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I/S AND C/S MIXED LAYERS, SOME INDICATORS OF RECENT PHYSICAL-CHEMICAL CHANGES IN ACTIVE GEOTHERMAL SYSTEMS: THE CASE STUDY OF CHIPILAPA (EL SALVADOR).

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ABSTRACT

I/S and C/S mixed layers from the geothermal field of Chipilapa (El Salvador) have been studied in details in order to reevaluate their potential use as indicator of the thermodynamic conditions in which they were formed. It is funded that overprinting of clay bearing alteration stages is common. For a given alteration stage, the spatial variation of I/S and C/S mixed layer minerals is controlled by kinetics of mixed layer transformation and not only by temperature. Clay geo-thermometers cannot give reliable results because the present crystal-chemical states of the I/S and C/S mixed layers is not their initial state, it was aquired during the overall hydrothermal history which post dated the nucleation of smectitic clay material at high temperature.

Occurrences of smectites or smectite-rich mixed layers at high temperature in reservoirs is a promising guide for reconstruct the zones in which boiling or mixing of non isothermal fluids occurred very recently or still presently.

INTRODUCTION

In geothermal fields, clay minerals have received considerable attention during the last twenty years. Being extensive products of water-rock interaction processes within a wide range of hydrothermal conditions, they are reliable indicators of spatial organization of active or fossil geothermal fields. Furthermore, due to their high reactivity to change in physical-chemical conditions, crystal chemical variations of clay minerals have been investigated as petrogenetic guide. In geothermal systems, illite/smectite (I/S) and chlorite/smectite (C/S) mixed layers are by far the most widely extended clay minerals. Both mixed layer series are well known to be of interest for geothermometry (Velde, 1977). They represent the progressive conversion of di and tri-smectite respectively to illite and chlorite via series mixed layered minerals which crystal-chemical properties (especially the content of smectite layers and the degree of ordering of interstratification) changes in response to thermal conditions ranging between less than 50°C to about 230-240°C (Henley and Ellis, 1983, Srodon and Eberl, 1984, Bettison and Shiffman, 1988 among others). Consequently, in geothermal systems, the compositional variations of I/S and C/S have been interpreted in term of geothermometry. Unfortunately, several works concerning active geothermal fields (Seki et al., 1984, Reyes and Cardile, 1989, Papapanagiotou et al. 1992, Inoue et al. 1992) indicated that occurrences of I/S and C/S mixed layers is not strictly temperature dependant, particularly within the permeable horizons of the geothermal reservoirs.

In this paper we use the data of a detailed study of alterations within the geothermal field of Chipilapa (El Savador) for reevaluate the significance of I/S and C/S mixed layer minerals at the view of other factors as overprinting of clay assemblages, hydrodynamic constraints on clay nucleation, kinetic control on conversion of mixed layers. Emphasis will be put on "high temperature" smectite rich mixed layers as guide of the very recent hydrothermal history of the active systems.

GEOLOGICAL SETTING

The Chipilapa geothermal field is located on the eastern margin of the Ahuachapan geothermal field, at 80 km west of San salvador, near the border to Guatemala. The geology of the Ahuachapan-Chipilapa geothermal zone has been described by Gonzalez et al. (1995). The geothermal zone emplaced in a Plio-Quaternary volcanic chain extending parallel to the Pacific Coast as response to subduction of the Cocos Plate under the Caribbean plate. The magmatism shows characteristics of a calcakaline series with predominance of pyroclastics and lava flows of dacitic to andesitic composition. According to Gonzalez et al (1995), the geothermal zone of Ahuachapan-Chipilapa post dated the last magmatic manifestations within the Late Pleistocene period (the age of the youngest volcanic manifestation was estimated to about 17000 years). Since 1989, four exploratory wells (CH7, CH7bis, CH8 and CH9) which depth range from 1300m to 2600m allow to propose the conceptual model presented figure 1. The present day thermal anomaly of Chipilapa is centered on an area delimited by interconnected active faults and presents a typical mushroom shape. Two major zones of total drilling mud losses have been reported: a shallow zone (A) located at depth between 500 and 650m has characteristics of a vapor cap containing fluids at temperature higher than 185°C. The deep zone (B) has characteristics of liquid dominated reservoir containing fluids at temperature higher than 200°C. It should be noted that the well CH8 crosscuts a fossil part of the field in which the hydrothermal activity is very weak (absence of fluid production) despite of a strong fossil hydrothermal alteration.

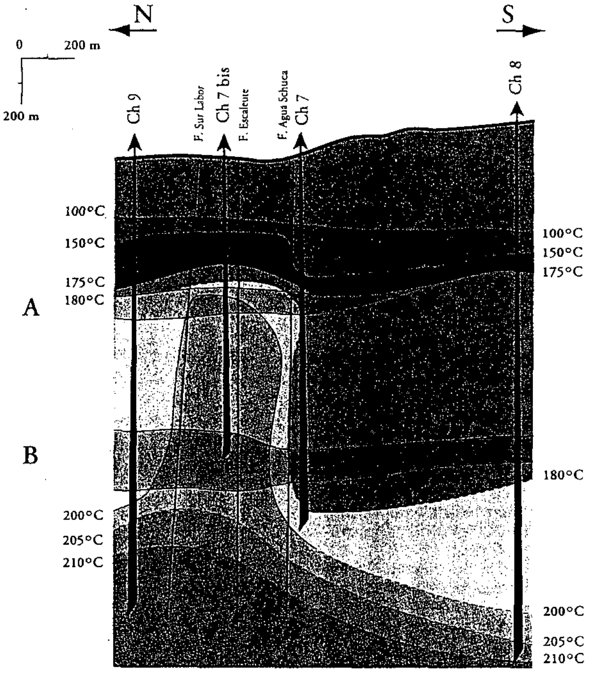

Fig. 1. Conceptual model of distribution of aquifers and isotherms in the field of Chipilapa (after CFG).

MULTI-STAGE ALTERATION

All the volcanic formations drilled in the geothermal field have been subjected to strong hydrothermal alteration. A detailed study coupling alteration petrography and fluid inclusions microthermometry evidenced a vertical zoning of alteration which results from time-space super-imposition of at least three hydrothermal stages during I/S and/or C/S mixed layers series crystallized (Papapanagiotou, 1994, Bril et al. 1996).

The first stage of hydrothermal alteration affected the totality of the geothermal zone and led to a zoned distribution of mineralogical facies ranging from clay-zeolite to propylitic facies with increasing depth and temperature (figure 2). Alteration paragenesis and fluid inclusions data suggest that temperature graded from less than 100°C at surface area (saponite-clinoptilolite assemblage) to about 300°C at 2500m depth (chlorite-epidote-prehnite assemblage). This stage represents a thermal event typical of the external part of thermal aureoles during which zoned alteration developped in environment of inactive flow regime in response to mainly conductive thermal gradient. The economic potential of the geothermal field was non existent during this period.

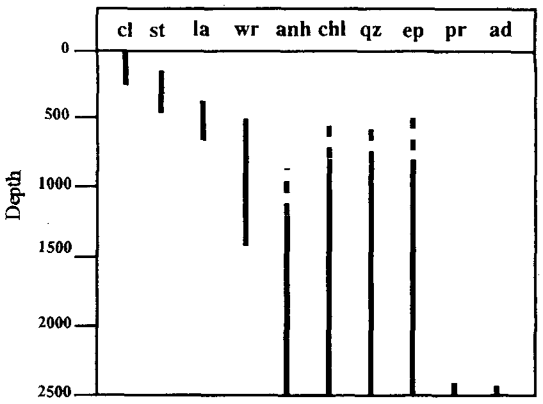

Fig. 2. Distribution of secondary minerals of the first hydrothermal stage as a function of depth. Ad: adularia, anh: anhydrite, chl: chlorite, cl: clinoptilolite, ep: epidote, la: laumontite, pr: prehnite, qz: quartz, st: stilbite, wr; wairakite.

The second stage of hydrothermal alteration was initiated by an extensive hydraulic fracturation of the upper part of the system (over an average thickness of 1700m). In a first step, infiltration of the permeable newly fractured horizons by aqueous fluids of meteoric origin promoted the intense alteration of the wall rocks. Fluid inclusions data and morphology of calcite evidence boiling during to this alteration stage. The energetic potential of the field was probably maximal at this moment. Great amounts of clay material, haematite and calcite formed during this event. Calcite precipitated mainly in open fractures at rather homogeneous temperature of about 240°C over all the depth range of 1700m. Clay minerals and haematite formed also in open fractures and replaced preexisting igneous and hydothermal minerals of the early stage in surrounding wall rocks. Clays are essentially composed I/S and C/S mixed layers which composition varies over the whole range from tri-smectite to chlorite and from di-smectite to illite apparently more as a function of depth than as a function of in-hole temperature. The crystal-chemistry and the spatial distribution of these mixed layers will be examined in details in the following section. Clays-carbonate alteration contribute to self sealing of the fracture network and provoked a rapid decrease of the hydrothermal activity in the field of Chipilapa.

Today, active circulations of hydrothermal fluids are channeled by three active vertical faults. They control the observed narrow thermal plume in which two reservoirs are located in fractured zones in which the frequency of permeable horizon is high. In permeable horizons, coatings of very fine grained clay material intimately associated to haematite overprint the coarser grained I/S and C/S formed during the previous clays-carbonate stage (figure 3). This newly formed clay material occurs at high temperature (about 200°C) along the fractures of permeable horizons; it is composed of di- and tri-smectite and smectite rich I/S and C/S mixed layers which crystal chemistry will be detailed in the following section.

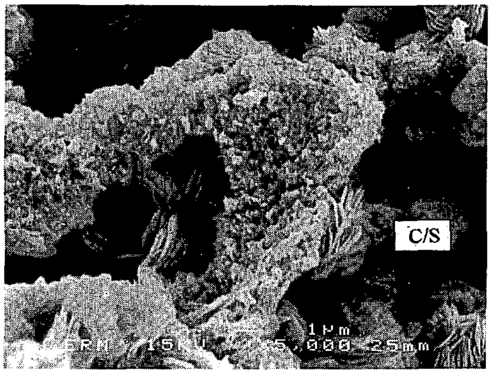

Fig. 3. Newly formed very fine grained smectitic material overprinting coarser and euhedral C/S mixed layers at the wall of a fracture in a permeable horizon of the shallow vapour dominated reservoir.

As a summary, mixed layer minerals observed in core samples of Chipilapa cannot be considered as representative of a single stage of water-rock interaction. They were formed during three distinct hydrothermal stages which were spatially superimposed during the hydrothermal history which probably did not exceed 17000 years. The two younger alteration stages emplaced in fracture controlled permeable horizons submitted to active flow regime (reservoirs). The hydrothermal activity of the system collapsed in response to clays-carbonate precipitations which plugged the permeable horizons. At present time, the main part of the fracture network is sealed by alteration; it constitutes a past reservoir which activity ceased recently. Smectite-rich mixed layers still crystallise within permeable horizons associated to active faults which constitute the current active reservoirs.

I/S AND C/S MIXED LAYERS: NATURE AND DISTRIBUTION

X-ray diffraction (DRX) is the most useful method for identification of I/S and C/S mixed layer minerals in altered rocks. However, we must keep in mind that DRX gives a structural identification of the whole clay material, without distinction of petrological assemblage.

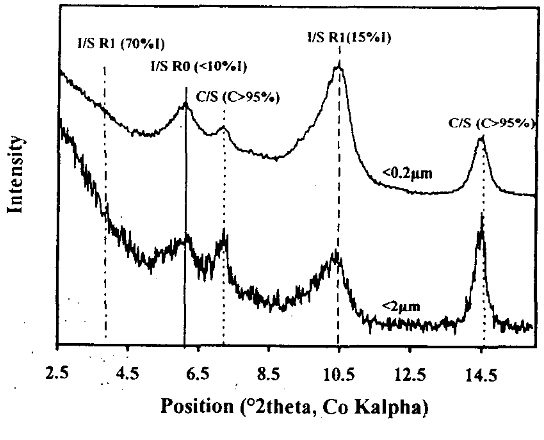

Fig. 4. XRD diffractograms of fraction size <2µm and <0.2µm of sample CH9 796m. R1: ordered mixed layer, R0 random mixed layer.

The identification of I/S and C/S formed in reservoirs was improved by analyse of the fraction less than 0.2µm of altered rocks according to the method described by Patrier et al., 1992. Analyses of the fraction less than 0.2µm rather than 2µm strongly minimize the contribution of coarser C/S mineral from propylitic and/or clay-zeolite facies (Fig. 4).

In past hydrothermal reservoir:

I/S and C/S mixed layers of this part of the geothermal field have been extensively studied by Patrier et al., (1996) and Papapanagiotou et al, (1995). From these works, it appears that I/S mixed layers display progressive variations of structure, which may be better correlated to sample depth than to current in-hole temperatures (Fig.5).

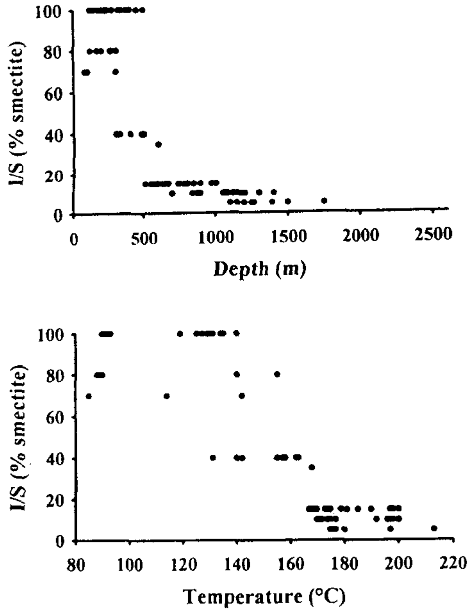

Fig. 5. Variation of smectite content in I/S mixed layers from past reservoirs as a function of depth and temperature.

I/S conversion series grades from nearly pure dioctahedral smectite near the surface area to I/S mixed layers with less than 5% of smectite at depth of 1750 m via regularly ordered R1 structure (35% of smectite) at depth near 400-500m (Figure 6).

C/S mixed layers display also a structural variation which may be better correlated to depth than to current in-hole temperatures (Fig.7).

C/S conversion series grades from pure trioctahedral smectite (saponite) near the surface area to C/S mixed layers with less than 10% of smectite at depth

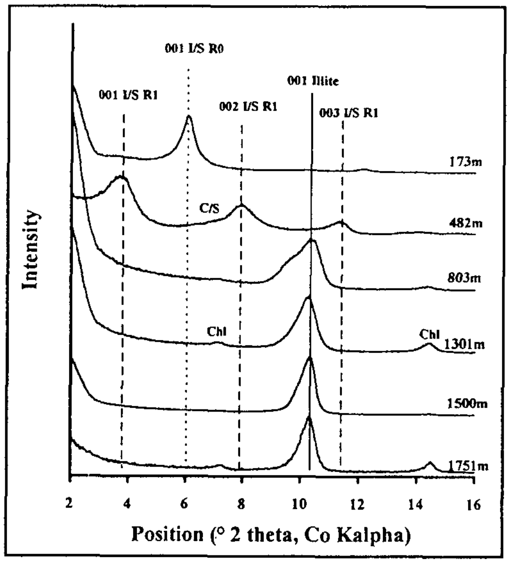

Fig. 6. Characteristic XRD diffractograms showing the general evolution of I/S mixed layers versus increasing depth in past reservoirs.

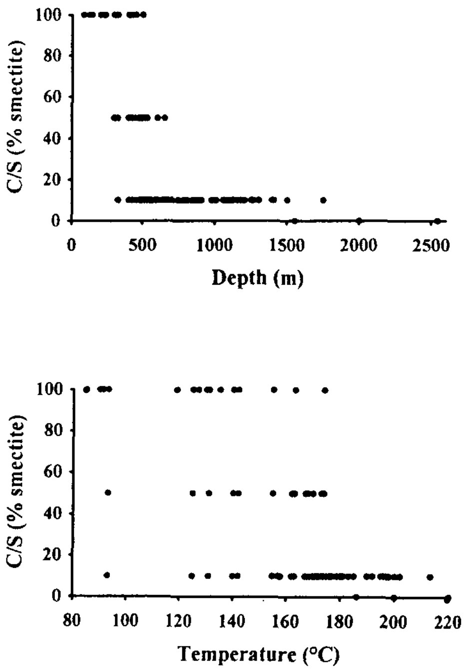

Fig. 7. Variation of smectite content in C/S mixed layers from past reservoirs as a function of depth and temperature.

of 1750 m via corrensite (50% of smectite) at depth near 400-500m (Figure 8).

In present reservoirs:

Detailed DRX investigation the <0.2µm fraction of samples from both zones which are the current reservoirs (Papapanagiotou, 1995) indicate a very heterogeneous spatial distribution of mixed layer minerals. I/S as C/S mixed layers are frequently polyphased. I/S and C/S mixed layers which conversion rate to non expansible end member (i.e. illite or chlorite) agree with the general trend observed in surrounding past reservoirs are mixed with di- and tri-smectites or smectite rich I/S mixed layers. These smectitic minerals correspond to the very fine grained crystals which are presently going to crystallize at the wall of the active fracture network (fig. 3). Figure 9 shows an example of heterogeneous distribution of mixed layers within the shallow reservoir crosscut by the well CH7. The great amounts of smectite observed at 540 m (rather tri-smectite) and at 580 and 606m (rather di-smectite) coincidate with fractured horizons infiltrated by fluids at temperature higher than 185°C.

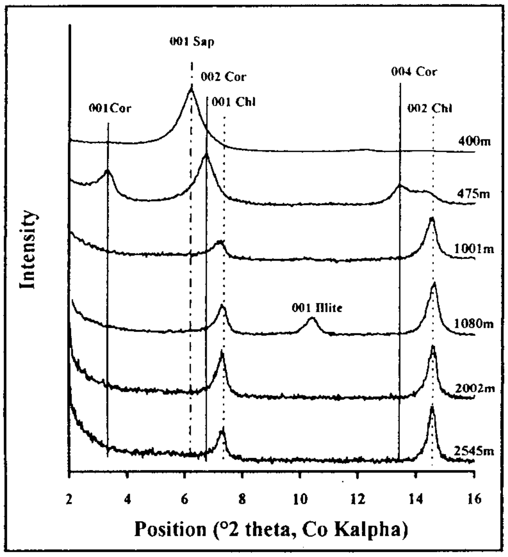

Fig. 8. Characteristic XRD diffractograms showing the general evolution of C/S mixed layers layers versus increasing depth in past reservoirs.

The structural evolution of the newly formed I/S versus depth and temperature is presented figure 10. It should be noted that all these minerals occur at high temperature in close relation with the fracture controlled permeable zones. Their structural variations are apparently independant of depth and temperature.

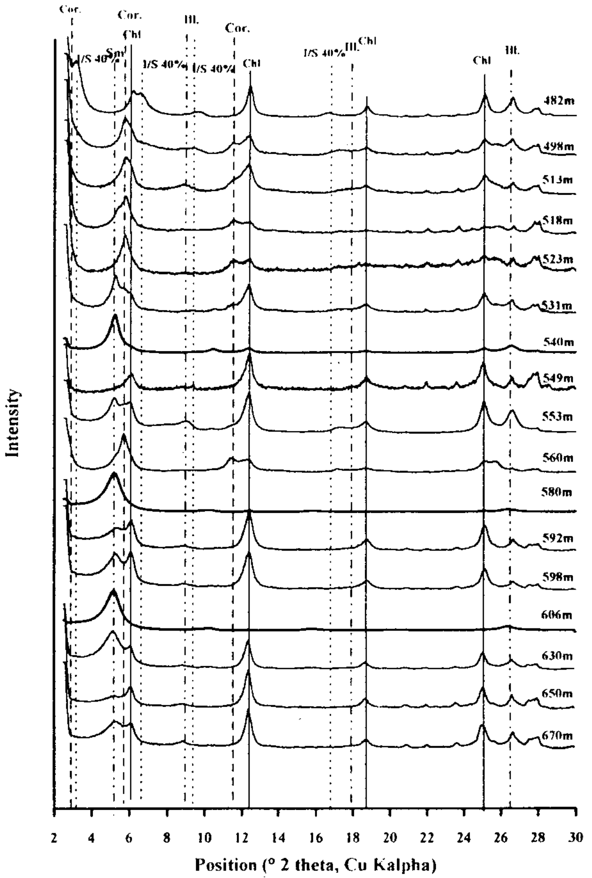

Fig. 9. XRD diffractograms of <0.2µm fraction of samples from the shallow reservoir (well CH7).

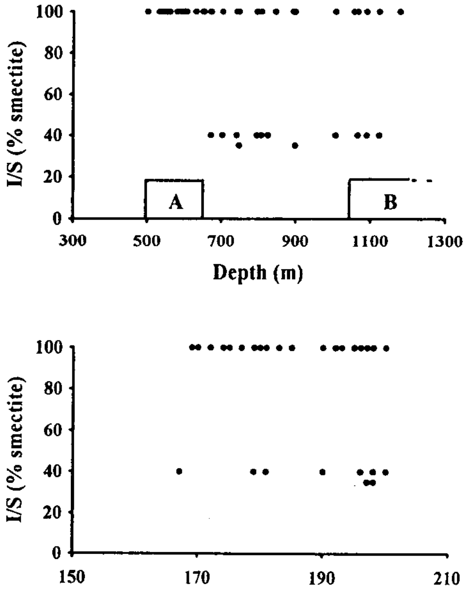

Fig. 10. Variation of smectite content in newly formed I/S mixed layers as a function of depth and temperature in present reservoirs.

Pure di and tri-smectites are particularly observed within both reservoirs, even though ordered I/S mixed layers are rather observed between the two reservoirs, particularly in the well CH7bis which parallels two major active faults (see fig. 1).

I/S AND C/S MIXED LAYERS: CHEMICAL COMPOSITION

Crystal-chemical investigations (Papapanagiotou, 1994, 1995) indicate that smectites occuring at high temperature within the reservoirs are high-charge saponite and high-charge beidellite which average structural formulas are given table 1. They differ from superficial smectites formed at much lower temperature (<100°C) which are rather montmorillonitic.

	Si	Al	Fe^{3+}	Mg	Ti	Mn	Ca	Na	K
(1)	6.90	1.46	1.82	3.72	0.00	0.02	0.40	0.04	0.02
(2)	7.01	4.07	0.73	0.19	0.04	0.01	0.38	0.02	0.22

Table 1. representative structural formulas (calculated on the basis 22 oxygens) of saponite (1) and beidellite (2) newly formed in the shallow reservoir.

The microprobe analyses of mixed layer minerals observed in thin sections of 20 samples selected in past and present reservoirs at depth ranging from 300 m to 1750m (about 500 analyses) have been plotted on the coordinates MR3-2R3-3R2 (Velde, 1985) and are presented figure 11. At Chipilapa, all the I/S mixed layers occuring at temperature higher than 130°C are distributed along the line beidellite-illite without any distinction due to their occurence in present or past reservoirs. These minerals are associated with trioctahedral mixed layers distributed along the line saponite-chlorite. It should be noted that mixed layers of the montmorillonite-illite series do not exist.

Oxygen isotope data given by Papanagiotou et al, (1995) indicate that newly formed smectite-rich I/S mixed layers from both reservoirs are in equilibrium with a fluid of $\delta^{18}O$ values ranging from -1.85 to 0.37 per mil. These values differ from the values of the present geothermal fluids ($\delta^{18}O = -4$ per mil) but are close to $\delta^{18}O$ values of fluids measured in boiling zones. The $\delta^{18}O$ values of fluids at equilibrium with I/S mixed layers from the past reservoirs at the current temperature average -6 per mil, suggesting that they are out of isotopic equilibrium with the present day geothermal fluids.

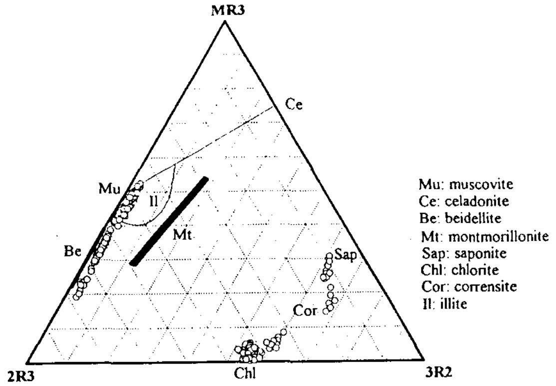

Fig. 11. Plot of the structural formulas of I/S and C/S mixed layers from the geothermal field of Chipilapa on the coordinates MR3-2R3-3R2.

DISCUSSION

During the last twenty years, most of the studies concerning clay minerals in geothermal fields focused on their potential as indicator of the thermodynamic conditions in which they were formed. Several clay geothermometers were proposed on the basis of the structural or the chemical variations of minerals of the C/S and the I/S series. Unfortunatly, their use gave often inconsistent results. The detailed petrographic and crystal-chemical investigations of the I/S and C/S mixed layer series from the geothermal field of Chipilapa demonstrate that clay geothermometers must be treated with much reserve for at least two major reasons:

(1) Clay minerals from I/S and C/S mixed layer conversion series encountered in samples of altered rocks were not necessarily formed at the same moment of the geothermal history. They did not constitute assemblages, and, in absence of a careful (and consequently time consuming) study, empirical use of the crystal-chemical properties of these mixed layer minerals for geothermometry may lead to dramatic misinterpretation.

(2) Recent works focusing on processes and mechanisms of crystal growth of phyllosilicates demontrated that conversion series of mixed layers is the most usual way by which illite or chlorite are finally formed in natural or synthetic hydrothermal or diagenetic systems (Inoue, 1988; Whitney and Northrop, 1988 among others). According to these works, the conversions of di-smectite to illite or tri-

smectite to chlorite proceed by dissolution precipitation mechanisms by which the smaller grains of early formed smectitic material even though growing, will dissolve to give larger, more stable mixed layers phases which smectite content decrease with increasing time and temperature of reaction (Velde and Renac, 1996).
A major consequence of this concept of crystal growth is that formation of illite and chlorite end-members is controlled by kinetics of the reactions of conversion of the mixed layers and not only by temperature as previously expected. In other words,. smectites which first nucleated were transformed to illite or chlorite via mixed layers series which the rate of conversion depends on the length of time during which the thermal conditions were applied to the system (i.e. the amount of energy provided to the system).

At high temperature, conversions of di and tri-smectites to illite and chlorite will be completed over short length of time. Consequently, the smectite rich mixed layers can be observed only in case of very recent or present crystallisation events. So, smectite-rich mixed layers in geothermal system of high enthalpy are indicators of horizons in which very recent or present processes of water-rock interaction or fluid discharge occur in response to local thermodynamic nonequilibrium. The best candidate to rapid nucleation and growth of clay minerals in active geothermal are the horizons in which geothermal fluids are boiling or are mixing (Gunnlaugsson, and Einarsson, 1989).
An other consequence of the kinetic control on the transformation of mixed layers is that, in past alteration, the distribution patterns of mixed layer minerals represent the integration of the elapsed thermal history since their nucleation and not close thermal conditions. Mixed layers minerals are only indicators of the mean thermal energy received by the system since they crystallized in the rocks and have a poor potential in recording the brief thermal episodes which are frequent in geothermal systems.
A good example of this phenomenum is given by the comparison of the fluid inclusion microthermometry in calcite and the alteration data obtained in the past reservoirs from the field of Chipilapa (Bril et al. 1996). Fluid inclusions trapped in calcite recorded only instant of the hydrothermal history and indicate deposition of calcite in nearly isothermal condition (240°C) over a range of 1700m even though crystal-chemistry of mixed layers associated to calcite suggests a wide range of depth dependant thermal conditions (more than 150°C). These inconsistencies may be reconciled if we consider that smectites coprecipited with calcite at 240°C as observed in present reservoirs at chipilapa and in many other geothermal fields (Papapanagiotou et al., 1992, Inoue et al. 1992, WoldeGabriel et al, 1992, Reyes, 1990) and the zonal distribution of mixed layers results of the subsequent thermal history which is rather dominated by restoration of a conductive thermal regime.

CONCLUSION

The detailed study of the geothermal field of Chipilapa demonstrates that spatial distribution of I/S and C/S mixed layer minerals in geothermal fields cannot be satisfactorily interpreted without careful petrographic study of alterations and apply of the kinetic concept of the crystal growth of phyllosilicate. It shows that use of clay geothermometers in such environments, particularly in reservoirs, cannot give reliable results because the present crystal-chemical properties of the I/S and C/S mixed layers was progressively aquired during the overall hydrothermal history which post dated the nucleation of smectitic clay material. They do not represent a frozen initial state but rather a kinetically controlled rate of conversion of di-and tri-smectite to illite and chlorite. Occurrences of smectites or smectite-rich mixed layers in reservoirs at high temperature is a promising guide for reconstruct the very recent or present zones in which boiling or mixing of non isothermal fluids occurred.
Further investigations are needed on the kinetic law which govern the transformation of mixed layers. Some interesting models have been proposed recently for the transformation of di-smectite to illite. However they consider montmorillonite to illite transformation on the basis of what is observed in diagenesis. Our data indicate that in geothermal reservoirs, the di-smectite which occurs at high temperature is beidellite and that the overall conversion series of dioctahedral clay minerals in geothermal systems involved rather beidellite to illite conversion.

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