OCCURRENCE OF SMECTITES AND SMECTITE-RICH MIXED LAYERS AT HIGH TEMPERATURE WITHIN RESERVOIRS OF ACTIVE GEOTHERMAL FIELDS

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ABSTRACT

The < 0 2 µm clay fraction of samples coming from drill holes from the geothermal field at Milos (Greece) and from the geothermal field at Chipilapa (El Salvador) have been investigated by X-ray diffraction. The low permeability zones are characterized by the conversion of smectite to illite and to chlorite with increasing depth and temperature. The high permeability zones (present-day reservoirs) are characterized by the occurrence of smectites at high temperatures. These smectites are in isotopic equilibrium with the modern fluids. The precipitation of these « incompatible » clays at so high temperatures is related to boiling.

INTRODUCTION

Alteration assemblages in hydrothermal systems have received considerable attention during the last twenty years. From a prospecting point of view, petrological studies of fossil and active geothermal systems have tried to correlate the occurrence of newly formed minerals (calc-silicate minerals, feldspars, clay minerals etc.) with fluid temperature, fluid chemistry and permeability.

The occurrence of clay minerals and mixed-layer clays has been recognized as a powerful indicator, in particular, for geothermometry. Dioctahedral smectites transform to illite with increasing temperature through a series of mixed-layers illite/smectite (I/S) with the smectite ratio decreasing to 100% illite at about 230°C (Henley and Ellis, 1983). According to Henley and Ellis (1983). alteration to montmorillonite occurs at temperature lower than 120°C. Srodon and Eberl (1984) determined that the smectite to illite conversion is complete in the temperature range of approximately 50°-230°C. The trioctahedral clay sequence is characterized by the transformation of saponite to chlorite at temperatures higher than 190°-200°C through a series of mixed layers chlorite/smectite (C/S) (Kristmannsdottir, 1976 ; Browne, 1978 ; Seki et al., 1984). According to Bettison and Schiffman (1988). C/S are observed at temperatures lower than 200°-240°C. At higher temperatures, the saponite to chlorite transformation is complete Because swelling component transformations are essentially complete at temperatures close to 230°-240°C, illite + chlorite is the expected paragenesis at higher temperatures. In fact, the application of clay minerals to the study of hydrothermal systems is often complicated by the superimposition of clay parageneses which leads to incompatible assemblages. This phenomenon depends on the temporary evolution of the hydrothermal activity in different parts of a geothermal system.

In this study, we present a detailed characterization of the clay minerals sequences from the geothermal field at Milos (Greece) and from the geothermal field at Chipilapa (El Salvador). We have focused our investigation on the < 0.2 µm clay fraction. The vertical distribution of these clay minerals is discussed in order to point out the influence of host rock permeability and reaction kinetics on the present crystallization of clays in high-enthalpy geothermal systems. Furtermore, a study of stable isotopes (O) of these clays was undertaken in order to characterize the relationship between these clays and the geothermal fluids.

GEOLOGICAL CONSIDERATIONS.

Milos is one of the main volcanic centers of the Aegean volcanic arc. This arc, which presently extends from the Saronic Gulf in the west to Nissyros Island in the east, was formed during the Pliocene as a consequence of the northward subduction of the African plate beneath the Aegean plate (Smith, 1971). In 1975-76, two exploratory wells were drilled on the island of Milos. These wells proved the existence of a high-temperature geothermal reservoir. In 1980-81, three additional productive wells were drilled. The MI-1 well penetrates alluvial deposits (0-20 m depth), above a sequence of calcareous and volcanic rocks before encountering the metamorphic basement (60-1 180 m depth). These basement rocks have been metamorphosed to greenschist and locally blueschist facies. The reservoir is located below a depth of 900 m, and is hosted in the fractured metamorphic formations containing abundant micas (muscovite, biotite), chlorite and locally talc. Measured temperatures range from 130° to 320°C According to Liakopoulos (1987), the hydrothermal fluid in the reservoir consists of boiling sea water at temperature between 250° and 350°C.

Chipilapa is a geothermal field situated in western El Salvador (Central America). It is located on the eastern margin of the Ahuachapan geothermal field. Both fields lie in the northern foothills of the Plio-Quaternary Volcanic Chain that have formed at the margin of Central America in response to the subduction of the Cocos plate under the Caribbean Plate (Molnar and Sykes, 1969). Since 1989, four exploratory wells have been drilled (Ch-7. Ch-7b, Ch-8 and Ch-9). Well depths range from 1.3 to 2.6 km and maximum bottom hole temperatures reach 220°C in the deepest well Ch-8 (C.F.G., 1992). The rock penetrated in Ch-8 consist of interbedded lava flows and pyroclastic deposits of andesitic to dacitic composition and of Pliocene to Pleistocene age (C.F.G., 1992). Two permeable horizons were documented by circulation losses during drilling and temperature profiles (C.F.G., 1992). The first is characterized by the presence of a steam phase and is considered to be a "steam cap" The second zone is located between 1100 and 1400 m depth. This zone produces liquid water and has measured temperatures ranging from 180" to 210°C. Production tests were carried out after the drilling operations. Well Ch-7b is characterized bv the highest productivity, followed by well Ch-9 On the other hand, well Ch-7 has a very low productivity below 1000 m depth. Unfortunately, the 530-650 m depth interval which shows a prominent inflexion on temperatures profiles was covered by casing before the tests, and no data on its productivity was gained (C.F.G., 1992). No permeable horizons were observed in well Ch-8. Thus, the formations crossed by this drill hole are considered to be the parts of the geothermal system that are not affected by the present stage of hydrothermal activity At Chipilapa. the origin of the hydrothermal fluids consists of heated meteoric water.

Sampling.

Forty-eight samples were collected from three wells from the Milos geothermal area (MI-1 24 samples , MI-2 13 samples and MI-3 9 samples) Samples are only regularly distributed in well MI-1 where the sampling interval is about 50 m. Samples from MI-2 and MI-3 were all collected within reservoir zones

Eighty-two samples were collected from four wells from the Chipilapa geothermal area (Ch-7 36 samples , Ch-7b · 15 samples , Ch-8 11 samples and Ch-9 20 samples) Samples are only regularly distributed in well Ch-7b with a sampling interval of about 100 m in the upper part and 50 m in the lower part. Ch-7 well was sampled more densely between 500 and *650* m (5-20 m spacing) because of the presence of a permeable zone characterized by a large positive thermal anomaly on temperature profiles, which seems to indicate hot fluid inflow (T > 185°C)

METHODOLOGY

Depending on the amount of material available, 5 to 25 g of each sample were ground in an automatic scatterbox. The powder was then dispersed in distilled water by ultrasonic vibration. The clay fraction (less than about 0 2 pm) was extracted by continuous ultracentrifugation (Beckmann J2 21, rotor speed 5000 tr/min, flow rate 152 ml/min) The < 0 2 µm clay fraction was drawn through a millipore filter Oriented preparations were obtained by putting the filter on a glass slide This method produces preparations that have fair crystallite orientation and give accurate intensity (Bish and Reynolds. 1989)

X-ray diffraction was carried out on air dried and ethylene glycol saturated preparations using a Phillips PW 1730 diffractometer (Co K a radiation, 40 kV, 40 mA and Cu K a radiation, 40 kV, 30 mA) equipped with a stepping motor drive on the goniometer Aquisition parameters were obtained using a DACO MP numerical system. Clay minerals were identified according *to* the methodology of Brindley and Brown (1980) , Keynolds (1980, 1988) and Moore and Reynolds (1989). Identification was primarily based on the position of the basal spacings after saturation with ethylene glycol Distinction between dioctahedral and trioctahedral clay minerals has been made on the basis of the *(06-33)* reflection of randomly oriented powders Complex bands were decomposed according to the method developed by Lanson and Besson (1992) The ordering and the illitic and chloritic content of I/S and *C/S* were determined by theoretical calculations using the Newmod computer program (Reynolds, 1985)

Isotopic analyses of clay minerals were conducted following the conventional procedure of Clayton and Mayeda (1963). Isotopic ratios were determined with a Finnigan Mat 252 mass spectrometer anti expressed as δ values $\delta\ ^{18}O$ values are reported relative to the SMOW standard

RESULTS.

Nature and distribution of clay minerals

Table 1 summarizes the nature and the criteria *of* identification of the major clay minerals encountered at Milos and Chipilapa

Trioctahedral clay sequences (table 1a) were observed in both geothermal fields In both fields, saponite, corrensite, chlorite rich C/S and chlorite are present However, at Milos, the trioctahedral clay sequence is more complex with additional presence of talc, talcisaponite mixed-layers and an unidentified mixed-iayer phase Talc/saponite mixed-layers are characterized by a second order reflection at intermediate spacing values between the (002) reflection of smectite and the (001) reflection of talc (fig 1) In the studied samples, the saponite component predominates over the talc component Considering the very large width of this reflection. it seems reasonable to consider that it represents the sum of several types of randomly interstratified talcisaponite The unidentified clay mineral is characterized by a broad reflection near 12Å, which does not shift after ethylene glycol saturation It may be an interstratification of non-swelling clay minerals such as talc and chlorite (9 3Å/14Å)

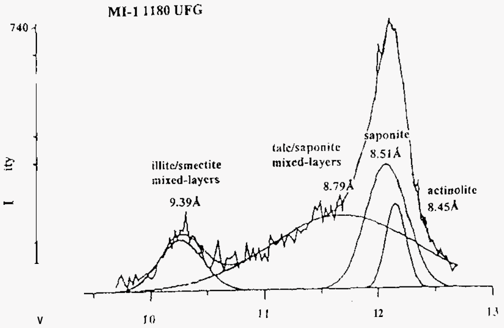


Fig 1 Decomposition of the X-ray diffraction pattern in the range 9 7-12.7°2Θ indicating the presence of talcisaponite mixcd-layers (MI-1 well, sample from 1180 m depth. after ethylene glycol saturation, Co Kα radiation)

The dioctahedral clay sequence (table 1b) is essentially observed at Chipilapa It is composed of dioctahedral smectites. rare smectite rich I/S R0, regularly ordered illite/smectite mixed-layers (I/S R1) containing 30-50% of smectite, illite/smectite mixed-layers (I/S R≥1) with a high illite content (> 85%) and illite

In addition to these clay minerals, actinolite has heen observed in

Tab 1a Trioctahedral clay sequence

Clay minerals	Criteria of identification	Found at :
Trioctahedral smectite (saponite)	17, 8.6, 5.6Å (E.G.) (06-33) reflection at 1.53Å	Milos and Chipilapa
Corrensite	31, 15.5, 7.75, 5.19, 4.46, 3.45Å (E.G.)	Milos and Chipilapa
Chlorite-rich chlorite/smectite mixed-layers (C/S)	14.7Å (E.G.)	Milos and Chipilapa
Chlorite	14.2, 7.1, 4.74, 3.53Å (A.D. and E.G.)	Milos and Chipilapa
Talc	9.38, 4.6Å (A.D. and E.G.)	Milos

Tab 1b Dioctahedral clay sequence

Clay minerals	Criteria of identification	Found at :
Dioctahedral smectite (beidellite or montmorillonite)	basal spacings similar to those of saponite , distinction on the basis of (06-33) reflection close to 1 50Å	Chipilapa
Regularly ordered illite/smectite mixed-layers (I/S R1, 30-50% smectite)	27-29, 13 5. 9-9 3, 6 7, 5 3, 4 5, 3 33Å (E G)	Chipilapa
Ordered illiteismectite mixed-layers (I/S R≥1, >85% illite)	asvmmetrical reflection at about 10Å, other peaks at 5, 3 34Å (E G)	Chipilapa
Illite	symmetrical **peak** at 10Å, 5, 3.34Å (A.D and E.G.)	Chipilapa

Table1 Nature and criteria of identification of clay minerals encountered at Milos and at Chipilapa (A.D · air-dried sample. E G sample after ethylene glycol saturation)

the geothermal field at Milos ; hematite is abundant and kaolinite has been locally observed in the upper permeable zone at Chipilapa.

The vertical distribution of the clay minerals (< 0.2 µm fraction) in MI-I well of Milos is reported on figure 2. With increasing depth and temperature, the trioctahedral clay sequence saponite - corrensite + saponite - 12Å mixed-layer + chlorite ± saponite - chlorite was established within the poorly permeable part of the field Saponite and talcisaponite mixed-layers coexist with talc and actinolite at depth below 900 m and temperatures higher than 300°C in the reservoir of the geothermal field at Milos.

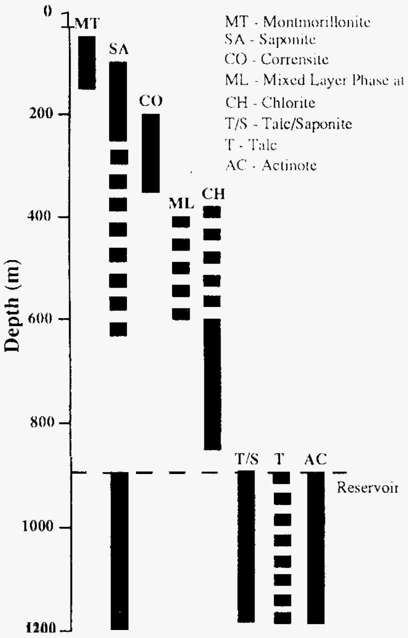


Fig 2 Distribution of clay minerals with increasing depth in MI-1 well of Milos

The vertical distribution of the clay minerals in wells Ch-7, Ch-7b, Ch-8 and Ch-9 of Chipilapa is reported on figure 3a,b with temperature profiles after thermal reequilibration

In the well Ch-8, the alteration sequence observed with increasing depth and temperature can be considered as typical The successive appearence of smectite, I/S RI, I/S R $\leq$ 1 is characteristic of the transformation from dioctahedral smectite to illite In the same way, the successive appearence of smectite, corrensite, C/S and finally chlorite is consistent with the commonly observed transformation from trioctahedral smectite to chlorite

In the well Ch-7. the clay mineral distribution shows a general decrease in smectite content of both C/S and I/S mixed-layers with increasing depth and temperature. similar to those observed in Ch-8 except between 530 and 670 m depth. where smectites crystallized in abundance in place of illite-rich and chlorite-rich mixed-layers Dioctahedral and trioctahedral smectites represent the main clay phase found at 540, 580 and 606 m depth (fig 4) and are accompanied by abundant hematite and minor kaolinite Smectites appear closely correlated to the sharp increase in the temperature profile, which is indicative of active circulation of hot fluids (steam cap)

In the well Ch-9, the clay mineral distribution also shows a general decrease in the smectite content of the mixed layer clays with increasing depth and temperature The most striking feature is the persistence of minor quantities of dioctahedral or trioctahedral smectites down to 1200 m depth where the top of reservoir is located

The clay mineral distribution observed in Ch-7b appears more complex that those observed in Ch-7 and Ch-9 'The general trend is one of decreasing smectite content in the mixed-layer clays with increasing depth and temperature, but smectites as a distinct clay phase are present troughout in the drill hole They represent the main clay phase found at 1090 and 1123 m depth, where the second permeable horizon is located. Another noteworthy feature is the concomittant precipitation of three illite/smectite mixed-layer clays with different smectite contents between 700 and 1123 m depth

Clay mineral distributions in the four wells at Chipilapa reveal several interesting results The non-permeable parts of the geothermal field are characterized by I/S and C/S conversion series This is well expressed in Ch-7 and Ch-8 The two permeable

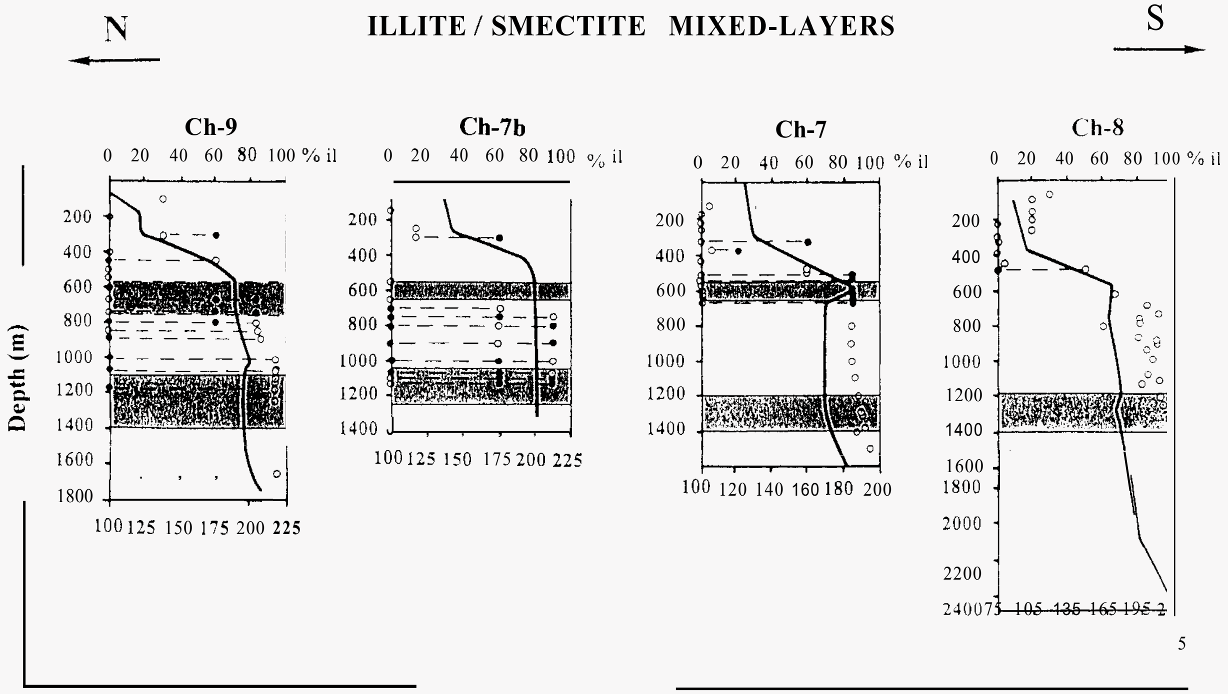
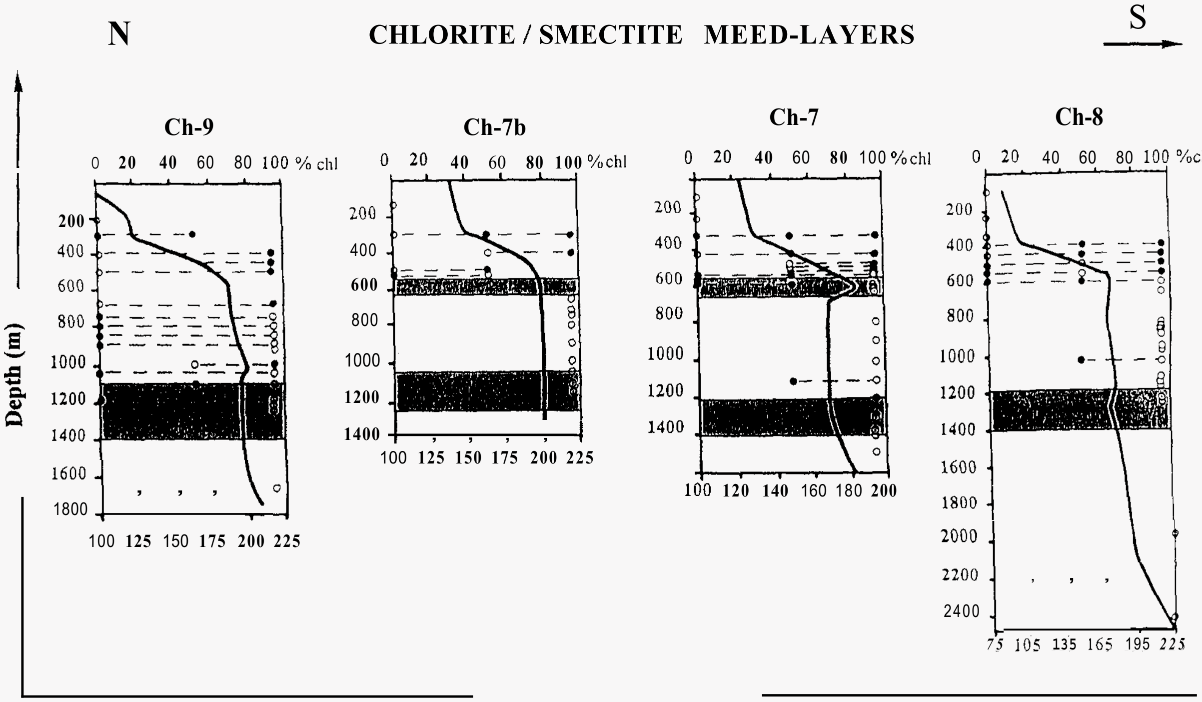


Fig. 3a Variation of the percentage of illite layers (% il) in illite/smectite (I/S) as a function of depth in the four wells from Chipilapa Continuous line represents measured temperatures after thermal reequilibration of the drill hole The dotted line shows the composition of coexisting illite/smectite mixed-layer clays in the same sample Circles and dots indicate the percentage of illite layers of the dominant and minor coexisting illite/smectite phases respectively The shadowed zones at Ch-9. Ch-7b. Ch-7 drill holes represents the present-day reservoirs.



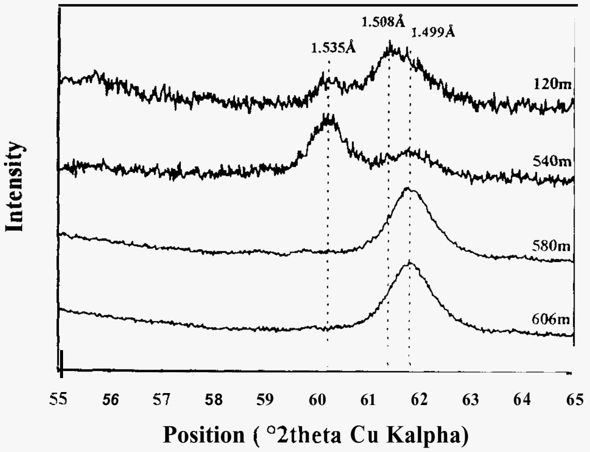


Fig 4 Distinction of dioctahedral and trioctahedral smectites on the basis of the position of their *(06-33)* reflection observed near the surface (at 120 m depth) and within the upper permeable zone (at 540, 580. *606* m depth respectively, Ch-7 dril hole).

horizons defined during drilling are characterized by the presence of smectites in addition to illite/smectite and chlorite/smectite mixed-layers clays Therefore, variations in permeability may be more important than slightly different temperature conditions prevailing within these exploratory wells in controlling the occurence of smectites

Isotope data.

Ten samples from Ch-7 were selected for oxygen isotope studies. Each sample contains an illite/smectite mixed-layer phase with a different smectite content (tab 2) The sample from 606 m depth contains smectite formed within the upper permeable zone

Measured $\delta^{18}O$ values of clays are presented in table 2. They range from 7.4 to 1.4 ‰ and show a progressive decrease with depth, with the exception of samples from *606* and 1404 m (fig. 5). The sample from 553 m displays a higher $\delta^{18}O$ values because of the presence of smectite with an illite/smectite mixed layer containing 80% illite

Sample	% illite	$\delta^{18}O$	Temp. (°C)	$\delta^{18}O_{fluid}$
173	20	7.4	114	-5.38
325	65	4.2	128	-6.89
480	65	4.2	150	-5.34
553	80	3.8	175	-4.11
606	10	8.5	183	0.37
803	85	1.9	170	-6.23
1203	90	2	170	-6.09
1301	93	1.4	172	-6.55
1404	90	5.7	180	-1.85
1500	95	1.4	180	-6.1

Table 2 Selected samples for oxygen isotope studies presented in function of depth (m), the percentage of illite layers and measured temperatures after reequilibration

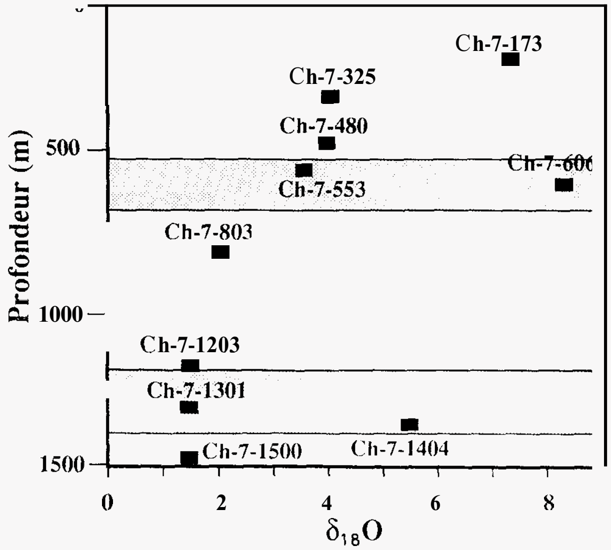


Fig 5 Distribution of $\delta^{18}O$ values of clay minerals with depth *in* Ch-7 drill hole The shadowed areas represent the permeables zones

On the basis of the following equation we have calculated the 6 ^{18}O value of the fluid in isotopic equilibrium with these clays under the present temperature conditions

$$\delta\,^{18}O_{ill/sm} - \delta\,^{18}O_{fluid} = -4.19 + (2.58 - 0.19i)\,10^6 / T^2$$

(Savin and Lee, 1988)

T measured temperature alter well reequilibration ,
i percentage of illite in illite/smectite mixed-layers

The data suggest that two types of geothermal fluids are present the samples from 606 and 1404 m, from the two permeable horizons, are in isotopic equilibrium with a fluid of δ^{18}O values ranging from -1 85 to 0 37 ‰ whereas the other samples, coining from non-permeable zones, are in isotopic equilibrium with a fluid whose δ^{18}O values is -6 ± 0 8 ‰ The δ^{18}O values of the present reservoir fluids at Chipilapa is -4 ‰ Higher δ^{18}O values ranging from -2 to 0 ‰ are encountered within the zones characterized by boiling The results of the calculations presented above compared with the δ^{18}O values of the reservoir fluids indicate that the smectite found within the permeables zones are in isotopic equilibrium with the modern geothermal fluids This is in agreement with the recent crystallisation of this smectite at 606 m depth This is confirmed by their small size and their poor crystallinity, compared to smectites observed near the surface

In contrast, clays from non-permeable zones appear to have preserved their original isotopic composition acquired during their crystallisation and are out of isotopic equilibrium with the present-day geothermal fluids

DISCUSSION.

These clay sequences have been described in fossils and active geothermal systems (Muffler and White, 1969, Browne and Ellis, 1970, Kristmansdottir, 1976, Elders and al.,1979; Inoue and Utada, 1983. Liou et al., 1985. Inoue, 1987. Inoue et al., 1992, among others) Much less classical is the association of clay minerals which appears in the permeable zones. The association of actinolite with saponite. mixed-layers talc/saponite and eventually talc observed in the reservoir at Milos at temperatures higher than 300°C is difficult to explain in terms of thermodynamic equilibrium. While actinolite and talc are common minerals at such thermal conditions in natural systems, saponite and mixed-layers talc/saponite generally are believed to form at much lower temperature (Reynolds, 1988). In the same way, the association of mixed-layers illite/smectite containg more than 80% illite with smectite and eventually regularly ordered mixed-layer illite/smectite, observed in the reservoir at Chipilapa, is not expected at such high temperatures (185°-210°C).

Crystallization of smectites at high temperatures has been already observed in other active geothermal fields including the Phillipines (Reyes, 1990), the Djibouti (Zan et al., 1990), the Valles caldera (Wolde-Gabriel and Goff, 1992) the Japan (Inoue et al., 1992) These occurences are interpreted as products of a dissolution-precipitation process affecting the drilling mud (Reyes and Cardile, 1989) or as relict minerals of a diagenetic origin (Hulen and Nielsen. 1986). Inoue et al (1992) have suggested smectite is a metastable phase which persists when illitization proceeds abruptly at high temperatures Saponite has been hydrothermally synthetized at temperatures as high as 850°C (Iiyama and Roy, 1963). Its hydrothermal reactivity has been experimentally investigated by Whitney (1979) This author demonstrated that the reactivity of saponite greatly increased with increasing temperature and that at a temperature of 400°C, saponite is not stable for more than 200 days Thereafter. it transformed into various mixed-layer clays The assemblage talc/saponite, talc and actinolite observed at temperatures higher than 300°C at Milos includes all the minerals experimentally synthetised by the hydrothermal transformation of saponite All these considerations lead us to interpret the occurrence of saponite, mixed-layer talcisaponite, talc and actinolite in the reservoir as the result of a continuous mineralogical transformation that is still in progress If this is true. saponite and mixed-layers talcisaponite represent metastable phases that are very young and are probably still forming Figure 6 presents the distribution of "anomalous smectite occurences" along Ch-7. Ch-7b and Ch-9 drill holes The Occurrence of these phases coincides mainly with the upper permeable zone which corresponds to a steam cap However, smectites also occur more erratically within the lower permeable zone which is a liquid dominant reservoir

The presence of abundant smectites in the reservoirs subjected to boiling still requires explanation It is well known that mineral precipitation in geothermal fields is closely associated with boiling because of rapid sursaturation of the liquid phase associated to steam As noted above smectites in the upper permeable zone of Ch7 are in isotopic equilibrium with fluids enriched in ^{18}O because of boiling Thus. it is possible that smectite precipitation may also occur at high temperatures where boiling takes place Furthermore, the presence of kaolinite and hematite with smectites in the < 0 2 µm fraction of samples from the upper permeable zone is consistent with the occurence of boiling at these levels These minerals are typical of high fO_2 and low pH conditions which are well known to be enhanced in environment of boiling waters The presence of regularly ordered illite/smectite mixed-layer clays with smectite within the interval between 600 and 1200 m depth in Ch-7b indicates that the interstratification of smectite with illite is under way Considering that the smectite to illite conversion is controlled by kinetic factors (e g. time, temperature) this assemblage suggests that this zone which is presently poorly permeable was probably permeable and up to a very recent period

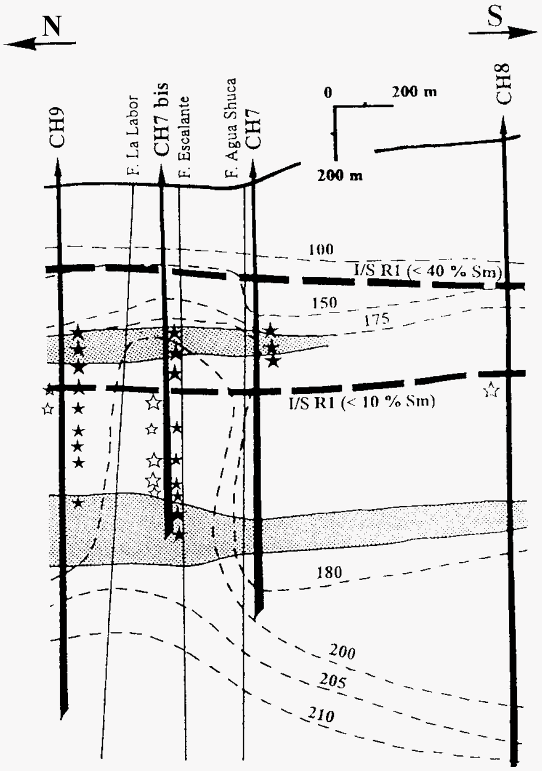


Fig 6 Distribution of isotherms (in °C) and permeables zones (shadowed zones) at Chipilapa geothermal field (C F G . 1992). A « thermal anomaly » is centered around the Escalante fault, whereas La Labor and Agua Shuca faults define the limits of the geothermal area.

Presentation of « anomalous smectite and regularly ordered illite/smectite mixed-layers (I/S R1) occurences » with depth solid star smectite , empty star I/S R1 , the large star .represents the dominant phase in the sample

I/S R1 (< 40 % Sm) first occurrence of regularly ordered illiteismectite mixed-layer? and I/S R1 (< 10 % Sm) first occurrence of ordered illiteismectite mixed-layers of the smectite to illite conversion sequence

CONCLUSIONS.

The study of the < 0.2 µm clay fraction may be considered as a powerful tool for understanding the present hydrodynamic and thermodynamic conditions of geothermal systems At Milos and at Chipilapa, the alteration mineralogy of the permeable zones associated with boiling differs from those. of the overlying low permeability rock formations by the presence of clay phases which are generally incompatible with the mesured temperatures (300°C at Milos. 185°-210°C at Chipilapa) These high-temperature smectites may be considered as very young metastable phases representing the first step of an ongoing conversion series towards illite and/or chlorite which are kinetically controlled (temperature and time) It is important to note that such phenomena are restricted to the levels in which the present hydrodynamic conditions favour a high degree of reactivity and the crystallisation process strong sursaturation of fluids and high nucleation rates of solid phases The occurrence of high temperature smectites in the < 0 2 µm clay fraction may be of great interest in determining zones of high fracture permeability; and particularly those were boiling presently occurs The nature of the coexisting clay phases are also useful for distinguishing between well-established and newly-formed geothermal reservoirs

REFERENCES.

Bettison L **A** and Schiffman P (1988) Compositional and structural variation of phyllosilicates from the Point Sal ophiolite, California *American Mineralogist*, 73, 62-76

Bish D L and Reynolds R C J (1989) Sample preparation for X-ray diffraction *Reviews in Mineralogy*, 20, 73-100

Brindley G W and Brown G (1980) Crystal structure of clay minerals an their X-ray identification *Brindley G.W. and Brown G., eds, Mineralogical Society, London*, 495p.

Browne P R L and Ellis A.J. (1970) : The Ohaki-Broadlands hydrothermal area, New Zealand Mineralogy and related geochemistry *American Journal of Science*, 269. 97-131

Browne P R L (1978) Hydrothermal alteration in active geothermal fields. *Ann. Rev. of Earth Planetary Science*, 6, 229-250

C.F G Report (1992) Proyecto desarrollo acelerado del campo geothermico de Chipilapa Contrato CEL-1684 Etapa 1: Estudios geoscientificos Informe de evaluation de la informacion existente *Rapport 92 CFG 10*

Clayton R N and Mayeda T K (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis *Geochim. Cosmochim. Acta*, 27. 43-52

Elders W **A**, Hoagland I R., MacDowell S D and Corbo J M (1979) Hydrothermal mineral zones in the geothermal reservoir of Cerro Prieto, Mexico *Geothermics*, 8, 201-209

Henley R W and Ellis **A** J (1983) · Geothermal systems ancient and modern a geochemical review *Earth Science Reviews*, 19, 1-SO

Hulen J B and Nielsen D L (1986) Hydrothermal alteration in the Baca geothermal system. Redondo dome. Valles caldera, New Mexico *Journal of Geophysical Research*, 91, B2, 1867-I886

Iiyama J T and Roy R (1963) Unusually stable saponite in the system Na2O-MgO-AL2O3-SiO2 *Clay Minerals Bulletin*, 5, 29, 161-171

Inoue A and Utada M (1983) Futher investigations of a conversion of dioctahedral mica/smectites in the Shinzan hydrothermal alteration area, Northeast Japan *Clays and Clay Minerals*, 31, 6, 401-4I2

Inoue A (1987) Conversion of smectite to chlorite by hydrothermal and diagenetic alterations, Hokuroko Koroko mineralisation area. Northeast Japan *Proc. International Clay Conference, Denver*, 1985, L G Schultz, €3 van Olphen and F **A** Mumpton. eds , The Clay Minerals Society, Bloomington. Indiana, 158-164

Inoue **A**, Utada M and Wakita K (1992). Smectite-to-illite conversion in natural hydrothermal systems *Applied Clay Science*, 7, 131-145

Kristmannsdottir H (1976) Types of clay minerals in hydrothermally altered basaltic rocks, Ryekjanes, Iceland. *Jokull*, 26. 30-39

Lanson B and Besson G (1992) Characterization of the end of smectite-to-illite transformation. decomposition of X-ray patterns *Clays and clay minerals*, 40, 40-52

Liakopoulos A (1987) Hydrothermalisme et mineralisations métallifères de lile de Milos (Cyclades, Grece) *Thèsis Univ. Paris-VI*, 279p

Liou J G., Seki Y., Guillemette R N and Sakai H (1985) Compositions and parageneses of secondary minerals in the Onikobe geothcrmal system, Japan *Chemical Geology* 49, 1-2n

Molnar P and Sykes L R. (1969) Tectonics of the Carribean and Middle America regions from focal mecanism and seismicity *Geological Society of America Bulletin*, 80, 1639-1684

Moore D.C. and Reynolds R C (1989). X-ray diffraction and identification of clay minerals *Oxford University Press, Oxford*, 332p.

Muffler P and White D E (1969) Active metamorphism of upper Cenozoic sediments in the Salton Sea geothermal field and the Salton Through. Souteastern California *Geological Society of America Bulletin*, 80, 157-182

Reyes **A** and Cardile C.M. (1989) Characterization of clay scales forming in Phillipine geothermal wells *Geothermics*, 3, 429-446

Reyes **A** (1990) Petrology of Phillipine geothermal systems and the application of alteration mineralogy to their assessment *Journal of Volcanology and Geothermal Research*, 43, 279-309

Reynolds R C J (1980): Interstratified clay minerals *Crystal structure of clay minerals an their X-ray identification. Brindley G.W. and Brown G., eds, Mineralogical Society, London*, Ch 4. 249-274

Reynolds R C J (1985) NEWMOD a computer program for the calculation of one-dimensional diffraction patterns of mixed-lavered clays *R.C. Reynolds, 8 Brook Rd., Hanover, New Hampshire 03755, U.S.A.*

Reynolds R C J (1988) Mixed layer chlorite minerals In « *Reviews in Mineralogy* », 19, 601-630.

Savin S M. and Lee M (1988) Isotopic studies of phyllosilicates In « *Reviews in Mineralogy* », 19. 189-223

Seki Y , Liou J., Guillemette R , **Sakai** H , Oki Y , Hirano T and Onuki H (1984). Investigation of geothermal systems in Iapan. I, Onikobe geothermal area *Mem.* 6, 206p , Hydrosci and Geotech Lab, Saitama Univ , Urawa, Japan

Smith **A** G (1971) Alpine deformation and Orogenic areas of the tethys. Mediterranean and Atlintic *Geol. Soc. Amer. Bull.*, 82. 2039-2070

Srodon J and Eberl D (1984) Illite *Micas, Reviews in Mineralogy, S.W. Bailey Ed*, 13, 495-544

Whitney G (1979) The paragenesi of synthetic phyllosilicates on the talc-phlogopite join *Thesis*, Uni of Illinois, 162p

WorldGabriel G and Goff F (1 992) K/Ar dates of hydrothermal clays from core hole VC-2B, Valles Caldera. New Mexico and their relation to alteration in a large hydrothermal system *Journal of Volcanology and Geothermal Research*, 50, 207-230

Zan L . Gianelli G , Passerini P , Troisi C and Hagas **A O** (1990) Geothermal exploration in the Republic of Djibouti Thermal and geological data of Hanlé and Asal areas *Geothermics*, 19, 6, 561-582

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