chachimbiro PEC1 as products of random events. They depend on the temperature of the fluids as well as their composition. The important question here is if these fluids were at equilibrium or not. It would help us to infer if the temperature of mineralization (in our case, the clays found) is true for the system or may still be changing. In this case, it would be useful to contrast our results with homogenization temperature of fluid inclusions and temperature measured in-situ at the time of drilling, unfortunately this data is not accessible until 2022.

Assuming that the system was in equilibrium and the illitization was a process caused by the thermal at the time, we can infer that the dominant hydrothermal alteration is argillic (Johnston et al., 1992). According to Inoue, (1995) the argillic zone would form the cap rock. Here two ideas are contrasted. First, according to geophysical studies of Chachimbiro system, the cap rock would be formed by smectite and would cover a depth of 340 meters (Pilicita, 2017). Our results support this statement because we find smectite within the first 300 meters depth. However, we do not consider that the cap rock ends at this depth. In fact, following Johnston et al (1992) and Inoue (1995), the cap rock is dominated by argillic alteration and since illitization is related to argillic alteration, we suggest that the cap rock may extend deeper than what Pilicita, 2017 holds.

Within the clay assemblage, there is a notable range of chlorite. The presence of this mineral, along with illite, reinforces the idea of illitization as it is a secondary product of this process. However, in order to know it with certainty, semiquantitative XRD analysis would be needed, to insure conservation of mass of the reaction. Moreover, textural analysis would be useful to know if the chemical elements for forming chlorite and illite (i.e. Al and K) are extracted from the I-S layer structures. A process that may release these elements is also albitization of plagioclase, which is likely occurring during hydrothermal alteration of the mother rock at depth. This is especially relevant given that the host rock of Chachimbiro system ranges from andesites to dacites, rocks rich in plagioclase.

Finally, we cannot dismiss that pressure at greater depths can be responsible for this illitization process. In fact, replacement of smectite by illite due to burial is a well-known process in basins (Brigatti et al., 2006). At this point, something to remark as you can see in Figures 4.2 and 4.3; are the picks of I-S. Their height increases considerably with depth. We can wonder if this is influenced by the increase of burial (and also the temperature). I would think that the crystallinity in these mixed clays are better developed as pressure goes on and it is reflected in to the diffractograms with better peaks.

The presence of kaolinite can also linked to burial. Moore and Reynolds (1989) spoke about how clays can evolve from one to another, for example illite to kaolinite and chlorite following burial. As kaolinite is a mineral that is not involved in illitization and we found it in our results, we can explain its presence at great depth by burial.

Another important result from our study is the temperature profile we can infer from the distribution of clays. There is information among authors about the stability range for various clay minerals. We compiled the information of five papers in Figure 4.6. As it is evident, some temperature ranges are similar but others are completely different. For example; in the case of Illite-Smectite according to Simmons and Browne (1998) and Reyes (1990).

As mentioned earlier, our results show the presence of illite at two different depth: from 190 to 350 m, and 605 to 765 m. We suggest that illite is produced by two different processes. The deeper one is related to the illitization process described earlier, with I-S in the medium depth range, and secondary product chlorite at greater depth. The shallower illite may be the result of localized fluid flow, transforming other minerals into clays only where these fluids are flowing. Further work on the samples, for example petrography study looking at the occurrence and distribution of illite or chemical analysis may help differentiating illite formed by different processes.

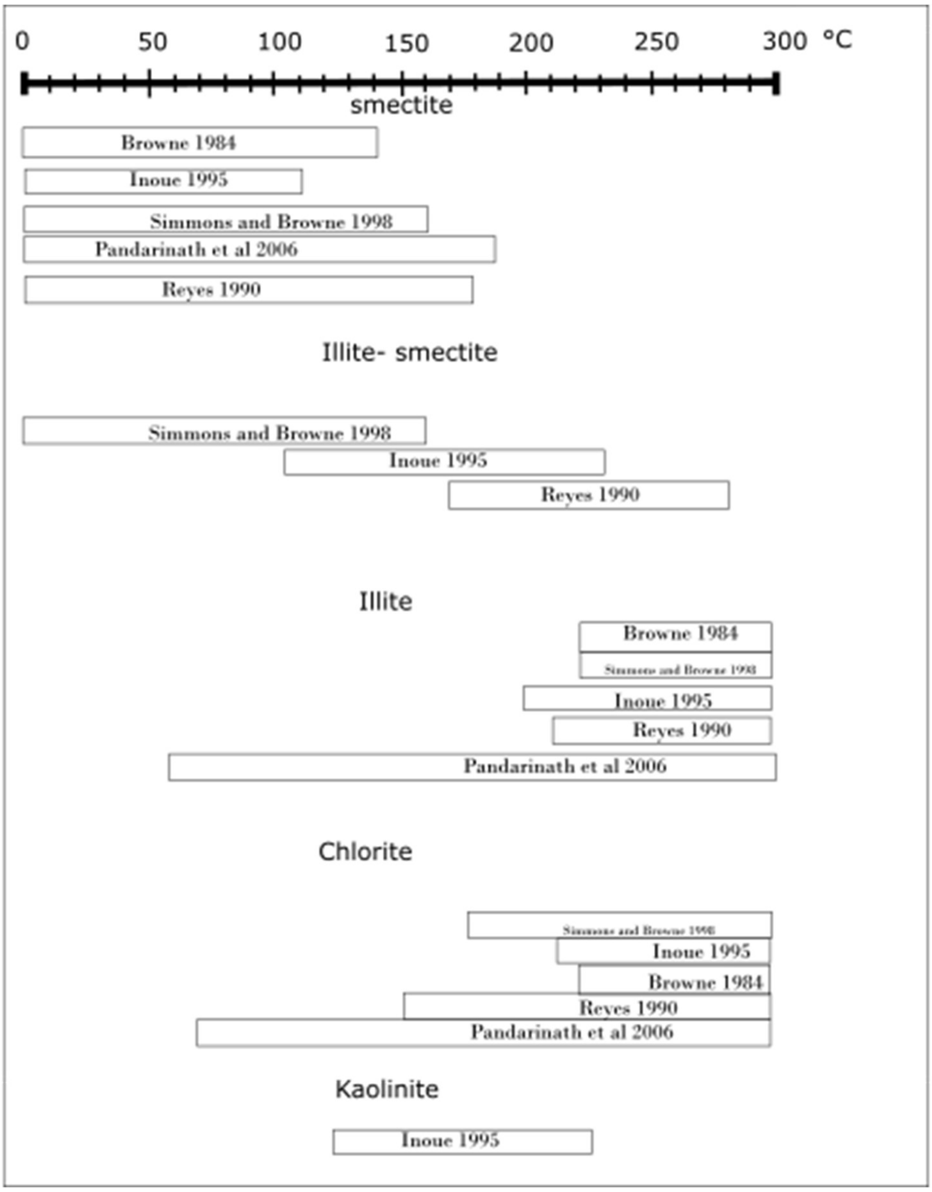

Figure 4.6: Clay minerals and their temperature ranges of stability following (Browne, 1984), (Reyes, 1990), (Inoue, 1995), (Simmons et al., 1998), (Pandarinath et al., 2006).

Despite variations between authors, the stability range for smectite is within 0 and 170 °C. This suggests that the temperature within the well does not exceed 170 °C until a depth of 310 m. The temperature range for I-S is very wide, from 0 to 280 °C, making interpretation of the temperature in the well difficult. Kaolinite, illite and chlorite, all present at the greatest depths, suggest a temperature between 120 and 220 °C. As mentioned earlier, comparison with temperature obtained by homogenization of fluid inclusions in minerals from the cuttings and temperature measured down the well during drilling would improve our interpretation. The maximum temperature for the deepest assemblage is however agreeing with estimates from geochemical studies (Aguilera et al., 2005; Gherardi and Spycher, 2014), suggesting a temperature between 240 and 260 °C of the water within the reservoir.

CHAPTER 5.
CONCLUSIONS

This research has inspected some concepts about geothermal systems and its linkage with energy generation. Also, has included a synopsis of Ecuador's trajectory on geothermal exploration until reach the current prefeasibility stage. Besides, has covered other deeply notions about hydrothermal alterations and clays structure and properties. All above with the purpose to highlight the importance of clays minerals to study geothermal fields and the necessity of producing national knowledge to contribute in sort sense, to Ecuadorian geothermal development, in this case through laboratory practices.

Regarding the manual of procedures about clays preparation for XRD analysis is properly to remark that can be improved, however, each step established, has been experimented, contrasted and chosen, among diverse literature, adding some extra advices that empirically were concluded. It was created for been utilized also for IIGE own procedures so it is expected to be a useful contribution.

Finally, our apport to Chachimbiro geothermal system comprises the identification of five type of clays from 190 meters to 785 meters depth. They necessarily were formed under the influence of geothermal systems conditions., e.g. high temperature, fluids circulation, burial, etc. It is not correct to considered them as product of randomly events because these conditions must not be dismissed. However, as homogenization temperatures and *in-situ* temperatures are not available until 2022, we cannot be sure about the equilibrium of the system likewise about clays stability. However, if we assumed the system is on equilibrium important consideration are able to notice.

First, there is an illitization process that strength the fact of high rate of temperature increase with depth. But also, shows the existence of argillitic alteration which is the driver factor of clay cap formation. This bring us to think that the clay cap is thicker than 340 meters as other authors has established. Moreover, our results hold the illitization hypothesis because of the presence of chlorite which is a product of this reaction. Second, a thermal regime with the clays obtained varies among authors, however, we can suggest that PEC1 Chachimbiro geothermal well has a maximum temperature of 170°C until 310 meters depth and can reach among 240°C to 260°C o the bottom.

REFERENCES

Aguilera, E., 1998. The Chalupas and Chachimbiro geothermal fields in Ecuador. Trans. Resour. Counc. 247–252.

Aguilera, E., Cioni, R., Gherardi, F., Magro, G., Marini, L., Pang, Z., 2005. Chemical and isotope characteristics of the Chachimbiro geothermal fluids (Ecuador). Geothermics 34, 495–517.

Barberi, F., Coltelli, M., Ferrara, G., Innocenti, F., Navarro, J.M., Santacroce, R., 1988. Plio-quaternary volcanism in Ecuador. Geol. Mag. 125, 1–14.

Beate, B., 2010. Plan para el aprovechamiento de los Recursos Geotérmicos en el Ecuador. Quito.

Beate, B., Salgado, R., 2005. Geothermal Country Update for Ecuador, 2000-2005, in: Proceedings.

Beate, B., Urquizo, M., 2015. Geothermal Country Update for Ecuador: 2010-2015, in: Proceedings World Geothermal Congress 2015. pp. 19–24.

Bellver-Baca, M.T., Chiaradia, M., Beate, B., Beguelin, P., Deriaz, B., Mendez-Chazarra, N., Villagómez, D., 2019. Geochemical evolution of the Quaternary Chachimbiro Volcanic Complex (frontal volcanic arc of Ecuador). Lithos 105237.

Benderitter, Y., Cormy, G., 1990. Possible approach to geothermal research and relative costs. Small Geotherm. Resour. A Guid. to Dev. Util. UNITAR, New York 59–69.

Bernard, B., Hidalgo, S., Robin, C., Beate, B., Quijozaca, J., 2014. The 3640–3510 BC rhyodacite eruption of Chachimbiro compound volcano, Ecuador: a violent directed blast produced by a satellite dome. Bull. Volcanol. 76, 1–20. https://doi.org/10.1007/s00445-014-0849-z

Brigatti, M.F., Galan, E., Theng, B.K.G., 2006. Structures and mineralogy of clay minerals. Dev. clay Sci. 1, 19–86.

Brown, C.E., 2002. Geothermal energy, in: World Energy Resources. Springer, pp. 157–165.

Browne, P., 1984. Lectures on geothermal geology and petrology. UNU Geothermal Training Programme, National Energy Authority Reykjavik.

Browne, P.R.L., 1978. Hydrothermal alteration in active geothermal fields. Annu. Rev. Earth Planet. Sci. 6, 229–248.

CELEC, SYR, 2012. Initial Prefeasibility Study to Develop a Conceptual Model for the Geothermal Project. Quito.

Dickson, M.H., Fanelli, M., 2013. Geothermal energy: utilization and technology. Routledge.

Eguez, A., Aspden, J., 1993. The Meso-Cenozoic Evolution of the Ecuadorian Andes, in: Proceedings Second International Symposium Andes Geodynamics, Oxford.

Farinango, F., 2017. Instructivo preparación de muestras para análisis de arcillas por DR-X. Corporación Eléctrica del Ecuador.

Francisco, A.R.L., 2013. Geothermal energy Utilization and technology, Journal of Chemical Information and Modeling. https://doi.org/10.1017/CBO9781107415324.004

Gherardi, F., Spycher, N., 2014. Application of integrated multicomponent geothermometry at the Chachimbiro thermal area, a difficult geothermal prospection case, in: Proceedings, Thirty-Eighth Workshop on Geothermal Reservoir Engineering. Stanford University, Stanford, California.

Granda, B., 2011. Geological mapping 1:25000 of pre-Quaternary rocks, Chachimbiro geothermal project, pre-feasibility phase.

Guillier, B., Chatelain, J., Jaillard, E., Yepes, H., Poupinet, G., Fels, J., 2001. Seismological evidence on the geometry of the Orogenic System in central-northern Ecuador (South America). Geophys. Res. Lett. 28, 3749–3752.

Gutscher, M.-A., Olivet, J.-L., Aslanian, D., Eissen, J.-P., Maury, R., 1999. The “lost Inca Plateau”: Cause of flat subduction beneath Peru? Earth Planet. Sci. Lett. 171, 335–341.

Hall, M.L., Beate, B., 1991. El volcanismo plio-cuaternario en los Andes del Ecuador. Estud. Geogr. 4, 5–38.

Hauff, P.L., Starkey, H.C., Blackmon, P.D., Pevear, D.R., 1984. Sample preparation procedures for the analysis of clay minerals by X-ray diffraction, Open-File Report. https://doi.org/10.3133/ofr82934

Hughes, R.A., Pilatasig, L.F., 2002. Cretaceous and Tertiary terrane accretion in the Cordillera Occidental of the Andes of Ecuador. Tectonophysics 345, 29–48.

Inoue, A., 1995. Formation of clay minerals in hydrothermal environments, in: Origin and Mineralogy of Clays. Springer, pp. 268–329.

Johnston, J.M., Pellerin, L., Hohmann, G.W., 1992. Evaluation of electromagnetic methods for geothermal reservoir detection. Trans. Geotherm. Resour. Counc.

Lagat, J., 2014. Hydrothermal Alteration Mineralogy in Geothermal Fields With Case Examples From Olkaria Domes. Short Course IV Explor. Geotherm. Resour. 1–24.

Lloret, A., 2014. Geothermal development in Ecuador: History, current status and future.

Lonsdale, P., 1978. Ecuadorian subduction system. Am. Assoc. Pet. Geol. Bull. 62, 2454–2477.

Moore, D.M., Reynolds, R.C., 1989. X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford university press Oxford.

Moya, D., Paredes, J., Kaparaju, P., 2018. Technical, financial, economic and environmental pre-feasibility study of geothermal power plants by RETScreen–Ecuador’s case study. Renew. Sustain. Energy Rev. 92, 2–6.

Nicholson, K., 2012. Geothermal fluids: chemistry and exploration techniques. Springer Science & Business Media.

Pandarinath, K., Torres-Alvarado, I.S., Pushparani, D.E., Verma, surendra P., 2006. X-ray diffraction analysis of hydrothermal minerals from the Los Azufres geothermal system, Mexico. Int. Geol. Rev. 48, 174–190.

Panichi, C., Noto, P., Belluci, L., 1992. MODELO GEOTÉRMICO PRELIMINAR DE ÁREAS VOLCÁNICAS DEL ECUADOR, A PARTIR DE ESTUDIOS QUÍMICOS E ISOTÓPICOS DE MANIFESTACIONES TERMALES. Estud. geotérmicos con técnicas isotöpicas y geoquimicas en Am. Lat. 219.

Pilicita, B., 2017. A 3D model of the Chachimbiro geothermal system in Ecuador using

Petrel.

Poppe, L., 2001. USGS OFR01-041: A Laboratory Manual for X-Ray Powder Diffraction [WWW Document]. Open-File Rep. 01_041. URL https://pubs.usgs.gov/of/2001/of01-041/htmldocs/clay.htm (accessed 5.19.19).

Reyes, A.G., 1990. Petrology of Philippine geothermal systems and the application of alteration mineralogy to their assessment. J. Volcanol. Geotherm. Res. 43, 279–309.

Scarpati, C., 2019. The encyclopedia of volcanoes (second edition), Geologos. https://doi.org/10.2478/logos-2019-0018

Scintag, I., 1999. Basics of X-ray Diffraction.

Simmons, S.F., Browne, P.R.L., Arehart, G.B., Hulston, J.R., 1998. Illite, illite-smectite and smectite occurrences in the Broadlands-Ohaaki geothermal system and their implications for clay mineral geothermometry. Water rock Interact. 9, 691–694.

Speight, J., 2015. Geothermal Energy: Renewable Energy and the Environment, by William E. Glassley: Boca Raton, FL: CRC Press. Hardback: 119.96;eBook: 104.97, 423 pp.(ISBN 9781482221749).

Utada, M., 1980. Hydrothermal alterations related to igneous activity in Cretaceous and Neogene formations in Japan. Min. Geol., Spec. Issue 8, 67–83.

Vallejo Cruz, C., 2007. Evolution of the Western Cordillera in the Andes of Ecuador (Late Cretaceous-Paleogene).

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. 134, 221–234.

Waseda, Y., Matsubara, E., Shinoda, K., 2011. X-ray diffraction crystallography: introduction, examples and solved problems. Springer Science & Business Media.

Yparraguirre, J.A., 2018. ANALISIS MINERÁLOGICO POR DIFRACCION DE RAYOS X PARA IDENTIFICACION DE MINERALES ARCILLOSOS MEDIANTE EL TRATAMIENTO ETILENGLICOL.