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**Stability fields of smectites and
illities as a function of temperature
and chemical composition**

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ABSTRACT

Besides arguments which suggest that clay minerals are metastable phases at the surface of the Earth, there are also indications that the chemical compositions of smectites and illites somewhat reflect the temperatures at which they form and the different chemical environments in which they may approximately equilibrate. Thus the thermodynamic properties of clay minerals must be further explored.

Almost all the standard XRD-determined pure clay phases, in fact, appear to be mixtures of particles of highly dispersed chemical compositions. Furthermore, within an apparent monomineralic population of particles, chemical variables are intercorrelated in such a way that correlations clearly reflect the temperatures at which these populations are supposed to have been formed. The $(\text{Fe}^{3+})_{\text{VI}}$ -content in octahedral position is positively correlated with the tetrahedral charge (glaucanites) at low temperature and with the octahedral charge (celadonite) at high temperature. The $(\text{Al}^{3+})_{\text{VI}}$ -content is negatively correlated with the tetrahedral charge at low temperatures (montmorillonite) and positively correlated to the tetrahedral charge (illite) at higher temperatures. The $(\text{Mg}^{2+})_{\text{VI}}$ -content is negatively correlated with the tetrahedral charge (stevensite) at low temperature, while it is positively correlated to the tetrahedral charge at high temperature (saponite).

A thermodynamic ideal solid solution analogue is proposed which accounts for such correlations. The solid solution is considered, at a particle scale, as an ideal mixture of individual layers, weakly bent each to the next. Each layer presents the chemical composition of a given end member, so that the proportions of the different end members change from one particle to another. Because the solid solution theory requires that several ideal solid solutions cannot be in equilibrium in the same environment, one must consider that each particle and its surrounding solutions forms an independent microsystem.

Considering one particle of a given chemical composition, the multipole solid solution theory allows to calculate the weighted contributions of each end member into the ideal clay solid solution along with the chemical composition of the aqueous solutions in equilibrium with the considered particle in its independent microenvironment.

This model is able to predict the nature of the chemical correlations which are expected, at a given temperature, within a given population. This model is also applied to the prediction of the temperature required for the conversion of smectite into illite during the burial diagenesis.

INTRODUCTION

In the last few years, a large number of works have been devoted to clay mineral geochemistry and to clay stability fields in natural conditions. Our knowledge has been considerably improved by additional natural observations, mineralogical data, crystallographic measurements and conceptual models.

Among the different families of clay minerals, smectites and illites have received particular attention, probably because, apart from chlorites, they offer a large variety of compositions, and they cover, in nature, a large range of stability fields. In fact, at and near the surface of the Earth, they form or survive over a wide range of temperature, pressure and solution concentration conditions. Smectites and illites are particularly interesting in the scope of the clay mineral geochemistry.

Furthermore, clay minerals are now introduced in computer models which simulate the mass transfers occurring in nature (Fritz, 1975, 1981, 1985). These computations are based on thermodynamic equilibria between a large number of chemical variables : simple and complex aqueous species, solid solutions and minerals of complex chemical compositions, so that mass transfer simulations are now supposed to work not only as idealized but also as realistic models. This paper is an attempt to analyze the difficulties and the possibilities to treat clay minerals as phases in thermodynamic equilibrium in their environment and to be able to interpret their chemical composition as indicator of salinities and temperatures of solutions in which they may form or equilibrate.

1. DIFFICULTIES OF DEFINING CLAY MINERAL STABILITIES

The abundance and the diversity of smectites and illites at the surface of the Earth suggest that these clay minerals can reflect differences among the chemical conditions in which they form and can exert control on their chemical environments. However, as perfectly pointed out by May *et al.* (1986) all of the experimentally determined solubilities or stabilities appear uncertain due to complications arising in part from the experimental techniques employed and in part from the nature of the minerals. Furthermore, both the accuracy of the selected free energy values and the validity of assumptions involved in their use are suspect in many instances for both technical and theoretical reasons. If gibbsite and kaolinite are simple and nearly ideal minerals, smectites appear on the other hand to be very complex with regard to their stability field evaluation. The difficulties come from several reasons : (i) variations in mineral crystallinity (May *et al.*, 1979b ; Tsuzuki and Kawabe, 1983), (ii) variations in particle size (Bassett *et al.*, 1979), (iii) uncertainty about mineral purity which may skew both the dissolution chemistry and the formula determination and (iv) compositional heterogeneity of the minerals themselves.

A second problem, which unfortunately cannot be entirely solved before the first questions will be completely answered, concerns the possibility for smectites, illites or interstratified minerals to survive as metastable phases in weathering profiles or in sedimentary columns. Lippmann (1977, 1979a, 1979b, 1982) developed several arguments which suggest that "only metastable systems are capable of carrying information. By virtue of their metastability, clay minerals are useful as stratigraphic markers, as indicators of diagenesis as distinct from metamorphism. If silicates would readily equilibrate at ordinary temperature, neither soils nor clays would exist and Earth would be covered by a shell of barren rocks to be classified near the greenschist facies" (Lippmann, 1982, p. 485).

It is clear that the metamorphic minerals such as muscovite, pyrophyllite or dickite have true stability fields in stability diagrams, although they do not readily form at 25°C (Lippmann, 1982). However, it would be very useful to be able to predict the domains of formation of clay minerals as function of their chemical composition, assumed to be exactly known.

If direct solubility measurements, and the concept of clay minerals as single phases, fail as the base of the prediction of their stability fields (May *et al.*, 1986), we must search for a new approach, based on the thermodynamics of metastable phases applied to inhomogeneous systems, and able to reproduce the large variety of mineral associations, observed in natural environments and persisting during a relatively short period of geological time.

2. THE STABILITY FIELD OF SMECTITES

Three important steps have marked the progressive recognition of the great variety of smectite stability fields in nature.

2.1. The aluminous montmorillonite

In the 1950's, soil scientists first clearly described the mineral succession : gibbsite-kaolinite-montmorillonite, in soils, as function of climate, topography and nature of the parent rock (Jackson *et al.*, 1948 ; Leneuf, 1959 ; Millot, 1964 ; Barshad, 1966). Gibbsite appears in leached conditions in the upper parts of the profiles, in the topographic highs and under humid tropical climates, when the percolating solutions are diluted. Montmorillonite appears in confined conditions, in the lower parts of the profiles, downstream in landscapes and under semi-arid climates, when the percolating solutions are concentrated by evaporation or by a long advance through the weathering zone.

At the same time, thermodynamic models and calculations based on natural observations or experiments in laboratory were undertaken. The first works are probably those of Garrels (1957), Linn (1959) and Hemley (1959) cited by Garrels and Christ (1965). They were followed by those of Wollast (1961, 1963), Hemley *et al.* (1961), Frink and Peech (1962), Orville (1963), Helgeson (1964), de Keyser (1964), Feth *et al.* (1964), Kittrick (1966, 1969), Kramer (1968) and Tardy (1969).

In weathering profiles, gibbsite, kaolinite and montmorillonite may form successively from humid to semi arid tropical climates. The solubility products and equilibrium reactions concerning the aluminous minerals are written in Table 1.

The kaolinite-gibbsite boundary is defined by :

$$\log [\text{SiO}_2] - 0.5 \log [\text{H}_2\text{O}] = - 4.5$$

The smectite-kaolinite boundary is defined for an idealized smectite stoichiometry by the following equation :

$$0.57 \log [\text{SiO}_2] + 0.071 \log [\text{Ca}^{2+}] / [\text{H}^+]^2 + 2.167 \log [\text{H}_2\text{O}] = - 1.042$$

The equilibrium diagrams of Fig. 1 shows clearly that gibbsite is stable in dilute and acid waters, while montmorillonite or beidellite is stable in more concentrated solutions of higher pH and higher soluble silica activities. Waters collected in different temperate or tropical regions are positioned as function of $\log [\text{Na}^+] / [\text{H}^+]$, $\log [\text{Ca}^{2+}] / [\text{H}^+]^2$ and $\log [\text{SiO}_2]$. Concentrated waters from arid countries fall in the montmorillonitic domain. Diluted waters collected in humid areas fall in the domain of kaolinite, close to the gibbsite boundary (Tardy, 1971).

At that stage of investigation, it has been clearly recognized that montmorillonite is more "soluble" than kaolinite, i.e. forms in solutions of higher pH and characterized by higher concentrations of cations and silica. However, the systems studied were supposed to be exclusively aluminous and the influence of smectite compositions on their stability fields was, at that moment, not yet very well discerned.

2.2. The four major smectite stages of weathering and sedimentation : nontronite, beidellite, montmorillonite and stevensite

In sediments, a clear distinction between the aluminous montmorillonite and the magnesian stevensite was quite early recognized (Millot, 1949 ; Millot *et al.*, 1960 ; Grim and Kulbicki, 1961 ; Millot, 1964 ; Bradley and Fahey, 1962).

The distribution of smectites in sedimentary environments was extensively examined by Huertas *et al.* (1970). Later on, Trauth (1977) studied in detail the sediments of the Paris Basin and clearly showed that the chemical composition of smectites changes progressively from paleosoils and moderately leached continental material to marine evaporites deposited in confined areas. A comprehensive sequence was established (Table 2). The chemical composition of the most frequent and widespread smectite, found in the continental deposits and in the detrital fraction of the coastal marine sediments, is close to that of the soil ferri-beidellite described by Paquet (1970).

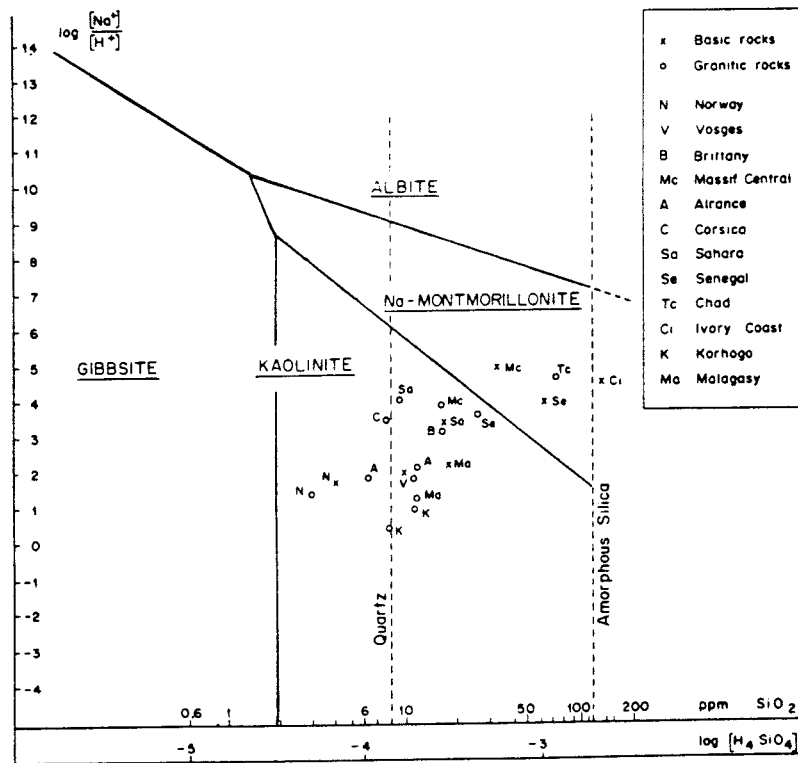
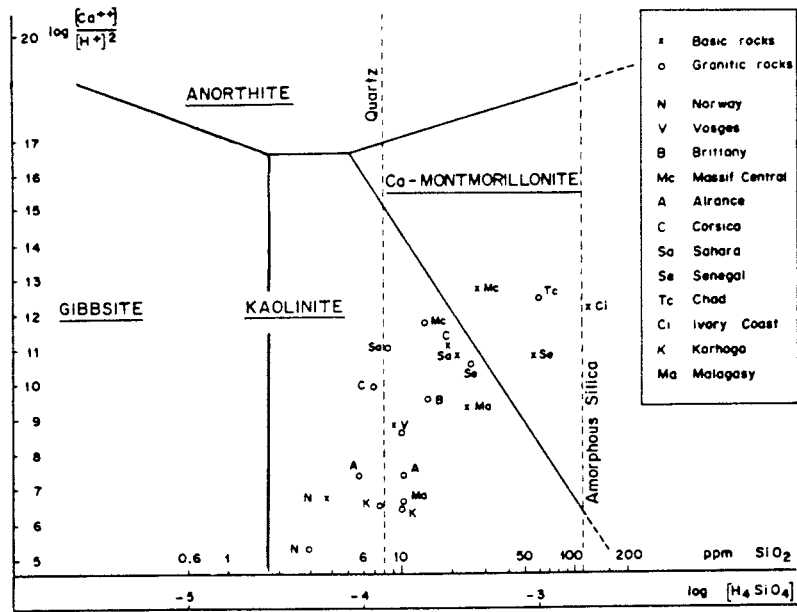
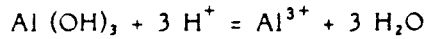


Figure 1. Stability field diagram of gibbsite, kaolinite and montmorillonite and position of drainage waters collected in different climatic environments (Tardy, 1971) (solubility data at 25°C)

Furthermore, in most of the facies deposited near the shorelines, the continental influence is marked by the formation of an aluminous Wyoming-type montmorillonite while in the evaporitic facies stevensite and sepiolite are predominant. In the intermediate stages, smectites are progressively enriched in magnesium and depleted in aluminium and iron. The bulk structural formulas indicate compositions somewhat in the middle between dioctahedral and trioctahedral minerals and also

TABLE 1- Equilibrium reactions and solubility product constants for gibbsite, kaolinite and an idealized Ca-beidellite, at 25°C (Fritz and Tardy, 1973; Droubi *et al.*, 1976)

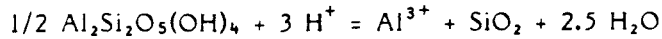
Gibbsite :



$$\text{with : } \log [\text{Al}^{3+}] / [\text{H}^+]^3 + 3 \log [\text{H}_2\text{O}]$$

$$= \log K_{\text{sp}} = 8.205$$

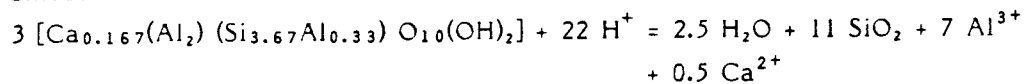
Kaolinite :



$$\text{with : } \log [\text{Al}^{3+}] / [\text{H}^+]^3 + \log [\text{SiO}_2] + 2.5 \log [\text{H}_2\text{O}]$$

$$= \log K_{\text{sp}} = 3.205$$

Smectite :



$$\text{with : } 7 \log [\text{Al}^{3+}] / [\text{H}^+]^3 + 11 \log [\text{SiO}_2] + 0.5 \log [\text{Ca}^{2+}] / [\text{H}^+]^2 + 14 \log [\text{H}_2\text{O}]$$

$$= \log K_{\text{sp}} = 18.60$$

$$\text{or : } \log [\text{Al}^{3+}] / [\text{H}^+]^3 + 1.57 \log [\text{SiO}_2] + 0.071 \log [\text{Ca}^{2+}] / [\text{H}^+]^2 + 4.667 \log [\text{H}_2\text{O}]$$

$$= \log K_{\text{sp}} = 2.66$$

Symbol [] designates activity of aqueous species in solution

TABLE 2- Smectite sequence from detrital to evaporitic sediments. Structural formulas and octahedral occupancies (Trauth, 1977)

Beidellite	: $\text{Ca}_{0.133} (\text{Al}_{1.327}\text{Fe}^{3+}_{0.5}\text{Mg}_{0.26}) (\text{Al}_{0.267}\text{Si}_{3.733}) \text{O}_{10}(\text{OH})_2$	2.09
Smectite Wyoming	: $\text{Ca}_{0.06} \text{K}_{0.5} (\text{Al}_{1.44}\text{Fe}^{3+}_{0.30}\text{Mg}_{0.30}) (\text{Si}_4) \text{O}_{10}(\text{OH})_2$	2.04
Smectite Cheto	: $\text{Ca}_{0.12} \text{K}_{0.16} (\text{Al}_{1.18}\text{Fe}^{3+}_{0.24}\text{Mg}_{0.60}) (\text{Si}_4) \text{O}_{10}(\text{OH})_2$	2.02
Saponite	: $\text{Ca}_{0.12} \text{K}_{0.13} (\text{Al}_{0.80}\text{Fe}^{3+}_{0.24}\text{Mg}_{1.35}) (\text{Al}_{0.21}\text{Si}_{3.79}) \text{O}_{10}(\text{OH})_2$	2.39
Stevensite	: $\text{Ca}_{0.08} \text{Na}_{0.08} \text{K}_{0.16} (\text{Al}_{0.21}\text{Fe}^{3+}_{0.07}\text{Mg}_{2.40}) (\text{Si}_4) \text{O}_{10}(\text{OH})_2$	2.68

indicate some important tetrahedral substitutions which may localize these smectites within the group of saponites.

Similar sequences were described in some weathering profiles and in the Lake Chad sediments. In weathering profiles located on basic and ultramafic rocks, Wildman *et al.*, 1968, 1971) have already remarked that nontronite appears in dilute environments and stevensite or saponite in more concentrated ones.

The Lake Chad system was extensively studied by Carmouze (1976), Lemoalle and Dupont (1973), Gac (1980), Gac and Tardy (1980). It was demonstrated that the

nature and the composition of the smectites, formed in the lake sediments, change from nontronite to beidellite or montmorillonite and to stevensite, when waters are progressively concentrated by evaporation (Table 3). Nontronite is formed within the ferruginous oolites (Carmouze *et al.*, 1977; Pedro *et al.*, 1978) and in the very dilute waters of the Chari river delta. Beidellite and montmorillonite were found stable together with calcite in the moderately concentrated waters of the northern part of the lake. Stevensite is formed in the sodium carbonate brines of the salines of Kanem.

TABLE 3- Chemical composition (millimoles/kg H₂O) of waters of the Lake Chad system (GAC, 1980). The most stable clay minerals is respectively kaolinite for water A (Chari River), nontronite for B (Delta), beidellite for C and D (Lake) and saponite or stevensite for E and F (interdune salines)

	Na	K	Ca	Mg	HCO ₃	SO ₄	Cl	SiO ₂	TDS mg/l	pH	fCO ₂ calculated
A	0.123	0.242	0.091	0.47	0.478	—	—	0.329	61.0	6.8	10 ^{-2.3}
B	0.141	0.060	0.126	0.099	0.626	0.010	0.020	0.385	76.0	7.4	10 ^{-2.8}
C	0.353	0.111	0.206	0.152	1.150	0.010	0.020	0.385	76.0	7.4	10 ^{-2.8}
D	2.060	0.605	0.625	0.480	3.950	0.090	0.150	0.879	548.3	8.8	10 ^{-3.3}
E	16.039	2.294	0.409	0.845	13.380	0.887	0.730	0.496	1759.2	8.9	10 ^{-2.9}
F	580.0	64.0	0.30	0.90	606.0	15.0	63.0	2.26	5567.5	9.9	10 ^{-3.4}

Equilibria in magnesian systems were experimentally studied by Hostetler (1963), Hostetler and Christ (1965), Hostetler *et al.* (1971), Bricker *et al.* (1973), Christ *et al.* (1973), Hemley *et al.* (1977a, 1977b). Stability fields of talc, sepiolite and other magnesium minerals were, since that time, precisely determined.

During the same period of time, the concepts of clay solubility and clay stability field have shown considerable progresses. Attempts to measure the smectite and illite solubilities were performed by Kittrick (1971a, 1971b, 1973), Routson and Kittrick (1971) and Weaver *et al.* (1971). At about the same time, attempts to estimate the thermodynamic properties of minerals were proposed by Karpov and Kashik (1968) and Eugster and Chou (1973). Therefore, Tardy and Garrels (1974) presented an empirical method for estimating ΔG°_f , the Gibbs free energies of formation of illites, vermiculites and smectites. This method has been generalized and applied to minerals of discrete chemical compositions. Other methods of estimation proposed later by Nriagu (1975), Chen (1975), Mattigod and Sposito (1978), Tardy (1979), Tardy and Fritz (1981) and Sposito (1985) have confirmed the consistency of the original approach. Tardy, Cheverry and Fritz (1974) and Tardy, Trescases and Fritz (1974) estimated the stability fields of nontronite, beidellite and stevensite by using the Tardy and Garrels (1974) method. Their results have been used to calculate the equilibrium reaction constants (Table 4) between kaolinite, goethite, nontronite, beidellite and saponite. Tardy and Gac (1979), Gac (1980) and Tardy (1981) showed (Fig. 2) the excellent agreement between the calculated stability fields and the observed sequence of smectites stables in the waters of the Lake Chad system.

Obviously, nontronite is the most stable and the least soluble smectite. In contrast, stevensite appears as the least stable and the most soluble clay mineral while beidellite and montmorillonite occupy intermediate positions :



The dioctahedral iron-rich smectites presenting a high tetrahedral charge can

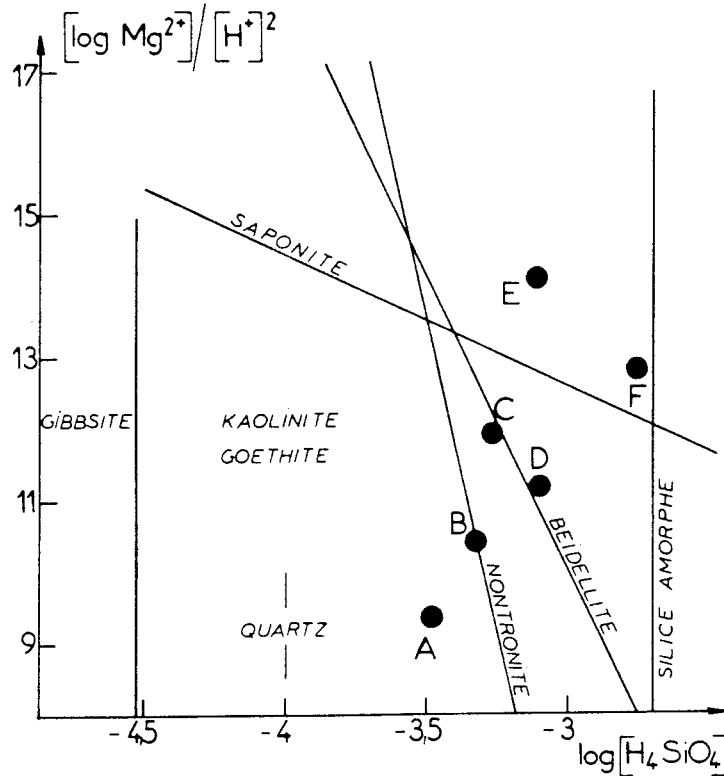


Figure 2. Stability fields (at 25°C) of nontronite, beidellite and saponite and characteristics of different waters of the Lake Chad system (Gac, 1980)

Furthermore, as pointed out by Robert (1973), the neoformed soil smectites are probably closer from true montmorillonites, characterized by a low tetrahedral charge, than from beidellites. However, Barshad (1966) and Barshad and Kishk (1969) have also described neoformed vermiculites, characterized by low tetrahedral charges, or mica degraded vermiculites characterized by high tetrahedral charges. Soil smectites, which are called ferri-beidellites probably differ from the beidellite *sensu stricto* which is a very rare mineral of hydrothermal origin (Weaver and Pollard, 1975). These smectites are probably mixtures of nontronites, Al- and Fe-vermiculites (degraded micas of high tetrahedral charges) and neoformed Al-montmorillonites (low tetrahedral charges).

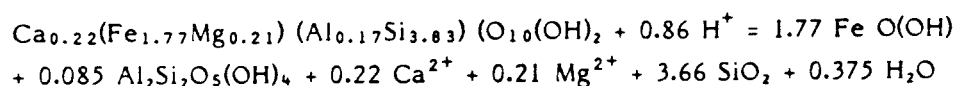
Similar considerations can be drawn for the sedimentary saponites. According to Weaver and Pollard (1975) most of the saponites described in the literature are of hydrothermal origin. A metamorphic origin is even proposed by Wilson *et al.* (1968), for a saponite in the Dalradian metalimestones of Scotland. Thus, it is probable that, in sediments, what was called saponites as described by Trauth (1977), are in fact intermediate stages between detrital beidellites and neoformed stevensites, both probably characteristic of low temperature smectites. As for soil beidellites, sedimentary saponites are probably mixtures. They may differ from the true saponites of hydrothermal origin.

Finally, at that stage of investigation, it seems clear that, in the conditions of weathering and sedimentation, each smectite type characterized by a given bulk composition appears also as characterized by a specific field of stability. In iron-rich environments and in dilute solutions, nontronite (high tetrahedral charge) is stable. In aluminium rich environments and in moderately concentrated solutions Al-vermiculite, beidellite and montmorillonite are formed or preserved together. In evaporitic and confined environments where solutions are concentrated, stevensite (low tetrahedral charge) appears as the most stable trioctahedral smectite.

The sequence ranging from nontronite, stable in diluted environments, to stevensite formed in concentrated brines, is the result of a progressive increase of Mg^{2+} in octahedral and Si^{4+} in tetrahedral sites and a decrease of Fe^{3+} or Al^{3+} from tetrahedral and octahedral positions.

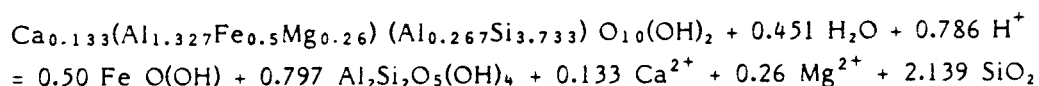
TABLE 4- Variations of the equilibrium constant at 25°C for the reaction : smectite = kaolinite + goethite from nontronite to beidellite and stevensite (Gac, 1980)

Nontronite = kaolinite + goethite



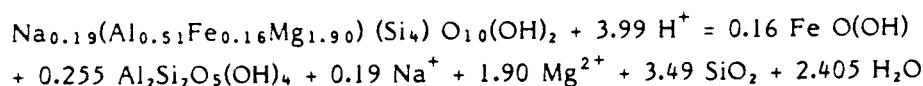
$$\text{with : } \log K_R = 0.22 \log [\text{Ca}^{2+}] / [\text{H}^+]^2 + 0.21 \log [\text{Mg}^{2+}] / [\text{H}^+]^2 + 3.66 \log [\text{SiO}_2] \\ + 0.375 \log [\text{H}_2\text{O}] \\ = - 7.636$$

Beidellite = kaolinite + goethite



$$\text{with : } \log K_R = 0.133 \log [\text{Ca}^{2+}] / [\text{H}^+]^2 + 0.26 \log [\text{Mg}^{2+}] / [\text{H}^+]^2 + 2.139 \log [\text{SiO}_2] \\ - 0.451 \log [\text{H}_2\text{O}] \\ = - 2.18$$

Stevensite = kaolinite + goethite



$$\text{with : } \log K_R = 0.19 \log [\text{Na}^+] / [\text{H}^+] + 1.90 \log [\text{Mg}^{2+}] / [\text{H}^+]^2 + 3.49 \log [\text{SiO}_2] \\ + 2.405 \log [\text{H}_2\text{O}] \\ = 14.731$$

form in very dilute solution environments. The trioctahedral magnesium-rich stevensite, presenting a very low tetrahedral charge can form in very saline and concentrated environments. The existence and the stability of beidellite, montmorillonite and saponite are perhaps more questionable.

In fact, the most typical smectites, found in soils i.e. in low temperature weathering conditions, generally show chemical compositions of ferribeidellites (Trauth *et al.*, 1967; Paquet, 1970). In iron-rich environments, nontronite, characterized by a large tetrahedral charge, may form instead of beidellite. Therefore, in the nontronite-beidellite dioctahedral serie, Paquet (1970) has pointed out that : higher the iron ((Fe³⁺)VI) content in octahedral position, higher the tetrahedral substitution of (Si⁴⁺)IV by (Al³⁺)IV ions. Weaver and Pollard (1975) have also found, in this mineral serie, a good positive correlation between (Fe³⁺)VI and (Al³⁺)IV.

Field observations suggest that the bulk composition of smectitic materials changes when the chemical composition of solutions, in which they form or reequilibrate, also changes. Thus, in thermodynamic models applied at a field scale or at a landscape scale, smectites can be considered as phases of variable chemical compositions, even if they may appear, at a crystal scale, as mixtures of apparently separate components.

3. THE STABILITY FIELDS OF ILLITES

The specific nature of illite is still an open question (Weaver and Pollard, 1975). In fact, pure monomineralic mineral samples are difficult to find, and consequently the mineral species characteristics and properties are not easy to define. Illite is, in fact, the dominantly potassic, dioctahedral, aluminous mica-like fraction of clay size materials in alteration products, sedimentary rocks and metasediments (Velde, 1977). Illitic minerals include also dioctahedral ferric minerals such as glauconite and celadonite.

Near the Earth's surface, two major situations seem to have provided most of the *sensu lato* aluminous illite materials : (i) the hydrothermal alteration of feldspars or other aluminosilicates into illites or sericites and (ii) the conversion by burial diagenesis or low grade metamorphism of smectitic or other detrital micaceous and feldspatic materials into illite, phengite or mica-like minerals.

The ferri-illites, glauconites and celadonites are also formed in two different environments (i) neoformation in slightly oxidizing or slightly reducing marine sedimentary environments and (ii) hydrothermal alteration of oceanic basalts.

Illite formation results of an alteration, at a given temperature, of an original material which was previously deposited either at a higher or at a lower temperature. Therefore, this material reacts with a given solution at the temperature of illite formation. Thus, illite chemical composition should reflect the bulk chemical composition of the original material, the chemical composition of the solution and the temperature of formation. Two mechanisms for the illite formation by transformation or by neoformation have been classically proposed. The layer-by-layer transformation of smectites as suggested by Lucas (1962), Millot (1964), Dunoyer de Segonzac (1969, 1970a, 1970b) and Hower *et al.* (1976) is a solid state transformation theory. It was successfully applied to the clay rich sediments such as shales, for example, and has drawn the attention to the fact that smectites provide most of the chemical material required for illite formation. The neoformation of filamentous diagenetic illite, precipitated from pore waters in sandstone reservoirs, was observed by Wilson and Pittman (1977) and by Mc Hardy *et al.* (1982). The neoformation theory is now adopted by several authors such as Lynch (1985), Nadeau *et al.* (1985), Nadeau and Bain (1986), as the fundamental mechanism for illite formation even when smectite are abundant and when interstratified I/S are present as intermediate stages. Therefore, the term conversion of smectite to illite will be used instead of transformation which, for historical reasons, involves a solid state mechanism (Nadeau *et al.*, 1985).

Conversion of smectites during compaction and burial diagenesis occurs along at least three geochemical and mineralogical pathways :

beidellites or montmorillonites	→ illites,
saponites or stevensites	→ corrensites or chlorites,
nontronites	→ glauconites or celadonites.

These conversions occur at different temperatures.

In a recent paper, Chang and Mackenzie (1986) reviewed the conditions of clay diagenesis and compared the evolution of dioctahedral and trioctahedral smectites subjected to burial diagenesis. As temperature increases, dioctahedral smectites (beidellites or montmorillonites) convert into illites, while trioctahedral smectites (saponites or stevensites) convert into corrensite or chlorite.

The compositional changes accompanying the smectite-to-illite conversion as deduced from published chemical analyses, were summarized by Hower and Mowatt (1966), Garrels and Mackenzie (1974) and Hower (1981) and more recently by Lynch (1985). The main chemical changes, with increasing number of illite layers, are a gain of interlayer potassium, increasing substitution of aluminum for silicon in the

tetrahedral layer loss of water and losses of octahedral magnesium or iron (Dunoyer de Segonzac, 1970a, b).

The compositional changes accompanying the saponite-to-chlorite conversion are a loss of interlayer cations, increasing substitution of aluminum for silicon in the tetrahedral layer and an overall increase of the total iron and magnesium content, followed by a fixation of magnesium in the brucitic layer. Chang and Mackenzie (1986) conclude that the ordering of illite/smectite takes place within a temperature range of 90°-115°C, whereas the ordering of chlorite/saponite (corrensite) occurs at a temperature of 60°-70°C. These authors also showed that the two different conversions may occur in the same sediments volume, that is, in the same chemical environment.

Glaucosite commonly forms in slightly compacted iron-bearing marine sediments at low temperature and during the earliest stage of diagenesis. In such environments, glaucosite may form directly but the dioctahedral-iron-rich smectite (nontronite) may also convert into mixed-layered nontronite/glaucosite (Porrenga, 1967 ; Lamboy, 1967 ; Giresse and Odin, 1973). The compositional changes accompanying these conversions result in a gain of aluminum substituting for tetrahedral silicon, and a loss of water (Burst, 1958 ; Thompson and Hower, 1975).

Celadonite is commonly found in vesicular cavities, formed during the hydrothermal alteration of basalts. Volcanic clastic rocks upon diagenetic alteration or low grade metamorphism (zeolite facies) often develop celadonite-bearing assemblages (Wise and Eugster, 1964 ; Weaver and Pollard, 1975). In the iron-bearing series, celadonites tend to form at higher temperatures and glaucosite at lower temperatures.

Trioctahedral illites were described by Walker (1950) and by Weiss *et al.* (1956), but they are very rare minerals and do not form commonly in nature. This is probably because the trioctahedral Mg-illite would be stable at a temperature higher than the one required to form an Mg-chlorite phase : phlogopite, the magnesian mica may form at very high temperatures. During the burial diagenesis of an Mg-rich sedimentary facies, an increase in temperature and pressure will act in favor of the conversion of stevensite into corrensite and chlorite and not into the trioctahedral illites which are generally absent (Fig. 3).

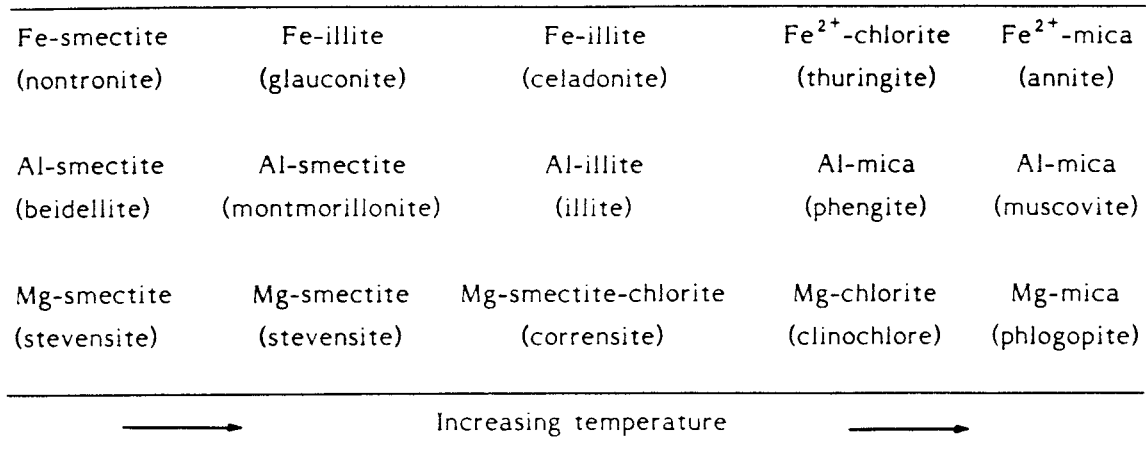
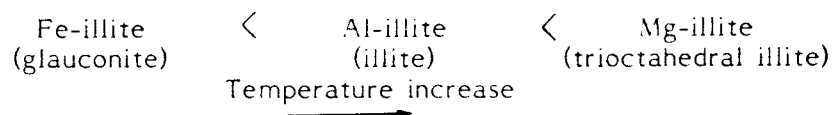


Figure 3. Schematic evolution of the smectites, chlorites and micas as function of temperature

It can be concluded that in environments which differ by their chemistry, the temperature of illite formation increases from iron-rich, to aluminum-rich, to magnesium-rich environments :



The micaceous minerals such as mixed-layer smectite/illite, illite, celadonite and the chloritic minerals such as corrensite or chlorite form at elevated temperature and pressure. The trioctahedral Mg-rich illite would form at even higher temperature but appears at the near surface of the Earth, less stable than chlorite. Glauconite is the unique mica that forms directly at low temperature and pressure.

The temperature of mica formation is the lowest for the iron-bearing mineral sequence, intermediate for the aluminous serie and the highest for the Mg-rich minerals.

Many recent studies have been devoted to the problems of the conditions of formation of clay minerals and to their stability in natural environments. However, solutions to these problems are not yet satisfactory and the conclusions generally have been turned around the same questions : are the clay minerals formed in near-equilibrium conditions ; do the thermodynamic principles, apply to clay minerals ? The answer to these two questions may be yes, but only if one admits that their mineralogical and chemical compositions reflect the macro- or the micro-environments in which they form or the temperatures at which they equilibrate. However, the procedure of experimental measurements, the way to investigate the extreme imbrication of natural systems or microsystems, and the appropriate thermodynamic approach to treat the natural complexity (previously supposed to have been understood) have not yet been clearly defined.

In the particular case of the smectite/illite mixed layers, thermodynamics seems to be so difficult to apply that many researchers are inclined to consider that clay mineral systems are not a field in which equilibrium can truly exist.

4. SMECTITE/ILLITE MIXED LAYERS CONSIDERED AS TWO SEPARATE SMECTITE AND ILLITE PHASES

One of the most interesting and debated questions regarding stabilities of clay minerals concerns the transformation of smectites into illites through the intermediate stages of mixed-layers illite/smectite, occurring in the course of the sediment burial diagenesis. The question was initiated by Zen (1972), discussed by Lippman (1979c) and clearly reactualized by Garrels (1985) as follows. Should the mixed layers smectite/illite be considered as single phases or as mixtures of two separate phases i.e. illite and smectite ?

It is commonly accepted that illite/smectite interlayered particles are composed of two discrete species. One is montmorillonite with low interlayer charge ; the second is illite with high interlayer charge. The illite layers are formed by diagenetic alteration of original montmorillonite layers. The conversion of a single isolated montmorillonite layer to an illite layer would clearly be a phase change because there are marked structural differences between them. However, the question resolves as to whether, in an intimate mixture, there are enough interactions between the constituent phases so that their properties may be modified. Two types of recently reported results may suggest that mixed layers are not continuous solid solutions but mixtures of two separate phases.

4.1. Physical mixtures of smectite and illite particles

In series of papers, Mc Hardy *et al.* (1982), Nadeau *et al.* (1984a, 1984b, 1984c), Wilson and Nadeau (1985), Nadeau (1985) have apparently resolved the question of the interaction between particles of different nature, within interstratified clay minerals of different types. Transmission electron microscopic (TEM) examination of the < 0.1 μm fractions of different smectites and interstratified smectite/illite show that these clays, when dried from suspension consist primarily of both 10 A and 20 A thick particles respectively (one or two individual layers), while X-ray diffraction (XRD) examination of sedimented aggregates of such smectite or mixed-layer clays, indicate that the effective number of unit cells that are diffracting coherently is systematically higher. The authors reconcile this discrepancy by postulating interparticle diffraction effects from the sedimented aggregates of oriented particles and conclude that standard XRD data from sedimented aggregates may not be able to distinguish between true interstratification and interparticle diffraction effects of intimate physical mixtures. As a consequence of this postulate, the naturally occurring mixed-layers smectite/illite or chlorite/illite may be

physical mixtures of thin particles which exhibit interparticle, intra-aggregate diffraction phenomena. Large particles are almost always aggregates of smaller particles and yield rotational turbostratic electron diffraction patterns rather than single crystal patterns (Fig. 4).

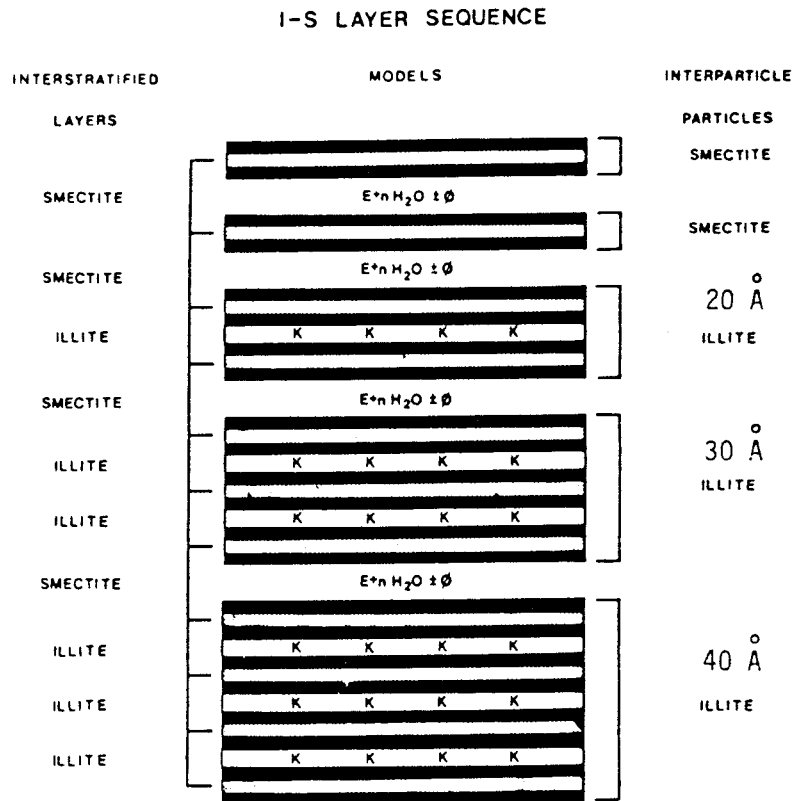


Figure 4. Diagrammatic representation of illite particles cross section (from Nadeau and Bain, 1986)

4.2. Montmorillonite/illite stability diagrams

The second element in favor of the two independent phase systems comes from Garrels (1985). There are two different ways to consider the montmorillonite/illite stability changes during the burial diagenesis: either (i) smectite and illite are one solid solution phase of variable composition, as proposed by Aagaard and Helgeson (1983) or (ii) smectite and illite are discrete separate phases. The solution compositions shown on Fig. 5 fit the two phase systems better than they fit a solid solution model. Aagaard and Helgeson (1983) stated that no compositions are available in the literature for waters that are known to coexist with illite. Garrels (1985) considers that data on coexisting aqueous solutions apparently are more nearly consistent with the interpretations of Nadeau *et al.* (1984c) stating that in mixed-layer smectite/illite, the two mineral species can be considered as two separate phases.

Nadeau *et al.* (1984c) concluded that "randomly interstratified smectite/illite would be composed of populations of illite and smectite particles. During diagenesis, smectite particles become unstable and dissolve, while illite particles are neofomed. As diagenesis continues, the thickness of the fundamental illite particles increases within the population. When the particles become sufficiently thick to produce diffraction maxima with 10-Å series, the clay material is identified by XRD as conventional illite".

Although these conclusions are fairly convincing, it seems that there are still some points i.e. energetic relationships between smectite and illite layers which may be subject to discussion.

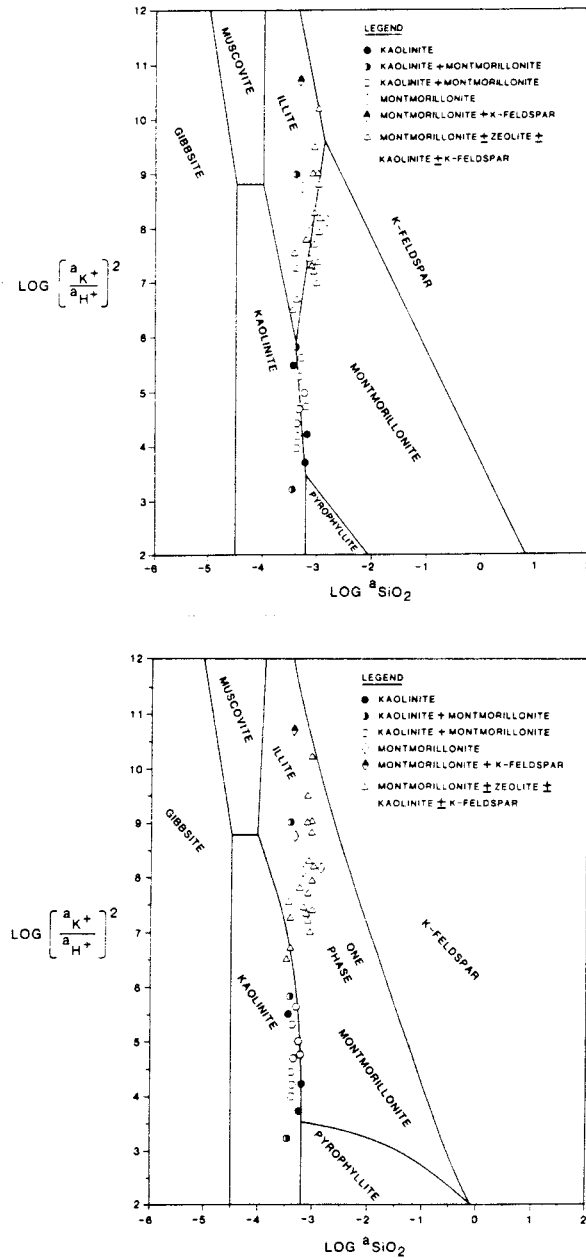


Figure 5. Ion activity diagrams illustrating the relations to be expected if montmorillonite and illite behave (a) as a solid solution or (b) as two discrete phases (from Garrels, 1985)

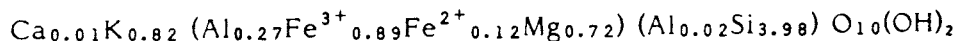
5. INTERLAYER ENERGIES

Among the two types of elementary 10 Å layers only the illitic layers are capable to organize into particles of different thickness (20 Å, 30 Å, 40 Å and 50 Å for example), while the smectite elementary layers are only present as particles of about 10 Å thick. In conception of NADEAU and his coworkers, the illitic layers are strongly organized in a face to face system, involving important interlayer energies. On the contrary, in a face-to-face system of two elementary smectitic layers (or between smectite and illite layers) the ordering is poor, the arrangement is turbostratic, and the resulting interlayer energy may be low or at least negligible compared to the energy involved in illite.

The turbostratic disordering due to the rotation or to the displacement of the individual layers, is a general phenomenon within the smectite group and is understood as a necessity for two layers to adapt and to fit the structure of the hydra-

The alteration of basalts generally yields series of clay minerals formed at the same place, in the same chemical environment but at different temperature conditions. The first stages may be typically hydrothermal, while the last ones may be formed at low temperature after the cooling of the basalts and the circulating fluids. A large number of examples are given in the literature.

The first example presented here concerns a celadonite found in the small cavities of the upper-Cretaceous basalt in the Troodos massif of Cyprus and described by Duplay *et al.* (1986). The chemical formula, calculated from the bulk analysis of 100 mg of separated material, is characteristic of a typical celadonite as defined by Buckley *et al.* (1978), Wiewiora *et al.* (1979), Köster (1982), Bailey *et al.* (1984), Bailey (1985) and AIPEA Nomenclature Committee :



A fraction of the powder was examined by TEM and microprobe and 42 individual particles were analyzed by the method of Duplay (1984). Selected data, shown in Table 5, indicate that particle compositions range from a true magnesian celadonite (1) to a true glauconite (2) ; some intermediate compositions mark some slight tendencies towards trioctahedral (3) or dioctahedral (4) K-vermiculite, K-saponite or K-montmorillonite.

Correlation diagrams (Fig. 7) show two clearly identified populations. Both present about the same layer charge and the same Mg- content (Table 6) but celadonite (1), characterized by a low tetrahedral and a high octahedral charges, contains less octahedral aluminum and less octahedral iron than glauconite (2). Furthermore, glauconite (2) is characterized by higher tetrahedral charge and a lower octahedral charge than is celadonite.

TABLE 5- Extreme compositions in the particle population of the Cyprus Celadonite

(1) $\text{Ca}_{0.00}\text{K}_{1.00} (\text{Al}_{0.28}\text{Fe}^{3+} 0.75\text{Mg}^{2+} 0.955) (\text{Al}_{0.00}\text{Si}_{4.00}) \text{O}_{10}(\text{OH})_2$
(2) $\text{Ca}_{0.002}\text{K}_{0.88} (\text{Al}_{0.017}\text{Fe}^{3+} 1.210\text{Mg}^{2+} 0.920) (\text{Al}_{0.405}\text{Si}_{3.595}) \text{O}_{10}(\text{OH})_2$
(3) $\text{Ca}_{0.12}\text{K}_{0.67} (\text{Al}_{0.10}\text{Fe}^{3+} 0.79\text{Mg}^{2+} 1.31) (\text{Al}_{0.19}\text{Si}_{3.81}) \text{O}_{10}(\text{OH})_2$
(4) $\text{Ca}_{0.00}\text{K}_{0.78} (\text{Al}_{0.40}\text{Fe}^{3+} 0.88\text{Mg}^{2+} 0.74) (\text{Al}_{0.10}\text{Si}_{3.90}) \text{O}_{10}(\text{OH})_2$

TABLE 6- Average composition of celadonites (1) and glauconites (2) within the particle population of the "Cyprus Celadonite"

(1) $\text{Ca}_{0.04}\text{K}_{0.835} (\text{Al}_{0.275}\text{Fe}^{3+} 0.800\text{Mg}_{0.980}) (\text{Al}_{0.10}\text{Si}_{3.90}) \text{O}_{10}(\text{OH})_2$
(2) $\text{Ca}_{0.02}\text{K}_{0.840} (\text{Al}_{0.14}\text{Fe}^{3+} 1.00\text{Mg}_{0.985}) (\text{Al}_{0.22}\text{Fe}_{0.05}\text{Si}_{3.73}) \text{O}_{10}(\text{OH})_2$

The second example presented concerns a celadonite and three smectites formed during the hydrothermal alteration of basalts under submarine conditions, collected in the Reykjanes ridge (SW Iceland, DSDP leg 49, hole 407) (celadonite 2V, saponite 2V, nontronite 2R, nontronite K2) or within the hydrothermal mounts of Galapagos (DSDP leg 70, hole 506, section 2) (nontronite V2). Three of these minerals have been formed under hydrothermal conditions while the nontronite K2 seems to have been formed at low temperature (Duplay, 1987) (Table 7).

In each of these samples, about fifteen particles were analyzed. The correlation coefficients between the three types of charges, tetrahedral negative charge (CHT), octahedral negative charge (CHO) and total layer charge (CHF), and the amounts of the octahedral cations (Fe, Al, Mg) were calculated and are given in

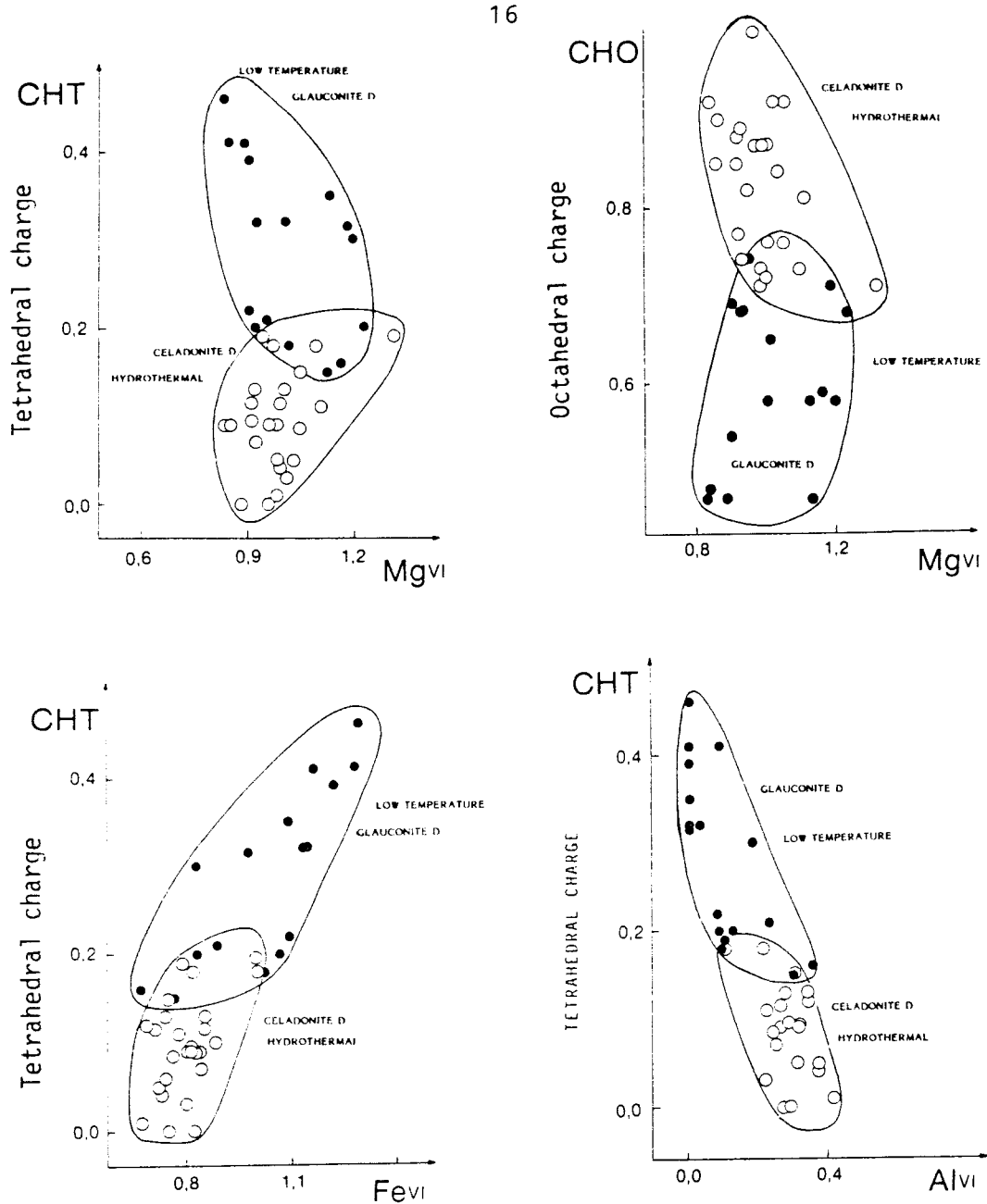


Figure 7. Correlation diagrams for a low temperature glauconite (D) and an hydrothermal celadonite (D) (open circles) from an altered basalt of the Troodos massif (solid circles) of Cyprus. CHO and CHT stand respectively for octahedral and tetrahedral charge

Table 8. Two groups of correlation appear, depending on the estimated temperature of mineral formation (low and hydrothermal temperatures) (Table 9, Fig. 8). The following conclusion can be drawn in the framework of a solid solution theory as already described by Tardy *et al.*, (1981), Fritz (1981), Duplay (1982), Fritz (1985) :

(i) At low temperature, the tetrahedral charge (CHT) is well correlated with octahedral iron (Fe^{3+})VI. This can be called the glauconite effect, which may correspond to an important contribution of the ferri-muscovite end member to the solid solution.

(ii) At low temperature, layer charge (CHF) is anticorrelated with the octahedral aluminum (Al^{3+})VI and to a lesser extent with octahedral magnesium (MgVI). This can be called the pyrophyllite and the talc effects which may correspond to important contributions of such end members to the presumed solid solutions.

(iii) At low temperature, octahedral charge (CHO) is not very well correlated with any of the octahedral ions. However, it seems that the Fe^{3+} -celadonite

TABLE 7- Average chemical formulas of a hydrothermal celadonite (1), a low temperature glauconite (2), a hydrothermal nontronite (3) and a low temperature nontronite (4)

(1) Celadonite 2V	$\text{Ca}_{0.008}\text{K}_{0.770}(\text{Al}_{0.10}\text{Fe}^{3+}_{1.135}\text{Mg}_{0.785})(\text{Al}_{0.06}\text{Si}_{3.94})\text{O}_{10}(\text{OH})_2$
(2) Glauconite D	$\text{Ca}_{0.020}\text{K}_{0.850}(\text{Al}_{0.10}\text{Fe}^{3+}_{1.030}\text{Mg}_{1.010})(\text{Al}_{0.22}\text{Fe}_{0.05}\text{Si}_{3.71})\text{O}_{10}(\text{OH})_2$
(3) Nontronite V2	$\text{Ca}_{0.007}\text{K}_{0.345}(\text{Al}_{0.315}\text{Fe}^{3+}_{1.235}\text{Mg}_{0.585})(\text{Al}_{0.18}\text{Si}_{3.82})\text{O}_{10}(\text{OH})_2$
(4) Nontronite K2	$\text{Ca}_{0.02}\text{K}_{0.54}(\text{Al}_{0.11}\text{Fe}^{3+}_{1.555}\text{Mg}_{0.30})(\text{Al}_{0.205}\text{Si}_{3.795})\text{O}_{10}(\text{OH})_2$

TABLE 8- Correlation coefficients among tetrahedral charge (CHT), octahedral charge (CHO), layer charge (CHF) and octahedral cations (Fe, Al or Mg) within particle populations of an hydrothermal celadonite (2V), an hydrothermal nontronite (V2), a low temperature glauconite (D) and a low temperature nontronite (K2)

	Tetrahedral charge			Octahedral charge		
	(CHT-Fe)	(CHT-Al)	(CHT-Mg)	(CHO-Fe)	(CHO-Al)	(CHO-Mg)
Celadonite 2V	- 0.41	-0.59	+ 0.76	+ 0.92	- 0.20	- 0.96
Glauconite D	+ 0.80	- 0.72	- 0.49	- 0.44	+ 0.25	+ 0.24
Nontronite V2	- 0.57	+ 0.28	+ 0.77	+ 0.40	- 0.34	- 0.62
Nontronite K2	+ 0.57	- 0.31	- 0.50	0.00	- 0.37	+ 0.22

	Layer charge		
	(CHF-Fe)	(CHF-Al)	(CHF-Mg)
Celadonite 2V	+ 0.89	- 0.75	- 0.67
Glauconite D	+ 0.50	- 0.61	- 0.37
Nontronite V2	+ 0.26	- 0.47	- 0.34
Nontronite K2	+ 0.54	- 0.74	0.00

($\text{K}(\text{Fe}^{3+}_{1.667})(\text{Si}_4)\text{O}_{10}(\text{OH})_2$) is the less important celadonite end-member. On the contrary, the Mg-celadonite ($\text{K}(\text{Mg}_{2.5})(\text{Si}_4)\text{O}_{10}(\text{OH})_2$) or the Al-celadonite ($\text{K}(\text{Al}_{1.667})(\text{Si}_4)\text{O}_{10}(\text{OH})_2$) end members may compete for the octahedral charge.

(iv) At higher temperatures, the tetrahedral charge (CHT) is correlated with octahedral magnesium (Mg^{2+})VI. This can be called the phlogopite effect which may correspond to an important contribution of the $\text{K}(\text{Mg}_3)(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$ end member to the supposed solid solution.

(v) At high temperature, layer charge (CHF) is negatively correlated with octahedral aluminum (Al^{3+})VI and almost equally to octahedral magnesium (Mg^{2+})VI. This can be due to a similar but important contribution of the pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$) and of the talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) end members for lowering the layer charge. By contrast, the octahedral iron (Fe^{3+})VI tends to act in favour of an increase of the total layer charge.

(vi) At high temperatures, octahedral charge (CHO) is mostly due to iron content (Fe^{3+})VI, and only partly due to octahedral aluminum (Al^{3+})VI but not at all due to octahedral magnesium (Mg^{2+})VI.

Then, in these series of minerals the same considerations can be presented differently.

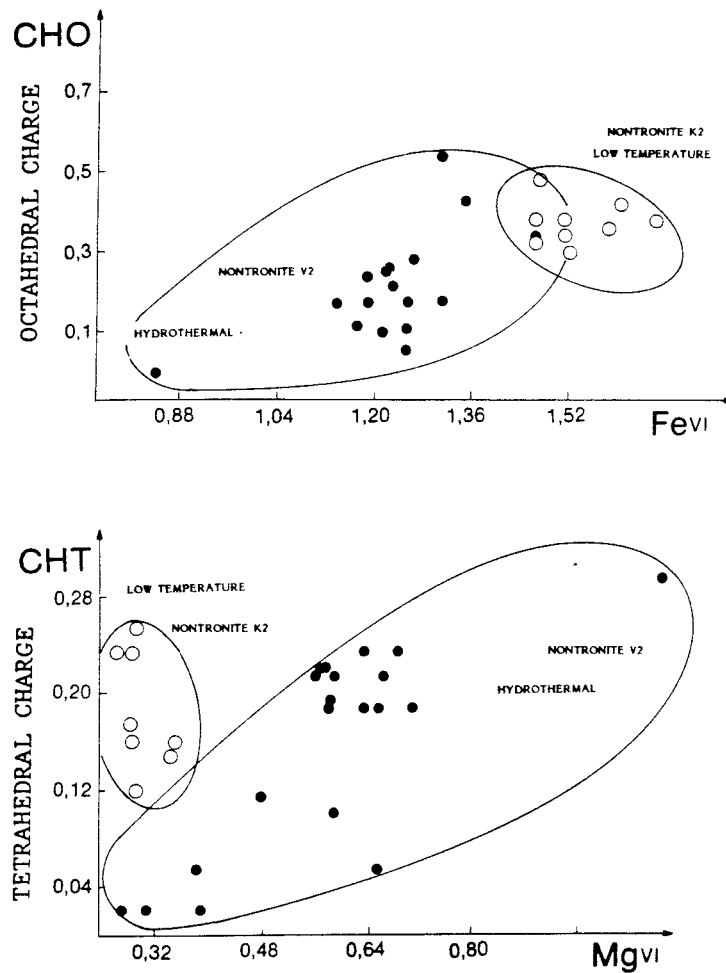


Figure 8- Correlation diagrams for a low temperature nontronite (K2) (Reykjanes ridge, Iceland) and an hydrothermal nontronite (V2) (Galapagos), in altered submarine basalts. CHO, CHT and CHF stand respectively for octahedral charge, tetrahedral charge and layer charge

the talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) end members for lowering the layer charge. By contrast, the octahedral iron (Fe^{3+})VI tends to act in favour of an increase of the total layer charge.

(vi) At high temperatures, octahedral charge (CHO) is mostly due to iron content (Fe^{3+})VI, and only partly due to octahedral aluminum (Al^{3+})VI but not at all due to octahedral magnesium (Mg^{2+})VI.

Then, in these series of minerals the same considerations can be presented differently.

(i) Octahedral iron (Fe^{3+})VI seems above all to be introduced as $\text{KFe}^{3+}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ at higher temperatures, while the weight of $\text{Fe}^{3+}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ as end member is low in any cases.

(ii) Octahedral aluminum (Al^{3+})VI at any temperature seems to be introduced more as $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ than as $\text{KAl}_{1.667}\text{Si}_4\text{O}_{10}(\text{OH})_2$, and to a lesser extent as the muscovite $\text{KAl}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$ end member.

(iii) Octahedral magnesium (Mg^{2+})VI seems to be better explained by the talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) than by the phlogopite end member ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$) at low temperatures, while the situation is reverse at high temperatures. In both cases, but especially at high temperatures, the Mg-celadonite end member contributions is relatively small.

TABLE 9- Correlation among tetrahedral charge, octahedral charge, layer charge and octahedral cations (Fe, Al or Mg) in low temperature and hydrothermal iron-rich clay mineral populations

Low temperature glauconite or nontronite	Hydrothermal celadonite or nontronite
The higher the octahedral iron (Fe^{3+})^{VI}	Higher the octahedral iron (Fe^{3+})^{VI}
the higher the tetrahedral charge	Lower the tetrahedral charge
the lower the octahedral charge	Higher the octahedral charge
the higher the layer charge	Higher the layer charge
The higher the octahedral aluminum (Al^{3+})^{VI}	Higher octahedral aluminum (Al^{3+})^{VI}
the lower the tetrahedral charge	Lower tetrahedral charge
the higher the octahedral charge	Lower the octahedral charge
the higher the layer charge	Lower the layer charge
The higher the octahedral magnesium (Mg^{2+})^{VI}	Higher the octahedral magnesium (Mg^{2+})^{VI}
the lower the tetrahedral charge	Higher the tetrahedral charge
the lower the octahedral charge	Lower the octahedral charge
the lower the layer charge	Lower the layer charge

These observations seem to support the idea that clay minerals are not only physical mixtures, in various proportions, of separate phases of discrete compositions which coexist independently. The temperature dependence of the solubility products of the end members and the temperature dependence of the weight of each of these defined end members within clay mineral populations indicate clearly that some thermodynamic relationships may take place to regulate these highly complex systems. However, the extreme diversity of the clay particle compositions, within a given population, indicates also that any overall equilibrium could not at all have been attained and suggests that equilibria may have been reached only locally in a large variety of aqueous microsystems.

7. AN IDEAL SOLID SOLUTION MODEL OF A LARGE NUMBER OF END MEMBERS

The tests of equilibrium in clay mineral systems may only be performed if the variety and the complexity of clay mineral compositions are taken into consideration.

Clay minerals and especially smectites and illites always present a large number of sites and cation substitutions. The interlayer sites may be occupied by Na^+ , K^+ , Mg^{2+} , Ca^{2+} at different hydration stages as functions of temperature, solution salinity, and degree of compaction of the sediment. The interlayer charge is balanced by variable tetrahedral and octahedral charge deficiencies. The octahedral sites may be occupied by at least four different cations: Fe^{3+} , Al^{3+} , Fe^{2+} and Mg^{2+} . Then the number of individual components which define a clay mineral composition, and determine - if admitted - clay mineral stability, is very high :

- 4 pyrophyllite-talc components
- 4 muscovite - phlogopite components, with 4 possible interlayer cations
- 4 celadonite components, with 4 possible interlayer cations.

Therefore the number of possible end members ranges between 12, if potassium micas components are only involved, and 36 if the four interlayer cations (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) are taken into consideration (for the micas and cela-

donite components).

Thermodynamics of equilibrium between multicomponent solid solutions and aqueous solution is extremely complex and a general model is not yet entirely available. The solubility products of many end members (celadonites for example) are not known. Data for the mixing energies of several cations in different structural sites are not available. Measured Gibbs free energy changes as function of crystallinity and grain size are not also available.

Despite these intrinsic difficulties, it seems interesting to explore what conditions clay minerals would have to satisfy in order to form solid solutions of a large number of end members. Truesdell and Christ (1968) and Stoessell (1979, 1981) adopted regular solid solution models to calculate the thermodynamic consequences of compositional variation in montmorillonites and illites. Helgeson and Mackenzie (1970) have adopted an ideal solid solution model while Aagaard and Helgeson (1983) proposed an ideal mixing of atoms on homological sites in montmorillonites and illites. All of these models have been applied to a rather small number of components and for that reason, fail to simulate the reality (see Merino and Ransom, 1982). In contrast, and for a very large number of end members, Fritz (1981), Tardy and Fritz (1981) and Fritz (1985) proposed an ideal multicomponent mixing model which simulate the variability of clay mineral compositions as they appear in nature.

In this model, it is supposed that end members can mix ideally either among the different sites of individual layers or among the different layers of individual particles. If one believes, for example, that dioctahedral and trioctahedral end members cannot mix ideally and in all proportions, at a molecular scale, one may admit that they can be interlayered and mixed at a layer scale to form particles without involving large interlayer energies.

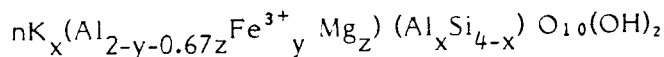
The equilibrium condition between a solid solution and an aqueous solution is described by the mass action law applied to each of the j end members which contribute in the solid solution (Fritz, 1981, 1985). For each of the j end member one has :

$$K_j = (Q_j/A_j) = (Q_j/X_j \lambda_j)$$

with K_j = the solubility product,
 Q_j = the corresponding ion activity product in solution,
 λ_j = the activity coefficient,
 X_j = the mole fraction,
 A_j = the activity,

of the j th end-member, in the solid solution.

Let us consider, for example, a simplified illite or smectite formula with no octahedral charge, the interlayer being saturated with only one cation (K^+) :



This formula is obtained by combining two sites of substitution (one tetrahedral and one octahedral site). Six end-members define this solid solution :

3 micas	muscovite	: $K(Al_2) (Si_3Al) O_{10}(OH)_2$
	Fe^{3+} -muscovite	: $K(Fe_2) (Si_3Al) O_{10}(OH)_2$
	phlogopite	: $K(Mg_3) (Si_3Al) O_{10}(OH)_2$
3 pyrophyllites	pyrophyllite	: $(Al_2) (Si_4) O_{10}(OH)_2$
	Fe^{3+} -pyrophyllite	: $(Fe_2) (Si_4) O_{10}(OH)_2$

That solid solution is completely defined by only three variables (x , y , z) for its composition and one additional variable (n) for the quantity (n = number of moles of solid solution per kilogram of water). Thus, one needs 4 relationships between the solid solution phase and the aqueous phase in order to define both amount and chemical composition of the clay solid solution in equilibrium with a given aqueous solution, along any geochemical process.

The relationships required are depending on the type of solid-solution involved. For a simple pure mineral, the equilibrium condition is written by using only one equation which is the classical Mass Action Law. This condition allows to calculate the unique unknown which defines completely the solid phase, that is the quantity (n) of solid phase in equilibrium with the aqueous solution (one unknown, one equation per pure phase).

For a binary solid solution, the Mass Action Law is applied for the two members. This allows to calculate the two unknowns : the total amount of solid solution (n) and one substitution or composition parameter (x), which corresponds to the mole fraction X_1 or X_2 of one of the two end-members. The second mole fraction is calculated from the relation $X_1 + X_2 = 1$.

If one considers now a generalized multipole solid solution, the problem becomes seriously more complex. There are two types of possible generalization : (i) a solid solution of j end members due to only one type of substitution and (ii) the general case involving several types of substitutions, which is the case of real clay minerals such as smectites, illites, chlorites, etc.

The first case (one type or site of substitution) is only an extension of the binary solid solution to j end-members, with j Mass Action Law equations (one per theoretical end-member). The unknowns are (n) and (j-1) substitution or composition parameters : x, y, z... which correspond also to (j-1) mole fraction X_i , the last jth being defined by the conservative rule ($\sum X_i = 1$). In that case, the number of independent unknowns is equal to the number of end-members.

The general case (two or more types of sites or substitutions) is characterized by linked relations among the solid solution parameters (K_j , X_j) as shown by Fritz (1981). It can be summarized, as follows, for the illite formula given above and formed by the mixing of 6 end-members. The corresponding aqueous ionic activity products Q_j obey to the four different following inter-relations :

$$\frac{[Al^{3+}]^2}{[Fe^{3+}]^2} = \frac{Q(\text{Al-pyrophyllite})}{Q(\text{Fe-pyrophyllite})} = \frac{Q(\text{Al-muscovite})}{Q(\text{Fe-muscovite})}$$

$$\frac{[Al^{3+}]^2}{[Mg^{2+}]^3} = \frac{Q(\text{Al-pyrophyllite})}{Q(\text{talc})} = \frac{Q(\text{Al-muscovite})}{Q(\text{phlogopite})}$$

They correspond to relations between solubility products and mole fractions of the end-members in the solid solution, due to the Mass Action Law, considered for each end-member j :

$$Q_j = K_j X_j \lambda_j$$

or for an ideal solid solution ($\lambda_j = 1$) :

$$Q_j = K_j X_j$$

Thus, it follows :

$$\frac{X(\text{Al-pyrophyllite}) K(\text{Al-pyrophyllite})}{X(\text{Fe-pyrophyllite}) K(\text{Fe-pyrophyllite})} = \frac{X(\text{Al-muscovite}) K(\text{Al-muscovite})}{X(\text{Fe-muscovite}) K(\text{Al-muscovite})}$$

and :

$$\frac{X(\text{Al-pyrophyllite}) K(\text{Al-pyrophyllite})}{X(\text{talc}) K(\text{talc})} = \frac{X(\text{Al-muscovite}) K(\text{Al-muscovite})}{X(\text{phlogopite}) K(\text{phlogopite})}$$

These relations show that there are six Mass Action Law relations, linked by two relationships among K_i and X_i values, *whatever the chemistry of the aqueous solution in equilibrium could be*. Finally, for the example chosen, the seven apparent unknowns (6 X_i and n) are linked by 2 relations due to the Mass Action Law and one conservative relation ($\sum X_i = 1$). It remains 4 independent unknowns and 4 independent equations. The resolution of the system gives the total number of moles of solid solution (n) and three composition parameters x, y, z if the solution chemistry is known (Q_j and consequently X_i). On the contrary, if the composition of the clay is known (n, x, y, z), the calculation leads to the knowledge of mole fraction distribution for the solid solution (X_i) together with indications on the ion activity products (Q_j) in the solution.

In conclusion, one may notice that, in an ideal model, the contribution of each end-member to the solid solution phase (X_i) is directly proportional to the saturation index of the end-member in the aqueous solution ($X_i = Q_i/K_i$). Therefore, considering a given aqueous solution chemistry ($Q_i = \text{constant}$), the contribution of an end-member is taken inversely proportional to its selected solubility product : the

lower the solubility product of an end member (the higher its stability) the higher its contribution to the solid solution.

8. CONTRIBUTION OF THE DIFFERENT END MEMBERS AS FUNCTION OF TEMPERATURE AND CHEMICAL COMPOSITION

Recently, the solubility product of the clay mineral end members have been refined in order to allow simulations of clay mineral formation during weathering, diagenesis and hydrothermal alteration. In such a research one tends to model real chemical compositions and distribution of charges of clay minerals as they appear in natural conditions (Tardy and Fritz, 1981 ; Fritz, 1981 ; Tardy, 1982).

The solubility products of eight clay mineral end-members are given in Table 10 (Fritz, 1981). They do not correspond to the values of the pyrophyllite or muscovite solubility products but to clay minerals end-members, with the chemical composition of pyrophyllite or muscovite. These values will be used to estimate the temperature and the composition dependence of the smectite to illite conversion.

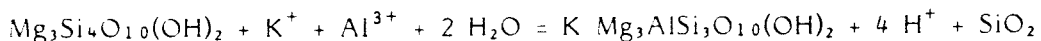
TABLE 10- Solubility products of some clay mineral end members, as a function of temperature (according to Fritz, 1981 and Duplay, 1987)

Mineral formulas	log K _{sp} , solubility products			
	0°C	25°C	100°C	200°C
Pyrophyllite-talc				
Al ₂ Si ₄ O ₁₀ (OH) ₂	2.613	1.061	2.801	- 6.116
Fe ₂ Si ₄ O ₁₀ (OH) ₂	- 13.162	- 13.700	- 15.459	- 17.126
Fe ₃ Si ₄ O ₁₀ (OH) ₂	8.894	7.235	3.118	- 0.141
Mg ₃ Si ₄ O ₁₀ (OH) ₂	27.671	25.162	19.063	14.030
Micas				
K Al ₂ AlSi ₃ O ₁₀ (OH) ₂	20.361	16.656	8.459	1.777
K Fe ₂ AlSi ₃ O ₁₀ (OH) ₂	4.321	1.088	- 4.542	- 9.187
K Fe ₃ AlSi ₃ O ₁₀ (OH) ₂	27.309	23.373	14.324	7.282
K Mg ₃ AlSi ₃ O ₁₀ (OH) ₂	46.907	41.913	30.749	21.736
Celadonites				
K Al _{1.667} Si ₄ O ₁₀ (OH) ₂	7.907	6.345	0.681	- 4.128
K Fe ³⁺ _{1.667} Si ₄ O ₁₀ (OH) ₂	- 6.169	- 6.956	- 11.087	- 14.803
K Fe ²⁺ _{2.5} Si ₄ O ₁₀ (OH) ₂	13.392	11.740	5.860	1.101
K Mg _{2.5} Si ₄ O ₁₀ (OH) ₂	29.289	26.929	19.401	13.160

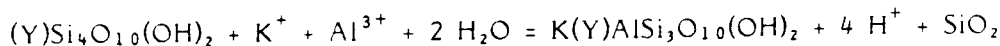
Fe³⁺-, Al³⁺-, Fe²⁺- or Mg²⁺-smectites are represented here respectively by clay minerals which have the composition of Fe³⁺-pyrophyllite, pyrophyllite, minnesotaite and talc.

Fe³⁺-, Al³⁺-, Fe²⁺- or Mg²⁺-illites are represented here respectively by clay minerals which have the composition of Fe³⁺-muscovite, muscovite, annite and phlogopite.

One may consider, for example, the equilibrium of talc and phlogopite :



and more generally, the equilibrium of an $(Y)Si_4O_{10}(OH)_2$ end-member with the corresponding $K(Y)AlSi_3O_{10}(OH)_2$ mica :



in which (Y) may stand respectively for (Fe_2^{3+}) , (Al_2^{2+}) or (Mg_3^{2+}) .

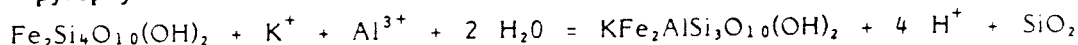
Let us call $\log K_R$ the difference between the two $\log K_{sp}$, respectively the solubility product of the micaceous end members and the solubility product of the corresponding pyrophyllite-talc-like end members :

$$\log K_R = \log K_{sp} (K(Y)AlSi_3O_{10}(OH)_2) - \log K_{sp} ((Y)Si_4O_{10}(OH)_2)$$

The data of Table 11 were calculated from the $\log K_{sp}$ in Table 5 (Fritz, 1981). They are reported in figure 9 and in Table 10.

TABLE 11- Equilibrium constants for conversion of smectites into illites

Fe³⁺-pyrophyllite = Fe³⁺-muscovite



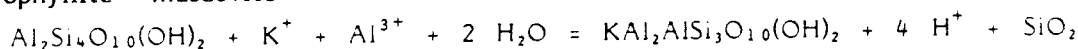
$$\log K_R = \log K_{sp} (KFe_2AlSi_3O_{10}(OH)_2) - \log K_{sp} (Fe_2Si_4O_{10}(OH)_2)$$

$$= 1.088 + 13.700 = 14.788 \text{ at } 25^\circ\text{C}$$

$$= -9.187 + 17.126 = 7.939 \text{ at } 200^\circ\text{C}$$

$$\log K_R (200^\circ\text{C}) - \log K_R (25^\circ\text{C}) = -6.849$$

pyrophyllite = muscovite



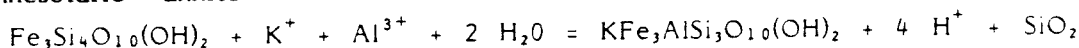
$$\log K_R = \log K_{sp} (KAl_2AlSi_3O_{10}(OH)_2) - \log K_{sp} (Al_2Si_4O_{10}(OH)_2)$$

$$= 16.656 - 1.061 = 15.595 \text{ at } 25^\circ\text{C}$$

$$= 1.777 + 6.116 = 7.893 \text{ at } 200^\circ\text{C}$$

$$\log K_R (200^\circ\text{C}) - \log K_R (25^\circ\text{C}) = -7.702$$

minnesotaite = annite



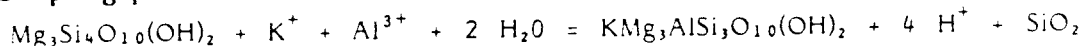
$$\log K_R = \log K_{sp} (KFe_3AlSi_3O_{10}(OH)_2) - \log K_{sp} (Fe_3Si_4O_{10}(OH)_2)$$

$$= 23.273 - 7.235 = 16.038 \text{ at } 25^\circ\text{C}$$

$$= 7.282 + 0.141 = 7.423 \text{ at } 200^\circ\text{C}$$

$$\log K_R (200^\circ\text{C}) - \log K_R (25^\circ\text{C}) = -8.615$$

talc = phlogopite



$$\log K_R = \log K_{sp} (KMg_3AlSi_3O_{10}(OH)_2) - \log K_{sp} (Mg_3Si_4O_{10}(OH)_2)$$

$$= 41.913 - 25.162 = 16.751 \text{ at } 25^\circ\text{C}$$

$$= 21.736 - 14.030 = 7.706 \text{ at } 200^\circ\text{C}$$

$$\log K_R (200^\circ\text{C}) - \log K_R (25^\circ\text{C}) = -9.045$$

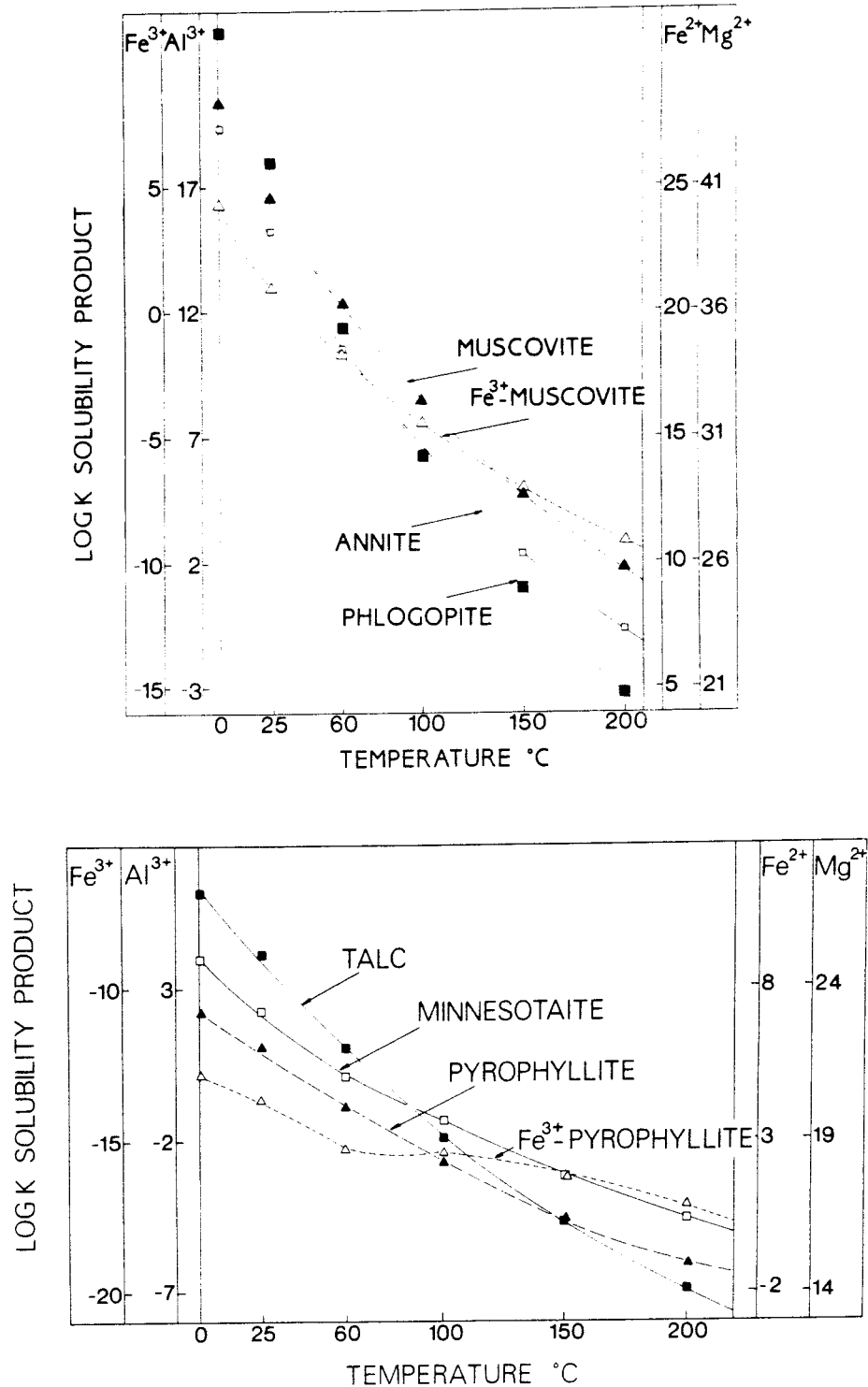


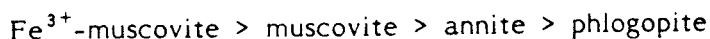
Figure 9- Variation of the solubility product (K_{sp}) of eight clay mineral components, as function of temperature

It appears that :

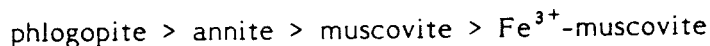
(i) $\log K_R$ increases from the ferric (Fe^{3+}), to the aluminous (Al^{3+}), to the ferrous (Fe^{2+}) and finally to the magnesian (Mg^{2+}) series at 25°C and at 200°C as well ;

(ii) the difference between $\log K_R$ (200°C) and $\log K_R$ (25°C) decreases regularly from the ferric (Fe^{3+}), to the aluminous (Al^{3+}), to the ferrous (Fe^{2+}), and finally to the magnesian series (Mg^{2+}) ;

(iii) at 25°C the relative stability of the micaceous end member compared to the pyrophyllite-talc-like end member decreases in the following order :



(iv) an increase of temperature will tend to reverse this sequence, becoming :



In other words, at low temperatures, the conversion of Fe^{3+} -pyrophyllite into Fe^{3+} -muscovite would tend to be much easier than the transformation of talc into phlogopite-like mineral. At high temperature, this advantage would be attenuated and the transformation of minnesotaite or a talc-like mineral into a ferrous or a magnesian tri-octahedral mica would be preferred. In conclusion, these data suggest that the temperature required for the transformation of a smectite into an illite would be as low if the Fe^{3+} content is high or if the Mg^{2+} content is low. The temperature of the transformation would be high if the Fe^{3+} content is low or if the Mg^{2+} content is high. In all cases, Al^{3+} and Fe^{2+} are in an intermediate position. These calculations confirm natural observations (Fig. 3).

When temperature changes, the solubility products also vary (Table 10 and Fig. 9) and if the model is correct, one may expect that in a given clay mineral with a given chemical composition the relative contribution (X.) of the end members also changes. Data of Table 10 represented on Figure. 9 shows, for example, that the solubility product of phlogopite is the highest at low temperatures and the lowest at high temperatures. Thus, one may expect that the contribution of the phlogopitic end member would be smaller at low temperatures and more important at high temperatures. Furthermore, for similar reasons, one can expect that the contribution of Fe^{3+} -muscovite would be more important at low temperature and negligible in hydrothermal conditions. These contributions were calculated (program CISS FIT) for the glauconite D, the celadonite 2V and the two nontronites given in Table 7. The diagrams of Figure 10 show the relative contribution of the three types of end-members : pyrophyllite, muscovite, celadonite for the three octahedral cations: Al^{3+} , Fe^{3+} and Mg^{2+} at 25°C and at 200°C.

It is interesting to note that the correlation coefficients (Table 8) which are also supposed to reflect the contribution of the end members almost perfectly confirm the distribution based on the multicomponent ideal solid solution model i.e. :

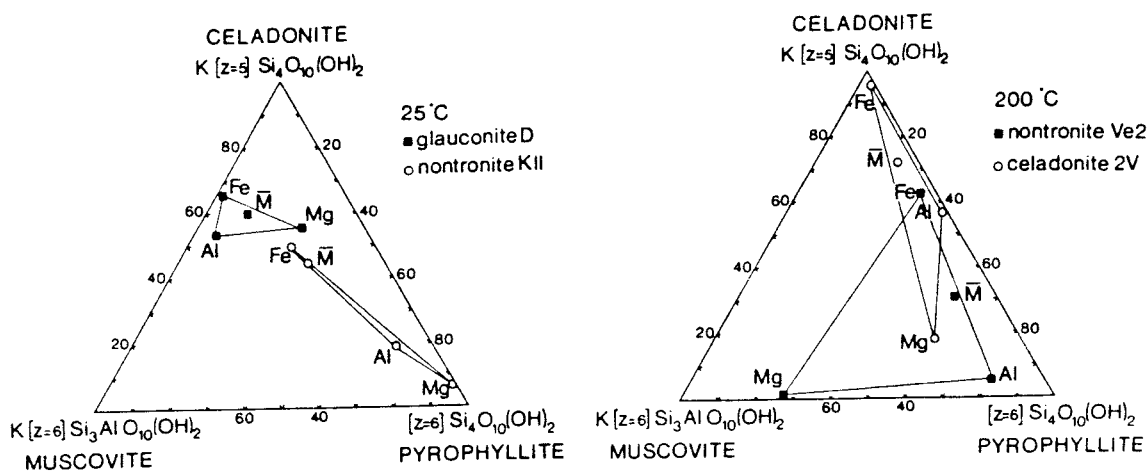


Figure 10- Triangular diagram showing the weighted contribution of the three types of end members (pyrophyllite, muscovite, and celadonite) in the three Fe^{3+} -, Al^{3+} - and Mg^{2+} -clay minerals at 25°C and at 200°C

- at low temperature, the tetrahedral charge is mostly due to the important contribution of the Fe^{3+} -muscovite (glauconite effect) ; Mg^{2+} is mostly related to the talc and Al^{3+} to the pyrophyllite ;

- at high temperature, the tetrahedral charge is mostly due to an important contribution of Mg^{2+} -mica (phlogopite effect) while the octahedral charge is particularly due to Fe^{3+} content (celadonite effect).

These data confirm the fact that the celadonite 2V and the nontronite V2 are of hydrothermal origin and that glauconite D and nontronite K2 are of low temperature origin so that specific compositional correlations obtained for a population of clay particles in fact characterizes its temperature of formation.

9. LOCAL EQUILIBRIA IN POPULATIONS OF MICROSYSTEMS

Chemical analyses of populations of clay particles within different clay samples have shown important variations of composition from one particle to another. If one tries to interpret these variations of composition through equilibrium conditions of multicomponent solid solutions with aqueous solutions, it appears that a true equilibrium condition can only be obtained in a microsystem of one particle and its surrounding solution. Equilibrium cannot be reached between the overall population of particles and the bulk solution. The multicomponent solid solution theory is able to predict, for each individual clay particle, the composition of the solution in which this particle has been equilibrated. One uses the general expression for ideal behaviour :

$$Q_j = K_j X_j$$

The determination of X_j allows also the calculation of the different Q_j (the ionic activity products in solution) and consequently the calculation of the following aqueous activity ratios or activities :

$$[\text{K}^+]/[\text{H}^+], [\text{Mg}^{2+}]/[\text{H}^+]^2, [\text{Al}^{3+}]/[\text{H}^+]^3, [\text{Fe}^{3+}]/[\text{H}^+]^3 [\text{SiO}_2] \text{ etc...}$$

in the corresponding equilibrium solution.

These calculated activity characteristics of the solutions in equilibrium with the different particles of the same clay samples (glauconite D and celadonite 2V) appear in Table 12. In this table, only four particles of celadonite and five particles of glauconite (extreme compositions) were represented among large numbers detected by analyses. The differences in activities of silica and in cation-to-proton activity ratios are more than significant and would correspond to important differences in element molalities (factors varying between 1 to 10). These values give an idea of the dispersion that would represent the real population of aqueous solutions corresponding to all the particles of a sample.

The next question is : what may be the origin of these differences in the activities and activity ratios from one aqueous microsystem to another ? Two major reasons may be found. First, we must remind that clays are built using about 7 to 10 major elements. Some of these elements, major in the solid solution are quite always traces in the solution because of their very low "solubility" (like Al, Fe^{3+} and even Fe^{2+}). The formation of any clay micro-sample will then have a drastic effect on the aqueous molalities of these elements and will strictly depend on their availability not only in the aqueous solution but also in the solid phase being destroyed. And then we reach the second point, the mobilities of the different elements in the solution, from one of these microsystems to another, which could also explain part of such chemical differences.

CONCLUDING REMARKS

Many natural occurrences, chemical experimental data, crystallographic observations and theoretical reasons together suggest that clay minerals are metastable phases at the surface of the Earth. This is also true for some other kinds of minerals such as Mg-calcites, iron and aluminum oxides and hydroxides and minerals which present crystal defects, cationic substitutions and grain size variabi-

TABLE 12- Calculated chemical composition of the solutions supposed to be in equilibrium with several clay particles of different compositions selected within the glauconite D population (at 25°C) and the celadonite 2V population (at 200°C)

	Temps	1	2	3	4	5	6	7	8
Glauconite D 32	25°C- 3.35	5.08	- 1.94	12.18	9.25	2.08	17.60	7.51	
Glauconite D 31	25°C- 3.15	5.45	- 1.79	12.23	8.14	1.00	2.45	7.55	
Glauconite D 4	25°C- 2.82	5.40	- 2.31	11.92	7.65	0.58	1.61	10.00	
Glauconite D 28	25°C- 3.01	5.27	- 2.16	12.07	8.18	1.08	15.57	10.37	
Glauconite D 9	25°C- 2.80	5.39	- 2.25	11.91	7.54	0.49	1.43	8.76	
Glauconite D Mean	25°C- 3.07	5.35	- 1.96	12.14	8.13	6.61	14.98	8.11	
Celadonite 2V 5N	200°C- 2.60	1.37	- 4.24	7.89	2.40	—	9.72	- 5.42	
Celadonite 2V 6N	200°C- 2.61	1.23	- 4.30	7.86	2.62	—	9.46	- 6.83	
Celadonite 2V 5B	200°C- 2.43	1.03	- 4.66	7.65	2.49	—	—	- 7.27	
Celadonite 2V 6B	200°C- 2.53	1.19	- 4.41	7.77	2.50	—	—	- 7.53	
Celadonite 2V Mean	200°C- 2.55	1.23	- 4.39	7.81	2.51	—	8.96	- 6.75	

(1) : $\log [\text{SiO}_2]$; (2) : $\log [\text{Al}^{3+}]/[\text{H}^+]^3$; (3) : $\log [\text{Fe}^{3+}]/[\text{H}^+]^3$; (4) : $[\text{Mg}^{2+}]/[\text{H}^+]^2$; (5) : $\log [\text{K}^+]/[\text{H}^+]$; (6) : $\log [\text{Na}^+]/[\text{H}^+]$; (7) : $\log [\text{Ca}^{2+}]/[\text{H}^+]^2$; (8) : $\log K_{\text{sp}}$ of the solid solution

lility.

However, the abundance, the diversity and the environmental specificity of the different smectites and illites, found in various sediment facies, weathering products and hydrothermal alterations, suggest that these clay minerals and their chemical composition variations, somewhat reflect the temperature at which they form and the differences of the chemical conditions in which they tend to equilibrate. Thus, the thermodynamics stability of clay minerals merits further exploration.

Almost all the XRD-determined pure clay phases are in fact mixtures of particles of highly dispersed chemical compositions. Furthermore, within a monomineralic population of particles, chemical variables are intercorrelated in such a way that the signs of the correlations clearly reflect the temperature at which that population has been formed.

A thermodynamic ideal solid-solution analogue has been proposed to explain such particle population behaviour :

(i) each particle is assumed to be - at a particle scale - an ideal solid solution of several end-members (mineral components) ;

(ii) there is no counter-indications to consider that each particle is a solid solution of discrete layers of various chemical compositions; the validity of the solid solution concept is unaffected by the scale at which the end-member mixing is organized : at a molecular scale, at a layer scale or at any intermediate scale (domains) ;

(iii) each individual particle is assumed to be in equilibrium, in its own micro-environment, with an aqueous solution, differing in composition from one particle to another ;

(iv) the chemical composition of each particle treated separately can be expressed as the weighted contribution of all end-members, the weight of which being variable as function of temperature and of the chemical composition of the microsite

aqueous solution ;

(v) according to the definition of the equilibrium condition ($X_i = Q_i/K_i$), the higher the solubility product of a given end-member, the lower its weighted contribution to the solid solution ; the lower the solubility product of a given end-member, the higher its weighted contribution into the solid solution. At low temperatures, the dominant end-members are :

- for iron, the Fe^{3+} -muscovite, so that glauconite is the only mica stable at room temperatures ;

- for aluminum, both pyrophyllite and Al^{3+} -celadonite, so that montmorillonite is the most stable aluminous clay mineral in hydrothermal conditions ;

- for magnesium, the talc and the Mg-celadonites end-members so that stevensites are stable.

In hydrothermal conditions :

- for iron, the Fe^{3+} - celadonites are more stable ;

- for aluminum the Al^{3+} - mica is dominant so that illite is stable ;

- for the magnesium, the phlogopite end-member is dominant, so that saponites are the hydrothermal stable smectites.

Glauconites (Fe^{3+} -mica) form at low temperatures. Illites (Al^{3+} -mica) form at higher temperatures. Mg-illite would form at much higher temperatures but chlorite is stable at lower temperature and becomes the most stable phase which involves magnesium.

Thus it can be imagined that a stock of individual smectite layers of different compositions, organized in particles, would be progressively used as temperature increases, to form illitic layers. At low temperatures, the first illitic layers formed are the Fe^{3+} -rich layers. When temperature increases, the illitic layers which form are aluminous. At the same time, the Mg-rich layers are progressively converted into saponite, then into corrensite and finally into chlorite.

In this schematic model, smectite may dissolve and be replaced by illitic layers at any temperature ranging from the lowest to the highest ones. When burial diagenesis increases, temperature increases, illites of different compositions form continuously and the number of illitic layers increases. Finally, smectite disappears and illite dominates, together with chlorite, in the clay fraction.

Thus, the model accounts for the compositional variabilities and for the observed correlations among chemical components within a population of individual particles constituting a given XRD determined clay mineral phase.

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Radar measurements performed at the Klipperås study site

Seje Carlsten, Olle Olsson, Stefan Sehlstedt,
Leif Stenberg

Swedish Geological Co, Uppsala/Luleå

February 1987

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Fuel rod D07/B15 from Ringhals 2 PWR: Source material for corrosion/leach tests in groundwater

Fuel rod/pellet characterization program part one

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Studsvik Energiteknik AB, Nyköping

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Calculations on HYDROCOIN level 1 using the GWHRT flow model

Case 1 Transient flow of water from a borehole penetrating a confined aquifer

Case 3 Saturated-unsaturated flow through a layered sequence of sedimentary rocks

Case 4 Transient thermal convection in a saturated medium

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Stockholm

March 1987

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Calculations on HYDROCOIN level 2, case 1 using the GWHRT flow model

Thermal convection and conduction around a field heat transfer

experiment

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Applications of stochastic models to solute transport in fractured rocks

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Royal Institute of Technology, Stockholm
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Harwell Laboratory, Oxfordshire
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Kåre Tjus* and Peter Wikberg**
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Combined interpretation of geophysical, geological, hydrological and radar investigations in the boreholes ST1 and ST2 at the Saltsjö tunnel

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Olle Olsson
Allan Stråhle
Swedish Geological Co, Uppsala
1987-06-30

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Geochemical interpretation of groundwaters from Finnsjön, Sweden

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August 23, 1987

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Corrosion tests on spent PWR fuel in synthetic groundwater

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Stockholm, September 1987

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The July – September 1986 Skövde aftershock sequence

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TR 87-18

Calculation of gas migration in fractured rock

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**Calculation of gas migration in fractured
rock – a continuum approach**

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September 1987