

CLAY MINERALS IN HYDROTHERMAL SYSTEMS

A. Meunier

Laboratoire des Argiles, Sols et Altération, Université de Poitiers, France

D. Aupart

Laboratoire des Argiles, Sols et Altération, Université de Poitiers, France

## ABSTRACT

*The aim of the present paper is to give an overview of clay formation processes using published data from laboratory experiments to field observations. Emphasis will be made on the time-temperature factor, which is the most important one in the clay crystallization processes, either for short-time laboratory experiments, or for long-time diagenetic evolution.*

### **Reactivity of dioctahedral smectites in short-time alteration processes**

*The study of Whitney & Northrop (1988) is the most exhaustive concerning the range of experimental conditions and the analysis of the run products (250 - 450°C, 1 - 220 days duration). It shows that the first reaction to occur in the smectite-to-illite conversion in experimental conditions is the formation of high-charge smectite layers from low-charge ones. This reaction was shown to be reversible in short time hydrothermal alterations (Meunier et al., 1992).*

### **Smectite to illite or chlorite conversion: long-time reaction processes**

*Smectite-to-illite conversion: In geothermal fields, three I/S particle populations coexist: pure or highly smectitic I/S, random or ordered I/S, which composition varies from 90 to 20 % Sm and pure illite. Several kinetic equations were proposed to model the smectite-to-illite conversion reaction. Huang et al. (1993) proposed a kinetic model which is first-order with respect to the concentration of  $K^+$  and second-order with respect to the fraction of smectite layers in the I/S fraction. The main difficulty is to estimate the  $K^+$  concentration. Using vitrinite reflectance and clay mineralogy data from the Cerro Prieto field (Salton sea), Velde & Lanson (1993) showed that the smectite-to-illite conversion can be modeled reasonably well by a single-step first-order reaction. They concluded that temperature is the most important variable for the smectite-to-illite conversion in the span of 104 to 105 years reaction time.*

*Smectite-to-chlorite conversion: The trioctahedral smectite to chlorite conversion is not a simple process controlled by the formation of brucite in the smectite interlayer region, as it is classically proposed (Bodine & Madsen, 1987). Two reactions proceed successively: (1) formation of a brucitic layer by fixation and polymerization of complex  $Al-R^{2+}$  ions in the interlayer region of the original smectite; (2) dissolution of the random mixed-layered minerals and recrystallization of an ordered chlorite-saponite phase. Corrensite is not a simple step in a continuous transformation process of saponite to chlorite; it is a true independent mineral phase.*

### **A case study: the active geothermal field of Chipilapa (Salvador)**

*Fossil alterations: The first widespread alteration is characterized by a typical propylitic assemblage (epidote + chlorite + quartz), which pervasively replaces plagioclase, pyroxene and glass. It is followed by a phyllic alteration observed along fracture-controlled veins filled with a phengite + quartz paragenesis. The last alteration event is characterized by a clay-carbonate assemblage along interconnected microfractures. Clay minerals belong to the smectite to illite and saponite to chlorite conversion series.*

*Present day alteration: Present-day alteration is strictly restricted to the open fracture network in the productive zone. It is characterized by the crystallization of nearly pure dioctahedral and trioctahedral smectites + haematite  $\pm$  kaolinite at the walls of the fractures. This assemblage overprints the conversion series I/S and C/S of the previous intermediate hydrothermal stage, creating spatial "clay anomalies" that closely corresponds to the present reservoir zones.*

## INTRODUCTION

Since the pioneer works of Loyering (1950) and

Bonorino (1959), the alteration minerals in hydrothermal systems have received considerable attention. The variation of

secondary mineral assemblages with depth (calc-silicate minerals, feldspars, clay minerals, etc.) were soon related to fluid

## REACTIVITY OF DIOCTAHEDRAL SMECTITES IN SHORT- TIME ALTERATION PROCESSES

### Experimental alteration

The study of Whitney and Northrop (1988) is the most exhaustive concerning the range of experimental conditions and the analysis of the run products (250 - 450°C, 1 - 220 days duration). It gives us the greatest insight into the reactions produced under the experimental conditions. In the figures which summarize the basic run results (see Figure 3), it is evident that there are two rates of reaction in the system, one rapid, found for short periods of time, and the other which establishes a much slower rate of change at longer time periods. A plot of the run results on  $\ln(a/a-x)$  vs time coordinates, where  $a$  is the initial 100% smectite concentration and  $x$  the amount of illite formed, shows these two types of reaction rates (Figure 2).

This plot follows the usage in Robertson & Lahann (1981) and Howard & Roy (1985). The most striking observation which can be made on this data is that, from the tables of run results and XRD diagrams presented in the studies, the reaction products are not the same for the two reaction rates. In the earlier rapid reaction, the products are I/S of R=O (disordered) structural type, quartz and a small amount of mica is often present. The second reaction, found after 40 days or so at 250°C and above, gives the products of I/S with an R=1 (ordered) structure, chlorite and quartz. These observations in-

temperature, fluid chemistry and permeability conditions (Steiner, 1968; Harvey and Browne, 1991). Most of the studies in the two last decades describe a double conversion series for clay minerals: smectite to illite and saponite to chlorite.

Based on present day temperature conditions in active geothermal fields, a set of geothermometers were calibrated using clay mineral compositions. Dioctahedral smectites are transformed to illite with increasing temperature through a series of mixed-layers illite/smectite (I/S), which smectite ratio decreases to 0% at about 230°C (Henley & Ellis, 1983; Srodon & Eberl, 1984). The trioctahedral clay sequence is characterized by the transformation of saponite to chlorite at temperatures higher than 190-200°C through a series of chlorite/smectite (C/S) mixed layers (Kristmannsdottir, 1976; Browne, 1978; Seki et al., 1984; Inoue and Utada, 1991). According to Bettison & Schiffman (1988), C/S are observed at temperatures lower than 200-240°C. At higher temperatures, the saponite to chlorite transformation is complete. Because of the swelling components of dioctahedral, as well as trioctahedral mixed-layers disappear at temperatures close to 230-240°C, illite + chlorite is the expected assemblage at higher temperatures.

In most of these studies, hydrothermal alteration reactions are considered to affect the whole rock and to produce secondary phases in equilibrium with local chemical and temperature conditions. This, of course, leads to use without caution the thermodynamical calculation codes to model the rock-water system at any tem-

perature. Unfortunately, even if this is satisfactory for mind, the results obtained depict rarely the actual phenomena which govern the formation of clay minerals through hydrothermal reactions. Indeed, accurate petrographical and mineralogical observations show that clay assemblages are systematically out of chemical equilibrium and sometimes out of phase equilibrium. It is now undoubtedly established that formation or transformation of clay minerals are controlled by kinetics even in diagenetic environments where physico-chemical conditions are stable for long period of time (order of magnitude: 107 years). The time-temperature factor is the most important one in all the clay crystallization processes from short time laboratory experiments to long diagenetic evolution (Figure 1).

The aim of the present paper is to give an overview of clay formation processes using published data from laboratory experiments to field observations. Emphasis will be made first on the nature of mineral reaction. Indeed, in spite of the fact that the I/S mixed-layer sequences produced in laboratory experiments seem to be identical to those observed in geothermal fields or in diagenetic formations, the smectite-to-illite conversion reactions are not equivalent. The main differences concern the layer charge and the composition of the smectite component. Secondly, recent progress in the interpretation of X-ray diagrams using the decomposition procedure (Lanson & Besson, 1992) allows now to better understand the complex distribution of clay species in hydrothermal systems and especially in active geothermal fields.

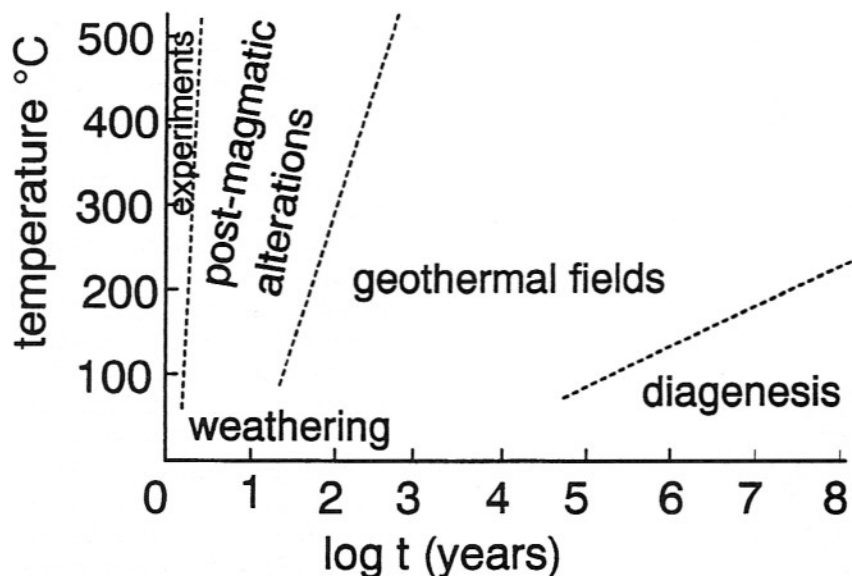


Figure 1 - Temperature versus time domains for the different types of hydrothermal reaction systems for clay minerals.

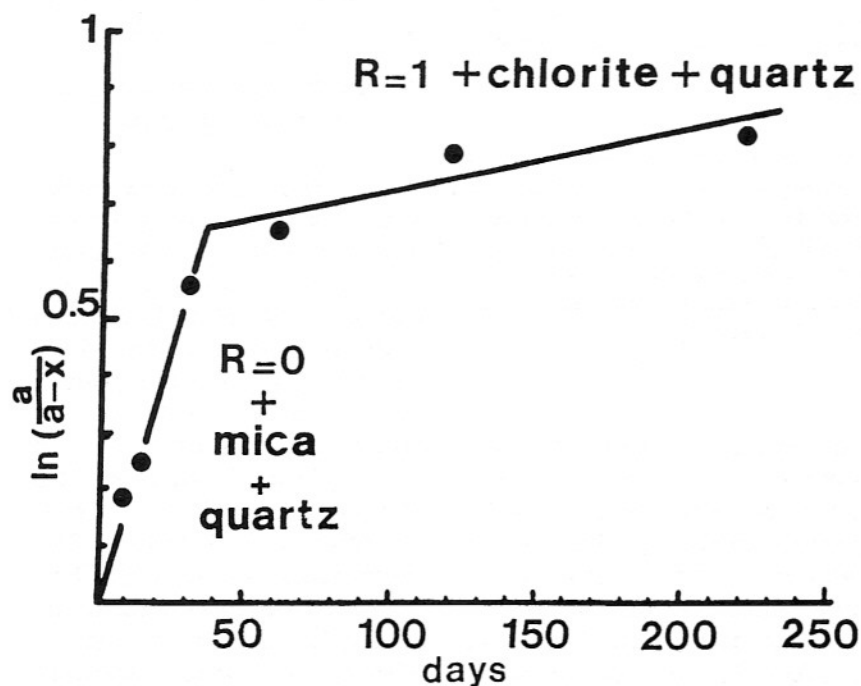


Figure 2 - Plot of hydrothermal reaction progress  $\ln(a/(a-x))$  of smectite to non-expanding layers in the potassium-saturated state, according to the data of Whitney & Northrop (1988). Two rates are apparent, that concerning the  $R=0$  structural I/S mineral type and that concerning the  $R=1$  structural type I/S mineral. The run product assemblage is different for the two apparent conversion rates. Temperature conditions were 250°C.

indicate that there are, in fact, two different reactions which occur in the experiments, as concluded by

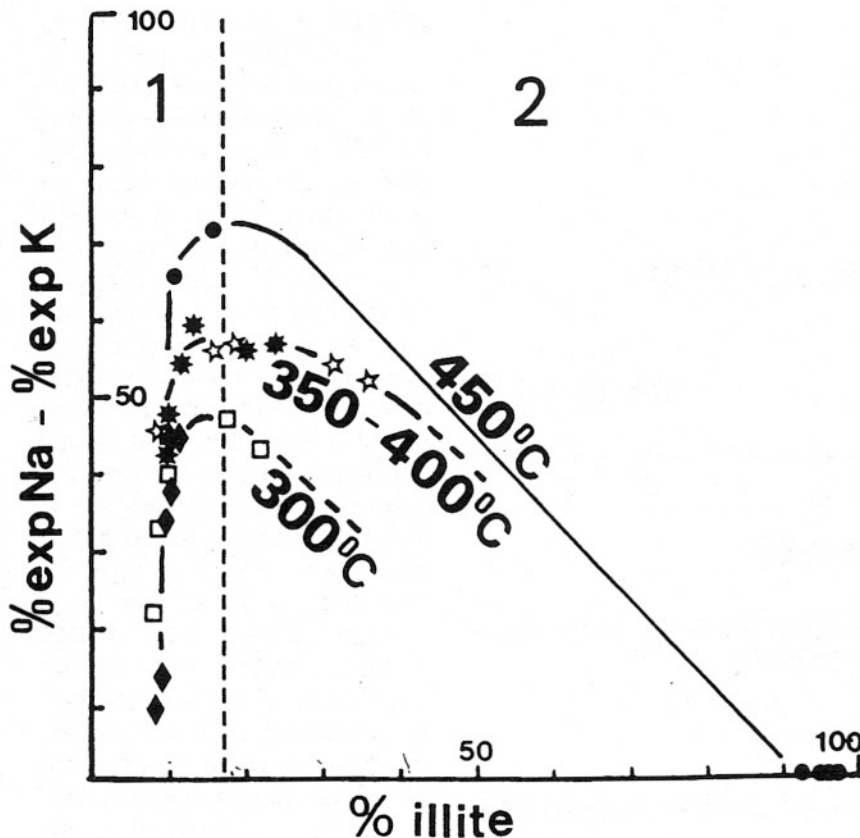
Whitney & Northrop (1988).

Nevertheless, the data given by Whitney & Northrop

(1988) indicate that the two reaction product assemblages in which the I/S phases are found are not similar. In determining the effect of potassium saturation on the I/S phase, these authors have indicated that the two different reaction series give smectites of different properties. The short duration (less than 40 days) reaction gives a disordered ( $R=0$ ) three component mixed layer mineral composed of illite and high charge and low charge smectites evidenced by the collapse of a portion of the layers when potassium is saturated (Figure 3). This complex I/S mineral is accompanied by quartz. As the reaction progresses, a higher proportion of the smectite layers collapses. Midway in the reaction sequence, when about 50% high charge smectite layers in the I/S mineral is approached, the mixed layer mineral has the  $R=1$  ordered type structure. The I/S mineral is accompanied by chlorite and quartz. These two reactions were noted by Whitney & Northrop (1988) to have different rates.

The authors assumed that the I/S mineral should be of a montmorillonite type, maintaining the Mg and Fe in its structure to create the charge on the unit layer. If this is the case, in runs with higher bulk aluminum content, the excess aluminum necessitates the production of a small amount of mica along with quartz. As above, the Fe and Mg remain in the smectite layers give a higher charge to the montmorillonite layers as the reaction progresses. Clay assemblages produced in the longer experimental runs indicate that the compositions of the I/S minerals formed are more illitic. Potassium saturation of the products does not affect the





**Figure 3** - Plot of run results for the data obtained by experimental illitization of a montmorillonite (Wyoming bentonite) by Whitney & Northrop (1988). The difference of expandability difference between the glycolated Na and K saturated samples (%expNa %expK) gives the proportions of high-charge smectite layers. The temperature at which the experiment was performed is 250°C (full lozenges); 300°C (squares), 350°C (black stars), 400°C (stars) and 450°C (points).

smectitic part of the I/S mineral. These reactions give the chlorite phase which contains Mg and Fe ions, indicating a relatively higher Al/R<sup>2+</sup> content of the I/S mineral. Therefore, in the second reaction, the charge increase is due to the production of illite layers, where the charge is in the tetrahedral site and beidellitic in nature. The compositional trends for the two I/S series are shown in Figure 4, as deduced from the expandability of the I/S structure and the phase assemblage produced.

In fact, it is not undoubtedly established that the

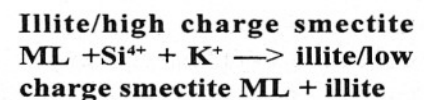
smectite component in the random and the ordered I/S mixed layers conserve the montmorillonitic structure of the original Wyoming clay. Another reaction should be envisaged for the first step of the illitization process. The low-charge montmorillonite could be transformed into a high-charge beidellite - saponite quartz mineral assemblage as indicated in Figure 5a. In such a case, the Fe and Mg chemical components are concentrated into a separate phase, as it was shown in experimental synthesis of clays in the Mg-Al-Si system (Grauby et al., 1993). Then, the

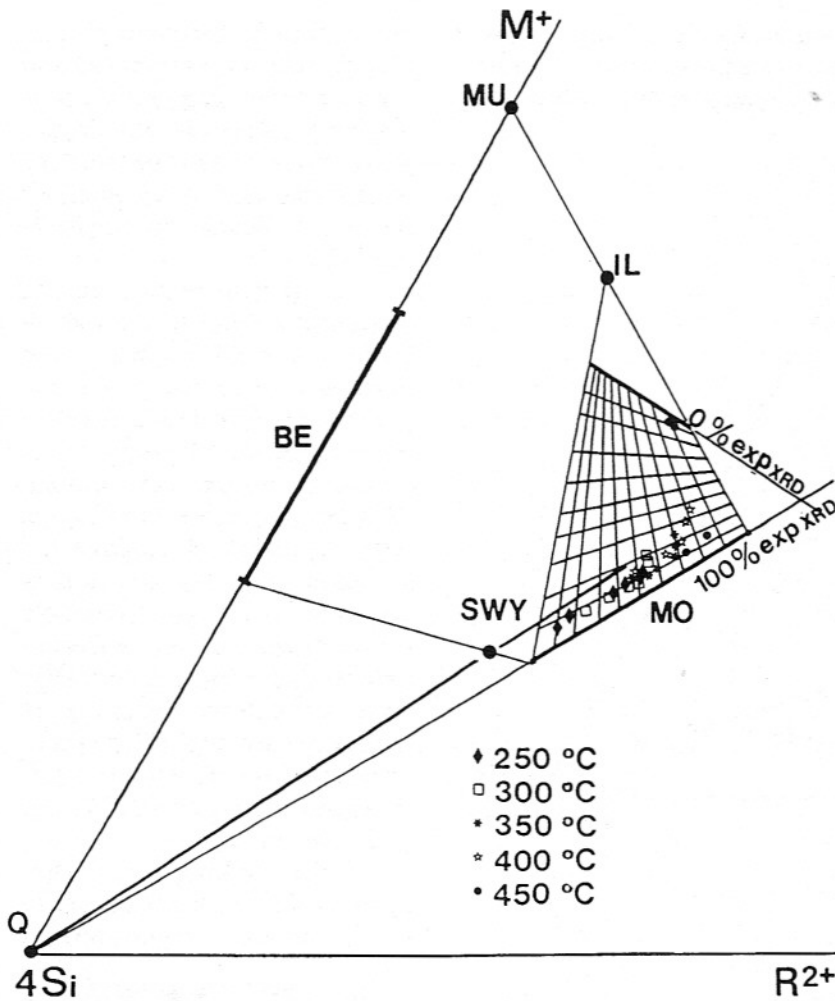
smectite component in the ordered smectite-illite mixed layers is beidellitic; I/S chemical composition must be located on the beidellite-muscovite joint, rather than on the montmorillonite-illite one (Figure 5b).

The Wyoming bentonite is classically used as a standard smectite in a great number of experimental works, especially in recent experiments devoted to illitization process kinetics (Huang et al., 1993). It is, of course, of great interest to determine the actual reaction processes because kinetic laws are calculated for a strict transformation of smectite to illite, ignoring that other processes are working. This means that new experiments have to be made in order to identify the mineral phases at each step of the reaction.

#### Hydrothermal alteration in natural systems

The reactions described above, i.e., smectites are transformed to illite-smectite mixed layers, were shown to be reversed in natural hydrothermal systems. This was described either in vein alteration systems or in geothermal field. The vein alteration was observed in an argillized dacite (La Martinique, Caribbean island) by Bouchet et al. (1988). The parent rock is composed of tiny debris of magmatic minerals embedded in a clay matrix, which is homogeneously formed of free illite + illite/high-charge smectite mixed layers (ML). A secondary hydrothermal alteration is observable along veins which cross-cut the argillized dacite. The reaction is the following:





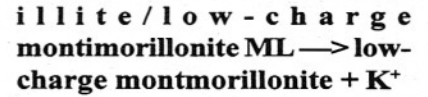
**Figure 4** - Interpretation of the data of Whitney & Northrop (1988) according to their assumption that the montmorillonitic structure of smectite component is conserved through the smectite-to-illite conversion series. I/S compositions are plotted in the  $M^+-4Si-R^{2+}$  coordinates using the high-charge montmorillonite - low-charge montmorillonite - illite layer proportions determined in Figure 3 (%expNa - %expK parameter). The line indicates that the stoichiometry is respected if the formation of high-charge montmorillonite layers is associated with the crystallization of quartz.

The intensity of the reaction increases toward the open fracture of the vein (Figure 6).

Clayey materials were shown to react under hydrothermal alteration conditions (high-temperature diagenesis) in the Colorado river delta. The sediments are composed of a mixture of detrital minerals including illite/low-charge smectite

ML, having different degrees of expandability, discrete illite or mica and kaolinite. They have experienced hydrothermal reactions due to hot fluid circulation (Jennings & Thompson, 1987). The <2mm fraction is progressively transformed into a pure low-charge montmorillonite as temperature increases from 39 to 68°C (Figure 7) ac-

ording to the following reaction:



The formation of low-charge smectite from I/S ML does not mean that the illitization process is strictly reversible. The smectite-to-illite and illite-to-smectite reactions do not follow the same trajectories but symmetrical ones in the  $M^+-4Si-R^{2+}$  chemical system (Meunier et al., 1992). Nevertheless, we ignore if these reactions produce or destroy a trioctahedral phase. Indeed, X-ray diffraction studies cannot detect a clay species which represents less than 5% in weight. Thus, the problem is still open.

### THE LONG-TIME REACTION PROCESSES IN SMECTITE TO ILLITE OR CHLORITE CONVERSION

The smectite-to-illite conversion processes

*Variation of I/S composition with depth in active geothermal fields*

The clay mineralogy of active geothermal fields has been described until the very recent studies as continuous series of trioctahedral and dioctahedral mixed layers in which the smectite content decreases regularly with depth, i. e., temperature. The illite-smectite ML series has been classically paralleled to the diagenetic one; the main difference being the rate of the transformation. This is the reason why kinetic models in both

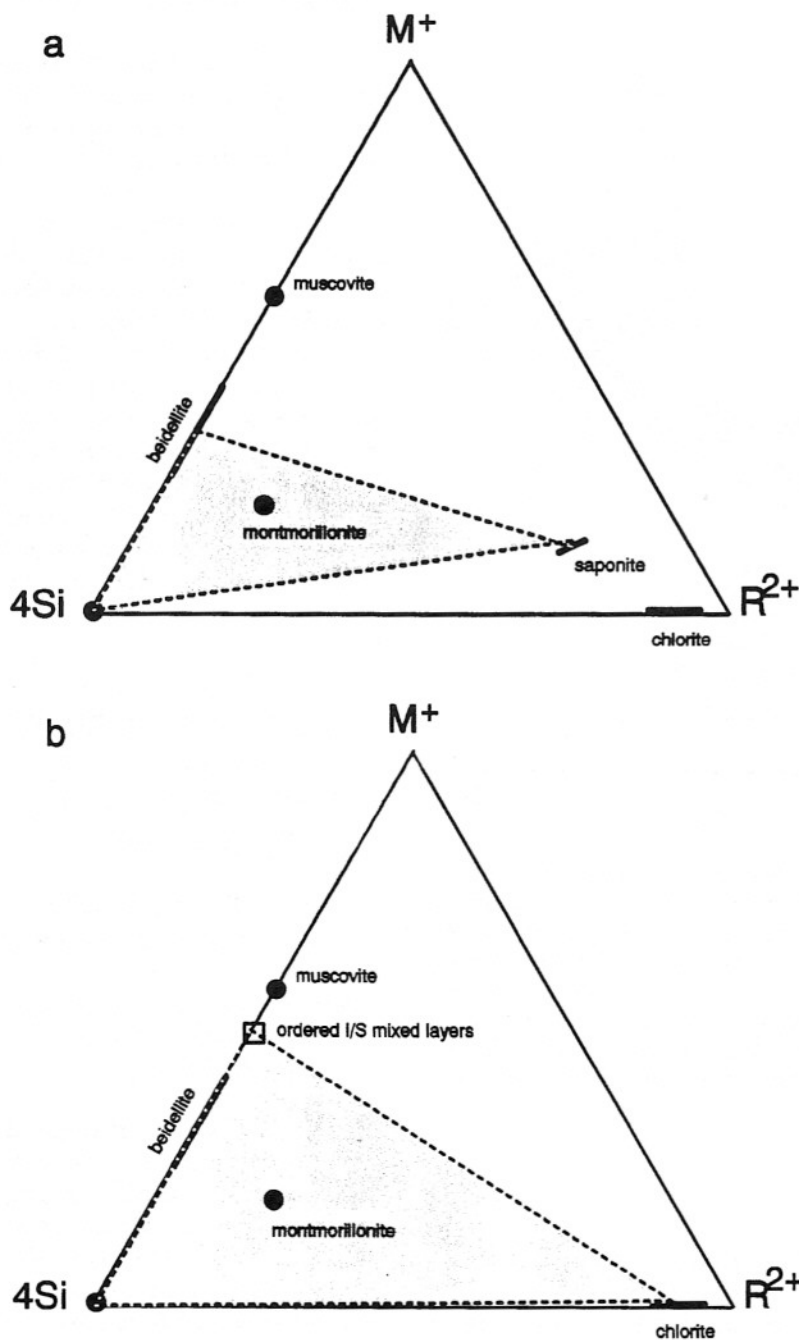
cases are based on the progress of a unique mineral reaction: the smectite-to-illite conver-

sion. In fact, the composition of the dioctahedral clay fraction is more complex than indicated by

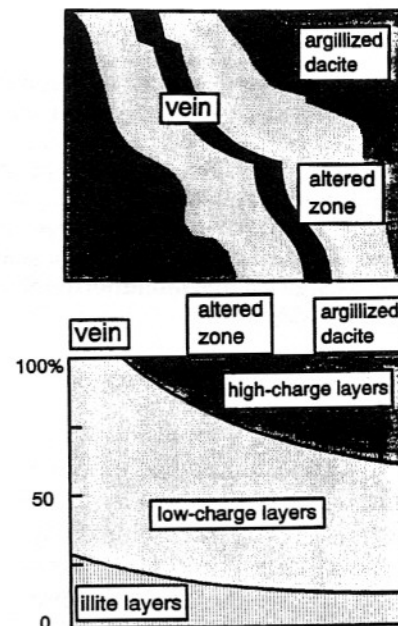
these studies. Most often, this clay fraction is polyphased and pure smectite frequently coexists with illite-rich ML in the same levels. These observations were interpreted as "anomalies" due to pollutions with the drilling mud.

The Sumikawa active geothermal field described by Inoue et al. (1992) will be taken here as a case study. As expected, the six studied boreholes (Figure 8) show a decrease of the smectite content of illite/smectite mixed layers with depth but in most of the samples, the clay fraction is composed of several I/S particle populations having different smectite content. Generally, three populations coexist: pure or highly smectitic I/S, random or ordered I/S which composition varies from 90 to 20 % Sm and pure illite.

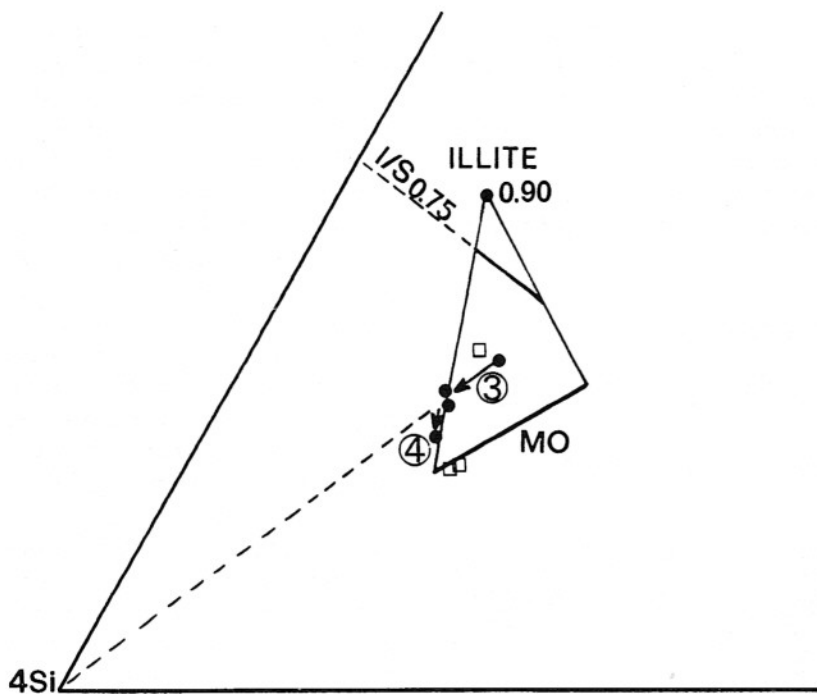
The striking fact is that pure smectite is observed in wells where the geothermal



**Figure 5** - Re-interpretation of the experimental alteration of a montmorillonite (Wyoming bentonite) from the data of Whitney & Northrop (1988). a) The stoichiometry in a closed indicates that the first reaction (short time, low temperature) may produce high-charge beidellite + saponite + quartz assemblage, instead of the random montmorillonite-illite mixed layer + quartz, as stated by the authors. b) Then, the second reaction would produce an ordered beidellite-illite mixed layer (instead of an ordered montmorillonite-illite mixed layer) + chlorite + quartz assemblage.



**Figure 6** - Composition change in I/S mixed layers in the hydrothermally altered veins crosscutting an argillized dacite at Les Trois Ilets, la Martinique (modified from Bouchet et al., 1988).



**Figure 7** - Hydrothermal alteration of illite-smectite mixed layers in natural environments. Full circles: vein crosscutting an argillized dacite at Les Trois Ilets, la Martinique (Bouchet et al., 1988); squares: Colorado River delta geothermal area (Jennings & Thompson, 1987). Increasing alteration degree is indicated by the arrow.

gradient is sharp (SN-7D, KY-2, S-4, SB- 1) and not so in the weaker gradient well (SN-8R).

This is due to the superimposition of two phenomena: 1) a progressive transformation of the rock similar to a high-temperature diagenesis; 2) direct precipitation from hot fluids in reservoir zones. The SN-8R well crosscuts a non-active zone, where the diagenetic type process is dominant. The direct precipitation of pure smectite clays was evidenced by Papapanagiotou et al. (1995).

#### *Kinetic models for the smectite-to-illite conversion*

The kinetics of the smectite-to-illite conversion reaction was investigated first by Eberl and Hower (1976) from experimental data. They found

19.6 kcal per mole for the activation energy of the reaction, using a first order equation. Several studies following this pioneer work concluded to different values of the activation energy, varying from 3 to 30 kcal per mole. The order of the kinetic equation may also vary. For example, Pytte and Reynolds (1989) derived a sixth-order kinetic equation based on the field observations of progressive illitization of smectite in bentonite beds close to intrusive basalt dykes. A similar sixth-order kinetic equation was used for modeling smectite-to-illite conversion in bentonites and in shales (Altaner, 1989; Elliot et al., 1991). As there is no formal justification on the choice of the order of the kinetic equation as well as of the value of the activation energy, Velde & Vasseur

(1992) proposed an empirical model based on a two step first-order reaction model, derived from a simultaneous fit of data from sedimentary basins of widely ranging ages. The pre-exponential factors and the activation energies for the two steps were  $e^{16.5} \text{ Ma}^{-1}$ ,  $e^{2.8} \text{ Ma}^{-1}$  and 56 kJ, 22 kJ, respectively.

Huang et al. (1993) proposed a kinetic model which is first-order with respect to the concentration of  $\text{K}^+$  and second-order with respect to the fraction of smectite layers in the I/S fraction. This model seems to predict well the extent of the smectite-to-illite conversion in a wide variety of geological settings including geothermal fields (calculations were made using data of the Salton Trough Geothermal area from Jennings & Thompson, 1987). However, the authors have encountered some difficulty to estimate the  $\text{K}^+$  concentration and the geothermal gradient. They gave a 33 to  $59^\circ\text{C.km}^{-1}$  geothermal gradient range and considered that  $\text{K}^+$  concentration varies between 12000 to 3000 ppm. The values of the two parameters are arbitrarily chosen to fit the % Sm versus depth curves.

In order to avoid such an arbitrary method, Velde and Lanson (1993) have determined the paleo-thermal conditions in the Cerro Prieto geothermal field (Salton Sea), by fitting simultaneously the smectite-to-illite conversion and the organic matter maturation. They used the kinetic equation set from Sweeney and Burnham (1990) to calculate the variation of vitrine reflectance with depth. They showed that the smectite-to-illite conversion can be modeled reasonably well by a single-step first-order reaction. They concluded that clays react rapidly to temperature in



geothermal areas and that thermal gradient does not influence greatly the reaction progress.

They claimed that temperature is the most important variable for the smectite-to-illite conversion in the span of

$10^4$  to  $10^5$  years reaction time.

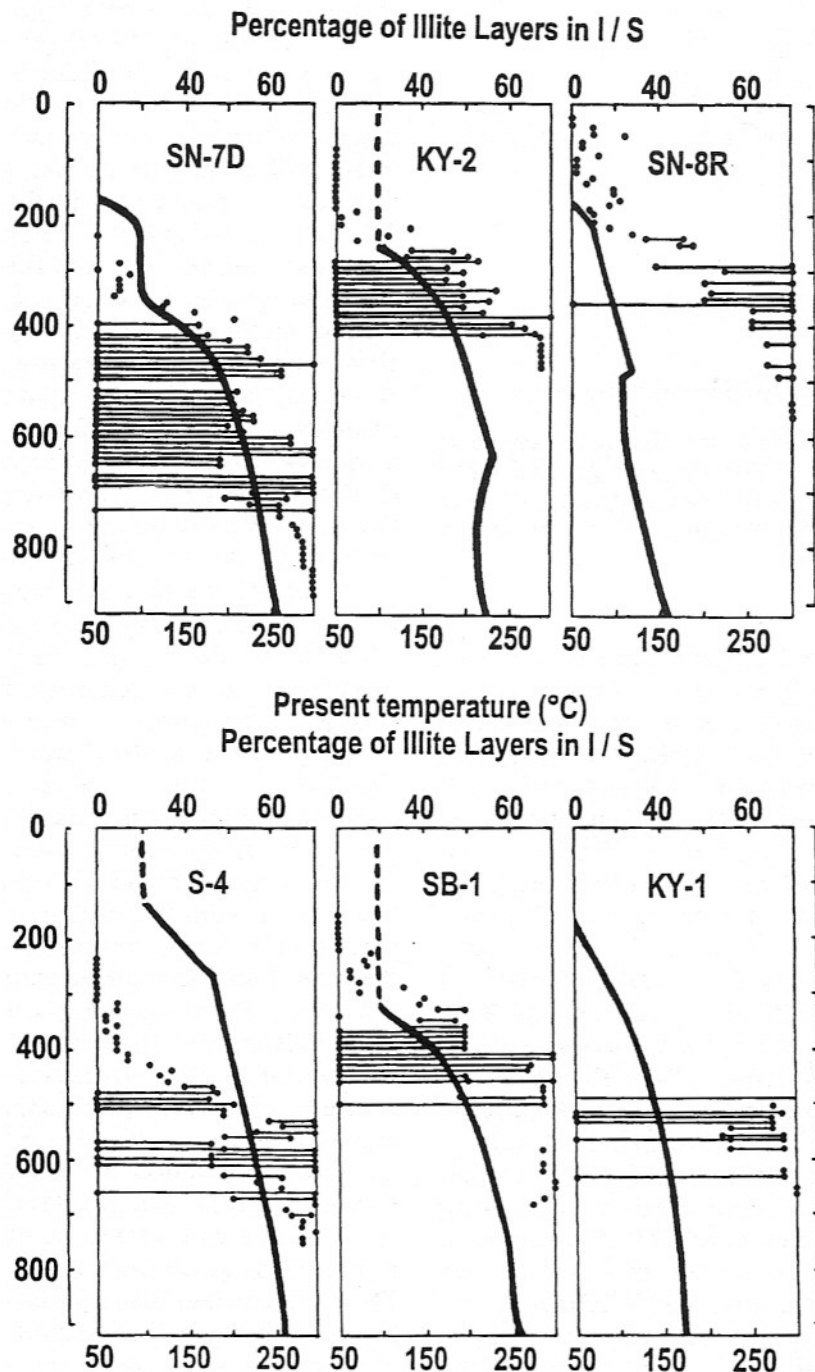
Whatever the model chosen, the major assumption they are based on is that the I/S clay fraction is homogeneous and can be depicted by a single composition. This assumption is in-

correct since highly smectitic mixed layers are frequently observed coexisting with highly-illitic ones in active zones of geothermal fields. The paradoxical presence of smectite-rich clays in high-temperature reservoirs is undoubtedly related to the quick nucleation of a phase out of equilibrium and out of any conversion reaction process. Whatever the kinetic equations the different models are based on, they must be used with care. The advantage of the empirical model of Velde and Vasseur (1992) is that both the smectite-to-illite conversion and the maturation of organic matter have to be modeled with the geothermal gradient conditions. In its actual state, this model is certainly the most powerful one to determine the paleo-thermal and the burial conditions, either in diagenetic series, or in geothermal field provided the % Sm of I/S and vitrinite reflectance are measured.

#### The saponite-to-chlorite conversion process

#### *The C/S mixed layer series in hydrothermal systems*

The C/S mixed layer series is classically considered to be the trioctahedral equivalent of the I/S one. According to this model, the smectite to chlorite conversion proceeds by a continuous variation of the relative proportions of the two end members and involves varying types (random and ordered) of mixed-layering. In such a model, corrensite is an intermediate term of the saponite-to-chlorite conversion series (Chang et al. 1986; Reynolds, 1980) corresponding to a regular mixed-layer recognized by a rational series of peaks having a coeffi-

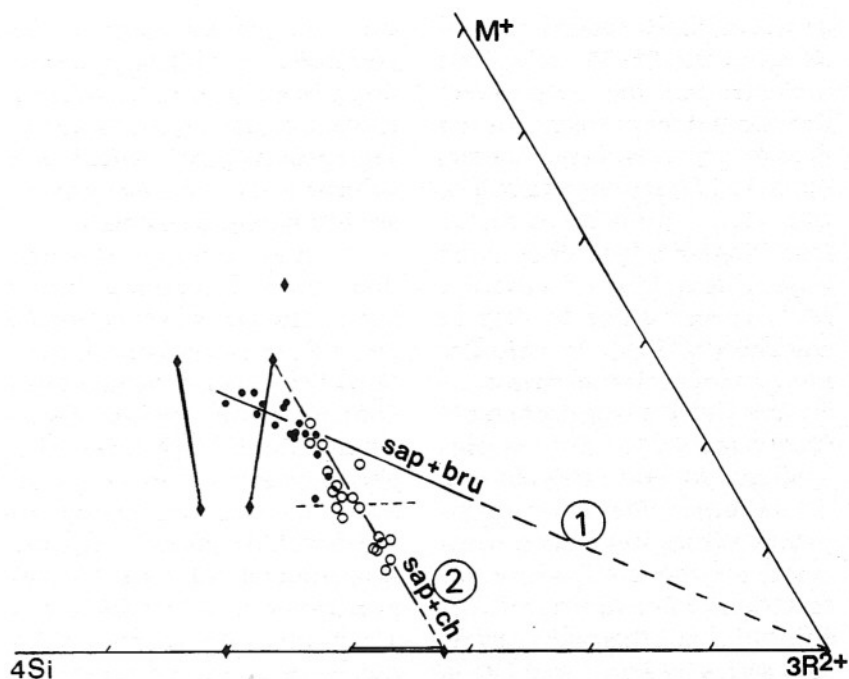


**Figure 8** - Variation of percentage of illite layers (%I) as a function of depth in six drill-holes from the Sumikawa field (modified from Inoue A.; Utada M.; Waldta K., 1992).

cient of variability lower than 0.50 (Bailey, 1982).

This classical model was discussed in numerous descriptions of a C/S series in hydrothermal fields. Among them, the Ohyu caldera one (Inoue et al., 1984) was the most documented since chemical compositions of mixed layers are given for a sequence of more than 20 samples. Three types of mixed-layered minerals were found with increasing depth: highly expendable mixed-layered minerals (100 to 80 % smectite), corrensite (55 to 40 % smectite) and slightly expendable chlorite (less than 15 % smectite). The series is not as continuous as expected in the classical model but the chlorite enrichment of C/S proceeds by composition jumps. This series was reinterpreted by plotting C/S chemical compositions in the  $M^+ - 4Si - 3R^{2+}$  coordinates (Figure 9). Surprisingly, the chemical compositions were not linearly distributed between the original trioctahedral smectite composition and a chlorite end member. Two trends were evidenced: (1) the original trioctahedral smectite-brucite (or brucitic layer) line for the highly expendable mixed layers; (2) a high-charge saponite (0.65  $M^+$  charge) - chlorite without octahedral vacancy trend for corrensite and highly-chloritic mixed layers. It was concluded that the trioctahedral smectite-to-chlorite conversion is not a single process controlled by the formation of brucite in the smectite interlayer region as it is classically proposed (Bodine and Madsen, 1987).

Two reactions were considered to proceed successively: (1) formation of a brucitic layer by fixation and polymerization of complex  $Al-R^{2+}$  ions in the



**Figure 9** - Projection in the  $M^+ - 4Si - 3R^{2+}$  system of the compositions of the "chlorite smectite" mixed layer minerals from Ohyu caldera formation (Inoue, 1985). Line 1: mixture of original smectite with an Al-MG brucitic layer; line 2: interlayering of high-charge saponite with octahedral-vacancy-free chlorite; extrapolation of line 2 gives the saponite composition (square) and the chlorite composition (triangle). The intersection with the dashed line represents the ideal 50-50 corrensite composition.

interlayer region of the original smectite; (2) dissolution of the random mixed-layered minerals and recrystallization of an ordered chlorite-saponite phase. The random mixed-layered minerals conserve the composition of the original 2:1 smectite layer and, as a consequence, they cannot be considered further as the direct precursors of corrensite in which the non-expendable layer is a true chlorite. The random mixed-layered phase is not progressively transformed into the ordered one; this means that it probably dissolves when corrensite crystallizes. This explains why there is not a continuous series from 100% to 50% expendable minerals in the Ohyu caldera sequence. As corrensite is the product of a

dissolution-recrystallization reaction, it behaves as a true independent phase in the thermodynamic sense. This was suggested by Velde (1985), Inoue (1985), Reynolds (1988) and Robertson (1988).

#### *The corrensite problem*

A recent XRD and HERTM study (Beaufort et al., 1995) based on extremely well crystallized saponite, corrensite and chlorite-rich C/S mixed layer samples from hydrothermal veins in the paleozoic basement at Sancerre-Couy (France) shows that corrensite behave as a single mineral phase. Considering the differences in the b dimension between smectite and chlorite, the coherent stacking of these two layer types

seems unlikely. Indeed, the position of the 06-33 reflections indicates that the b-parameter determined for corrensite is not median between b-parameters measured for saponite and chlorite, as it would be expected from Vegard's law. It is much higher than that of saponite (9.21Å) and close to that of chlorite (9.252Å). In chloritic mixed layers, b-parameter increases with the chlorite content (9.249 and 9.252Å for samples having 75% and 90% chlorite layers respectively). Very consistent values have been measured for saponite, corrensite and chlorite from a smectite-to-chlorite hydrothermal conversion series by Inoue and Utada (1991) in the Kamikita area (Japan). This suggests that the tridimensional structure of corrensite is not consistent with a 50/50 C/S ordered mixed layer for which the structural parameters should merely correspond to the mean of those of both individual phases.

HRTEM images clearly indicate that the corrensite layer can not be divided into sublayers of 'chlorite' and 'smectite'. All the 10Å layers observed in the corrensite or chloritic material are linked to chlorite in corrensite layers (24Å) even in case of edge dislocation or layer termination (Figure 10a). This indicates that the 24Å structure is the unit of crystalline growth. Thus, corrensite is a true independent mineral phase and not a chlorite/smectite mixed-layer. Further, discrete corrensite packets were observed in the so-called chlorite-rich C/S mixed layers (Figure 10b). These C/S mixed layers have crystallized according to two coexisting processes: 1) intergrowth within corrensite domains of coherently stacked chlorite layers leading to a mix-

ture of discrete chlorite and corrensite crystallites; 2) formation of small quantities of chlorite/corrensite mixed layers ( $\pm$  segregations?) in the case where chlorite and corrensite domains are intimately associated.

In a summary, the random chlorite/saponite mixed layers ( $R=O$ ) would probably result from the polymerization of Al-Mg<sub>2</sub> units in the interlayer domain of the saponite giving a non-chloritic 14Å layer. This phenomenon could be paralleled to the formation of 'gibbsite' like layers in expendable minerals of soils. Whatever the process by which they are formed, the random chlorite/saponite mixed layers are unstable at high temperature conditions. However, they are not progressively transformed in an ordered mixed layer as thought before, but they are dissolved while a new mineral appears: corrensite. At last, the chlorite-rich chlorite/saponite mixed layers are in fact corrensite/chlorite mixed layers or mixtures of crystallites.

## APPLICATION TO THE THERMAL HISTORY OF AN ACTIVE GEOTHERMAL FIELD: CHIPILAPA (SALVADOR)

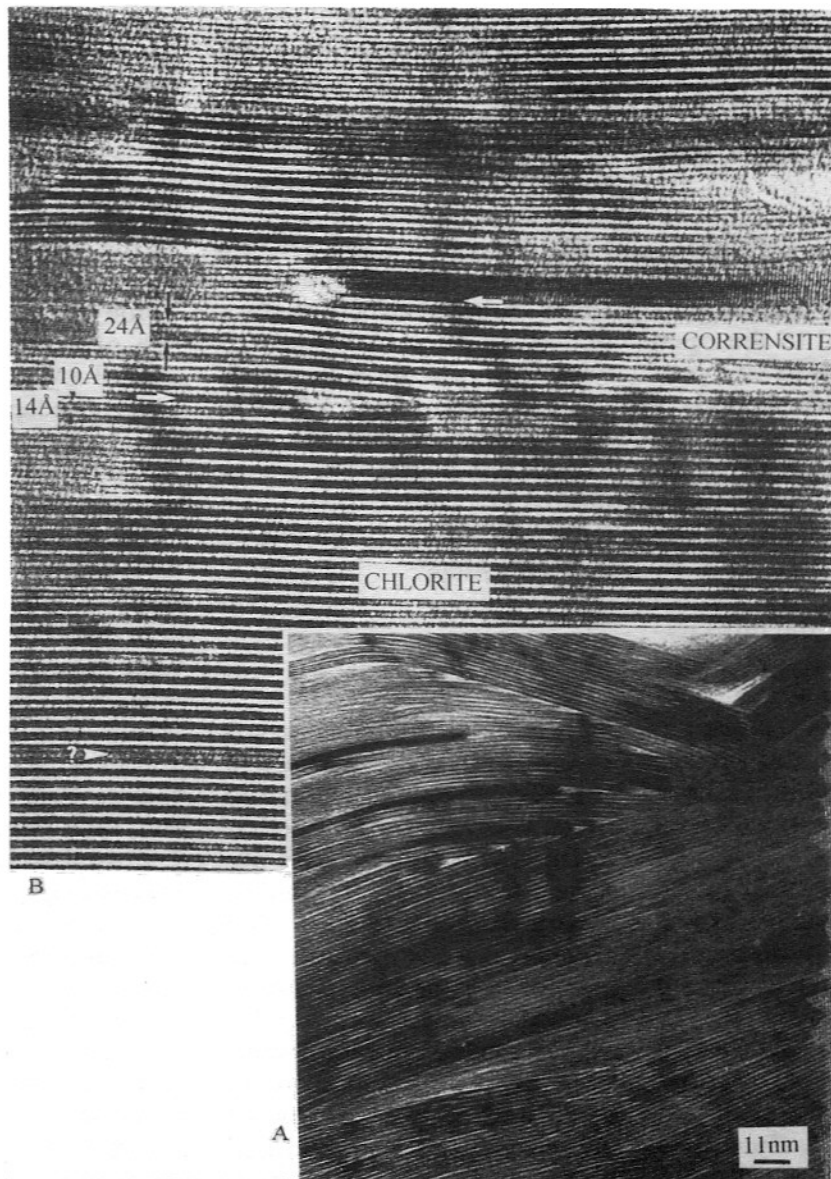
### Fossil alterations

A detailed petrographic study of core samples from the active geothermal field of Chipilapa, Salvador (Papapanagiotou, 1994) showed that fossil alterations are vertically zoned because of time-space superimposition of at least three hydrothermal stages. The first one is of propylitic type; its volumetric extension is of several cubic

kilometers. The typical assemblage is epidote + chlorite + quartz, which pervasively replaces plagioclase, pyroxene and glass. Authigenic quartz and epidote are commonly observed as vug fillings and chlorite  $\pm$  epidote replace the volcanic glass. Some mineralogical variations have been observed: prehnite, adularia and wairakite are observed at great depth (-1400 m); at shallow depth (above 800m), the assemblage epidote + quartz + chlorite progressively disappears, due to overprinting by later clay assemblages (relicts of epidote have been identified above 500m). From the depth of 500 m up to the present surface, zeolites progressively change in composition from laumontite to clinoptilolite-stilbite and chlorite is replaced by saponite. The second event is phyllic alteration strictly located around some large fractures, which are presently sealed by a phengite + quartz paragenesis. Its volumetric extension is difficult to estimate; it is probably of the cubic meter order.

The third event is characterized by a clay-carbonate widespread deposition in an interconnected network of microfractures, which is more developed in tuffs than in massive lava flows. In the surrounding host rocks, calcite partly replaces plagioclase and commonly seals the residual pore space of the vugs, which were previously filled by euhedral epidote and quartz. The clay minerals belong to the dioctahedral and trioctahedral series. The I/S series grades from nearly pure smectite, near the surface area, to illite-rich mixed layer-clays with less than 5% of smectite at 1750m through ordered  $R=1$  I/S (35% of smectite), at depth near 400-





**Figure 10 - a)** Corrensite sample "smectite 50%-chlorite 50%". Note the ubiquitous curvature of, and rare kink in, corrensite slabs. Image taken in the  $-1000\text{\AA}$  to  $-1200\text{\AA}$  defocus range. The three sub-layers (the  $9\text{\AA}$ -thick talc-like, the  $5\text{\AA}$ -thick brucite-like, and the  $10\text{\AA}$ -thick collapsed smectite) are imaged within the  $24\text{\AA}$  collapsed corrensite repeated distance in the upper left part of the microphotograph. However, most of the corrensite structure (e.g. upper middle and lower right) images as a regular succession of  $\sim 10\text{\AA}$  (collapsed smectite) and  $\sim 14\text{\AA}$  (chlorite) fringe spaces. The total lack of layer stacking error is remarkable even where subgrain boundaries (arrow) vanish, leaving parallel grains (left). This testifies for unsociable corrensite sublayers.

**b)** Corrensite - chlorite composite crystal (smectite 25%-chlorite 75%). HRTEM lattice image of the representative chloritic material displaying a flexuous, subparallel slab of corrensite (middle left to right) interlayered with a chlorite matrix, here chlorite, as well as chlorite-like, and collapsed smectite-like layers image as  $14\text{\AA}$  and  $9\text{-}10\text{\AA}$  fringes, respectively. Such matrix is moderately defective in the form of irregularly intergrown  $9$  to  $10\text{\AA}$ -thick layers (collapsed smectites?). Because  $9$  to  $10\text{\AA}$ -thick single layers are never contiguous, they may presumably be considered each as systematically associated with a chlorite-like layer, thus forming intergrown corrensite layers into chlorite. The regular corrensite is somewhat S-shaped due to a layer termination dipole (white arrows pointing to beam damages) which is formed on the left side (bottom) by a chlorite single layer and on the right side (top) by a collapsed smectite layer. This is best seen at grazing incidence from the left or right side of the photo. The upper arrow also marks a transition from I-D to 2-D imaging, i.e., the location of a turbostratic stacking surface; note the strong diffraction contrast change there. CORR = corrensite, CHL = chlorite, the  $28\text{\AA}$ -thick layer marked by the white arrow head is unidentified.



500m. The C/S series grades from pure saponite to C/S mixed-layer, with less than 10% of saponite at 1750m via corrensite, at depth near 400-500m.

### Present day alteration

Present day alteration is strictly restricted to the open fracture network in the productive zone. The secondary minerals produced are nearly pure dioctahedral and trioctahedral smectites + hematite  $\pm$  kaolinite deposited on the walls of the fractures. This assemblage overprints the I/S and C/S series of the third hydrothermal stage. The zones of crystallization are detected as "abnormal" ones, since the crystallizing mineral phases are fully expendable, in spite of local high temperature conditions.

Crystallization of smectites at high temperatures has been observed in numerous active geothermal fields: the Philippines (Reyes, 1990), Djibouti (Zan et al., 1990), Valles caldera (WoldeGabriel and Goff, 1992) and Japan (Inoue et al., 1992). Smectites were considered to result from a dissolution-precipitation process affecting the drilling mud (Reyes & Cardile, 1989) or as relict minerals of a diagenetic origin (Hulen & Nielsen, 1986). Inoue et al. (1992) have suggested that smectite is a metastable phase which persists when illitization proceeds abruptly at high temperatures.

The presence of abundant smectites in the reservoirs is closely associated with boiling zones. The rapid sursaturation of the liquid phase, while steam is produced, provokes the nucleation of growth

smectite crystals which are out of equilibrium regarding the local physico-chemical conditions. This is a typically kinetic controlled reaction. As a consequence, smectites in the permeable zone of Chipilapa geothermal field are in isotopic equilibrium with fluids enriched in  $^{18}\text{O}$ , because of boiling. They are associated with the hematite  $\pm$  kaolinite mineral assemblage, which is an indicator of high  $f\text{O}_2$  and low pH conditions. These conditions are well known to be enhanced in environment of boiling waters.

## CONCLUSION

Laboratory experiments and mineralogical analyses of samples from geothermal fields show that the smectite-to-illite conversion series observed are not strictly similar to the diagenetic one. The smectite component is beidellitic in the short duration processes and montmorillonitic in the long duration ones. The crystalline structure of beidellite is closer to that of the micas than the montmorillonite one, because of the layer charge located in the tetrahedral sheet. This could explain why disordered illite-beidellite mixed layers are rarely observed; order is quickly established during the conversion process to illite. The R=O I/S phases described by Whitney and Northrop (1988) could be three component mixed layers: high-charge beidellite, low-charge beidellite and illite layers. Such phases are unstable to temperature increase and produce quickly ordered illite-beidellite mixed layers.

The smectite composi-

tion in I/S series could explain the differences in activation energies and pre-exponential factors used in the different kinetic models. Indeed, the single step model is certainly more adapted to predict the reaction progress in short-time processes (Huang et al., 1993; Velde and Lanson, 1993). On the contrary, the two-step model (Velde and Vasseur, 1992) is adapted to predict the diagenetic illitization of montmorillonite as it is observed in sedimentary basins.

At present, it seems that two different ways exist for the smectite-to-illite conversion series: 1) a short time - high temperature process, in which a two-step reaction transforms first the dioctahedral smectites into a high-charge beidellite + saponite and, then, into beidellite/illite + chlorite mineral assemblages respectively.

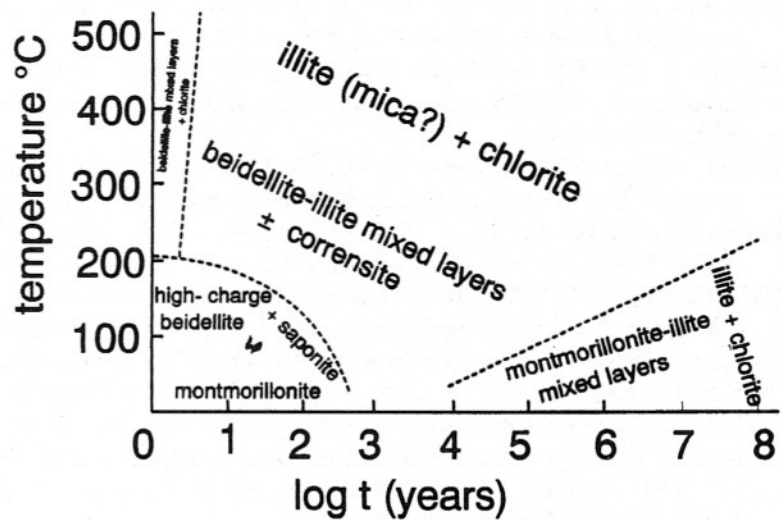
2) a long-time - low temperature process, which is also characterized by a two-step reaction process in which low-charge montmorillonite is first transformed into random montmorillonite/illite mixed layers and then into ordered ones. This reaction is controlled either by feldspar dissolution (Hower et al., 1976) or by mica dissolution (Boles and Franks, 1979).

This leads to a new question: what are the conditions required for the formation of montmorillonite? It is not exact to consider it as the stable low-temperature phase since most of smectites in soils or weathering profiles are beidellitic. The occurrences of the different clay minerals involved in experiments, geothermal fields, diagenesis and soils can be tentatively represented in the temperature ver-

sus time coordinates, as shown in Figure 11.

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**Figure 11** - Hypothetical representation of clay mineral domains in a temperature-time space. The remaining question is: what are the formation conditions of montmorillonite?

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