

DIAGENETIC ILLITE-CHLORITE ASSEMBLAGES IN ARENITES. I. CHEMICAL EVOLUTION

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Abstract—Authigenic chlorites and illites coexisting in clastic reservoir sandstones have been studied by energy dispersive X-ray spectroscopy (EDS) in the transmission electron microscope (TEM). All 16 samples studied are drill or sidewall cores from sandstones of relatively uniform age situated offshore Norway with burial depths ranging between 2400 m and 5000 m and representing temperatures between 90°C and 180°C. Chlorites and illites with authigenic equilibrium type texture and morphology were analyzed by EDS. Tetrahedral Al and octahedral Fe+Mg in chlorite increases with burial at the expense of Si and vacant octahedral positions in the chlorite structure. Illites show a clear increase in K. These factors indicate that a continuous chemical modification of these minerals takes place in the diagenetic interval studied through continuous dissolution and precipitation reactions.

Key Words—ATEM, Chlorite, EDS, Illite.

INTRODUCTION

Chlorites and illites occur together in many diagenetic environments. They are important because their structural and chemical reorganization is often related to temperature and because of their influence on petrophysical parameters like porosity and permeability in hydrocarbon reservoir rocks.

Following the lead of Chai (1974) and Baronnet (1982), Ostwald ripening-related recrystallization of minerals in natural systems has been studied by Eberl and Srodon (1988), Inoue *et al.* (1988) and Eberl *et al.* (1990). Their studies suggest that authigenic illites follow closed system grain coarsening kinetics. This means that larger illite crystals grow at the expense of smaller illite crystals with the difference in surface energy as the driving force.

Velde and Medhioub (1988), Jahren and Aagaard (1989), and Hillier and Velde (1991) have shown distinct temperature-dependent chemical compositional trends in authigenic chlorite. This supports continuous recrystallization of chlorite consistent with Ostwald ripening as found by Eberl *et al.* (1990) and Jahren (1991). Evidence for the dynamic growth of chlorite is also expressed in compositional trends within single chlorite grains from the core of the crystal to the rim (Jahren 1991). This implies that the surface of each chlorite crystal forms in equilibrium with the evolving porewater composition at any temperature during crystal growth and that the interior retains its original composition. The evolution of the porewater composition is a function of the minerals buffering the system. Because the solubility of silicates is so low, the saturation situation in diagenetic environments containing clay is fixed by equilibrium conditions between these high surface area minerals. This leads to a chemical evolution of the minerals precipitated (Hutcheon and Ab-

ercrombie, 1989; Aagaard *et al.*, 1990). The aim of the present paper is to establish illite, chlorite, and illite-chlorite compositional relations in sandstones in the temperature interval 90°–180°C.

METHODS

Core samples from the North Sea and Haltenbanken areas offshore Norway were studied. Samples containing both illite and chlorite were found in medium to deeply buried (2400–5000 m) relatively clean sandstones from the North Sea area and the Haltenbanken area of the Norwegian Continental Shelf (Table 1 and Figure 1).

The individual EDS analyses were performed on euhedral grains similar to the chlorite and illite crystals shown in Figure 2. Chlorites were analyzed in the rim area and illites towards the tip of the crystal to ensure that the morphologically youngest part of the crystals was analysed to delineate eventual temperature-dependent compositional variations related to dynamical growth of single crystals. The EDS results for the 16 samples studied containing coexisting illite and chlorite are presented in Table 2. The data presented are mean values based on analyses of between 5 and 15 individual grains of both illites and chlorites in each sample.

The core samples were gently crushed in an ethanol-filled mortar to suspend the clay content. A drop of this dilute alcohol suspension was transferred onto a Cu grid covered with a holey carbon film. After evaporation of the alcohol, the samples were investigated at 200 kV in a JEM 200 CX Transmission Electron Microscope (TEM) equipped with a TRACOR NORTERN TN2000 Energy Dispersive X-ray Analyzer utilizing modified TRACOR NORTERN software for quantitative evaluation of spectra.

EDS in a TEM can never become a quantitative

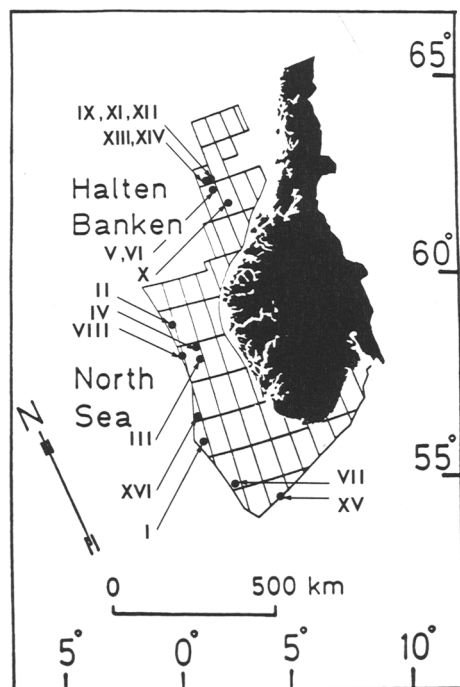


Figure 1. Well location map.

method in the sense wavelength dispersive spectroscopy (WDS) performed in a microprobe is a quantitative method, but it is the best method available for chemical analysis of individual clay-sized particles. In this study, which concentrates on relative differences in major components as a function of temperature, experimental *k*-factors have been used with estimated nominal uncertainties of around 2%. The analytical errors vary between 2–5% of the quantity reported for the major elements in both illites and chlorites rising to between 5% and 20% for Fe in illite and in some cases 50% for Mg in illite. Despite these statistical errors, the correlation between analyses of illite in the

a) chlorite

200 nm

b) illite

500 nm

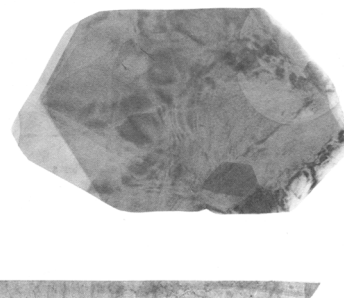


Figure 2. (a) Typical authigenic euhedral chlorite crystal from sample XV: The crystal is 4 μm across; (b) filamentous authigenic illite crystals from sample IX. The crystal has a width of 200 nm.

same sample is good for both major and minor elements. Each spectrum was fitted to a standard spectrum composed of Mg, Al, Si, K, Ca, Mn, and Fe peaks to minimize absorption, peak shifts, overlap, and statistical errors. The amounts of Ca and Mn in illites and chlorites were always very low (<1%) and are considered insignificant for this work. The structural formulas were calculated based on a charge of 22 and 28 for illite and chlorite, respectively, and all Fe was taken as Fe^{2+} . Formation temperatures were taken from corrected well measurements based on bottom hole temperatures and geothermal gradients.

RESULTS

Out of a selection of more than 30 core samples from generally feldspathic sandstones analyzed earlier by SEM and XRD, 16 samples contained both chlorite and illite as authigenic phases. The rest of the samples contained either only non-silicate iron minerals like pyrite, siderite, or ankerite, or various mixed-layer chlorite/smectite/illite iron and magnesium rich layer-silicates. These samples are not considered further here.

Table 1. Sample details.

Sample	Well location	Depth (m)	T (°C)	Formation	Age
I	Heimdal	2393	90	Heimdal	Paleocene
II	Statfjord	2852	110	Statfjord	Hettangian
III	Veslefrikk	3077	120	Intra Dunlin	Pliensbachian
IV	Oseberg	3463	130	Oseberg	Bajoc/Baton
V	Haltenbanken	3803	140	Garn	Bajocian
VI	Haltenbanken	3838	142	Garn	Bajocian
VII	Mime	4182	150	Ula	Kimmer/Volg
VIII	Hild	4258	150	Tarbert	Bathonian
IX	Haltenbanken	4357	155	Tilje	Sinemurian
X	Haltenbanken	4370	155	Garn	Bajocian
XI	Haltenbanken	4464	160	Tofte	Pliensb/Toarch
XII	Haltenbanken	4470	160	Tofte	Pliensb/Toarch
XIII	Haltenbanken	4504	162	Tilje	Sinemurian
XIV	Haltenbanken	4505	162	Tilje	Sinemurian
XV	Central Graben	4900	175	—	Rhaetian
XVI	S. Viking Gr.	4967	180	Intra Draupne	Kimmer/Volg

Table 2. EDS results from coexisting illites and chlorites. Al_o and Al_t represent the octahedral and tetrahedral Al, respectively.

Sample	Illites												
	K	±	Mg	±	Fe	±	Al _o	±	Al _t	±	Si	±	No. ana
I	0.72	0.029	0.25	0.046	0.16	0.012	1.60	0.046	0.40	0.012	3.60	0.072	5
II	0.75	0.027	0.08	0.018	0.07	0.008	1.87	0.062	0.67	0.021	3.33	0.071	6
III	0.75	0.031	0.15	0.040	0.20	0.014	1.71	0.039	0.60	0.014	3.40	0.051	5
IV	0.85	0.037	0.06	0.025	0.08	0.015	1.86	0.067	0.71	0.026	3.29	0.079	6
V	0.77	0.035	0.08	0.025	0.06	0.009	1.83	0.081	0.54	0.022	3.46	0.082	6
VI	0.82	0.026	0.12	0.032	0.08	0.014	1.81	0.058	0.64	0.020	3.36	0.067	7
VII	0.88	0.044	0.13	0.049	0.08	0.017	1.78	0.075	0.64	0.027	3.36	0.104	5
VIII	0.81	0.042	0.04	0.014	0.09	0.021	1.85	0.080	0.63	0.027	3.37	0.104	5
IX	0.89	0.048	0.10	0.039	0.11	0.020	1.78	0.075	0.64	0.027	3.36	0.098	10
X	0.90	0.027	0.08	0.024	0.04	0.005	1.88	0.059	0.72	0.018	3.28	0.068	7
XI	0.86	0.038	0.09	0.036	0.12	0.014	1.78	0.066	0.64	0.024	3.36	0.087	11
XII	0.87	0.030	0.10	0.040	0.10	0.013	1.81	0.051	0.69	0.019	3.31	0.060	10
XIII	0.87	0.052	0.11	0.061	0.12	0.024	1.71	0.087	0.50	0.026	3.50	0.112	4
XIV	0.92	0.040	0.15	0.045	0.22	0.022	1.65	0.063	0.63	0.024	3.37	0.081	7
XV	0.93	0.051	0.11	0.038	0.28	0.029	1.65	0.085	0.66	0.034	3.34	0.097	5
XVI	0.86	0.031	0.09	0.027	0.08	0.009	1.86	0.050	0.76	0.021	3.24	0.058	12

Sample	Chlorites											
	Mg	±	Fe	±	Al _o	±	Al _t	±	Si	±	No. ana	
I	1.61	0.061	2.36	0.050	1.68	0.040	1.01	0.024	2.99	0.051	10	
II	1.04	0.072	2.95	0.073	1.65	0.050	0.93	0.028	3.07	0.077	8	
III	0.90	0.053	2.98	0.055	1.82	0.036	1.22	0.024	2.78	0.074	9	
IV	1.24	0.074	2.79	0.140	1.68	0.072	1.09	0.049	2.91	0.108	7	
V	0.90	0.050	3.05	0.067	1.79	0.050	1.27	0.036	2.73	0.055	14	
VI	0.76	0.046	3.05	0.061	1.86	0.041	1.20	0.024	2.80	0.056	8	
VII	1.81	0.080	2.43	0.063	1.59	0.048	1.24	0.037	2.76	0.061	6	
VIII	0.62	0.059	3.24	0.063	1.76	0.044	0.99	0.025	3.01	0.069	9	
IX	0.65	0.052	3.30	0.066	1.79	0.043	1.27	0.030	2.73	0.074	12	
X	0.93	0.053	2.80	0.051	1.79	0.036	0.84	0.024	3.16	0.064	17	
XI	0.71	0.046	3.28	0.056	1.76	0.040	1.26	0.029	2.74	0.066	15	
XII	0.90	0.057	3.34	0.053	1.59	0.037	1.26	0.029	2.74	0.060	8	
XIII	0.93	0.062	3.19	0.073	1.66	0.045	1.25	0.034	2.75	0.080	14	
XIV	0.80	0.047	3.16	0.057	1.78	0.044	1.26	0.035	2.74	0.072	11	
XV	0.46	0.040	3.54	0.067	1.76	0.040	1.28	0.029	2.72	0.065	8	
XVI	0.39	0.040	4.13	0.087	1.46	0.039	1.32	0.036	2.68	0.075	6	

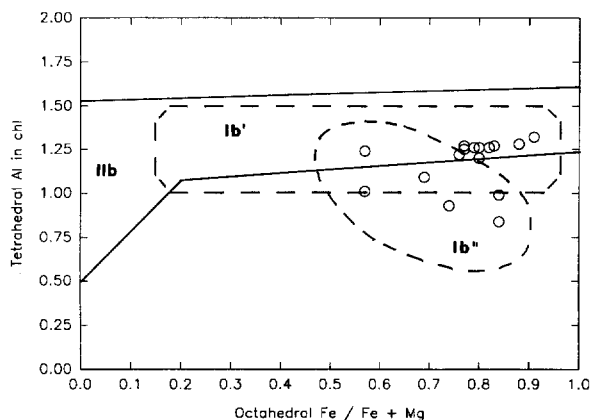


Figure 3. Chlorite analyses plotted as in Bailey and Brown (1962) with the compositional fields defined by the composition estimates in Bailey and Brown (1962), (field Ib'); Curtis *et al.* (1985), (field Ib''); and 95% of the metamorphic Ib chlorites compiled by Foster (1962), (field I Ib, solid lines).

Chlorites

With all Fe taken as Fe²⁺ all chlorite samples analyzed in this work are chamosites (Foster 1962). The Fe/(Fe+Mg) values range between 0.57 and 0.91 (Figure 3) and all samples plot inside the combined compositional ranges found by Bailey and Brown (1962) for Ib ($\beta = 90^\circ$) chlorites, and by Curtis *et al.* (1985) for authigenic chlorites of the same type. These results are similar to earlier studies of diagenetic chlorites (Hayes, 1970; Curtis *et al.*, 1984, 1985; Velde and Medhioub, 1988; Jahren and Aagaard, 1989; Jahren, 1991). Another feature of the chlorites is that they tend to have less total Fe + Mg than metamorphic chlorites (Curtis *et al.*, 1984). This could be due to change in polytype from Ib to I Ib, but as Figure 4a indicates there is an increase in the total amount of Fe + Mg as a function of temperature as well within the Ib authigenic chlorite group. The reason for this is a slight temperature-dependent decrease in octahedral vacancies and Si in chlorites (Figures 4b and 4c). This is not entirely compensated by a slight increase in the total amount

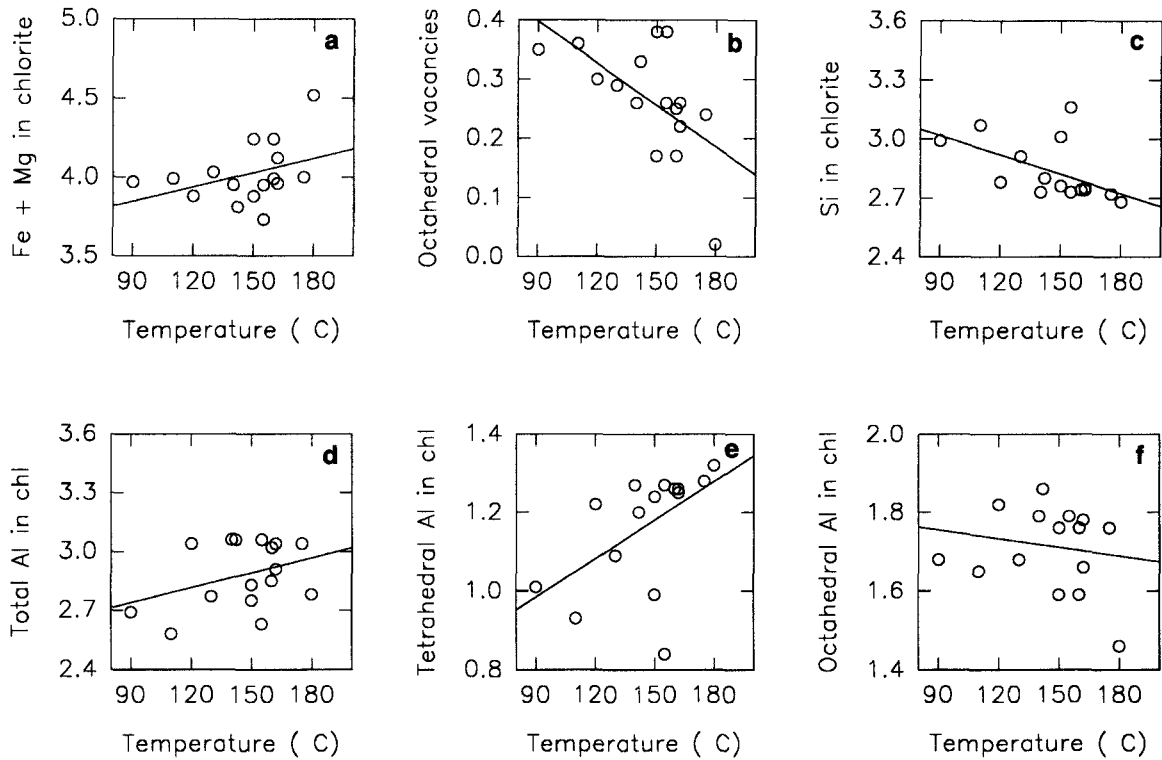


Figure 4. Temperature-dependent compositional trends in chlorite: (a) divalent cations with temperature, (b) octahedral vacancies, (c) decrease in Si, (d) total Al in the structure, (e) tetrahedral Al in chlorite vs temperature, and (f) octahedral Al. All solid lines are linear regression lines.

of Al (Figure 4d). The Al increase is confined to the tetrahedral positions (Figure 4e), with no definitive trend in octahedral Al (Figure 4f).

Another feature of the chlorites investigated is the apparent temperature-dependent variation in Mg and Fe. Mg decreases and Fe increases with increasing temperature (Figures 5a and 5b). This is rather surprising (Jahren and Aagaard, 1989) but can be explained by differences in host rock composition and precursor minerals because most of the iron-rich chlorites are found in deeply buried, relatively clean Haltenbanken

sandstones. The slightly less Fe-rich chlorites are generally found in shallower North Sea sandstones. The Mg vs Fe plot shown in Figure 5c fixes the Mg + Fe amount in all chlorites to around four formula units. This illustrates that the compositional range of chlorites in sedimentary environments is restricted.

Illites

The compositional trends in illites as a function of temperature are not as clear as in the chlorites. The best trend found in this study is the amount of K as a

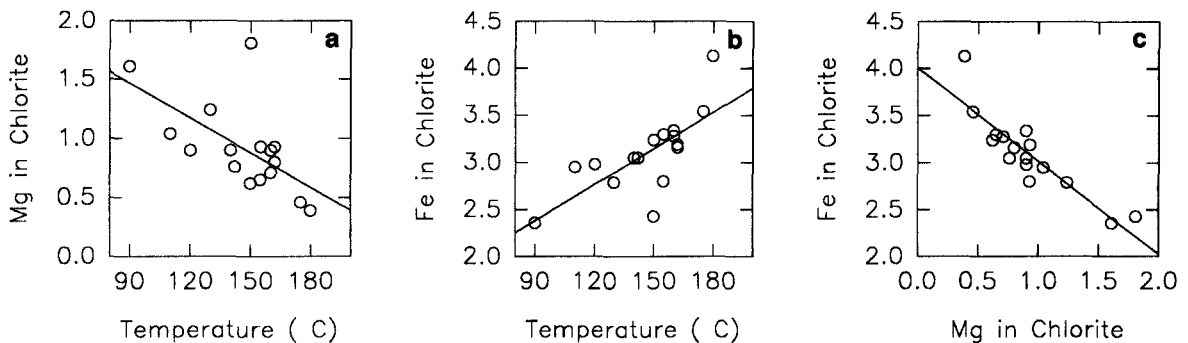


Figure 5. Fe-Mg relations in chlorites: (a) a decrease in Mg; (b) an increase in Fe as a function of temperature; (c) the sum of Fe and Mg in the chlorite structure, always around 4.

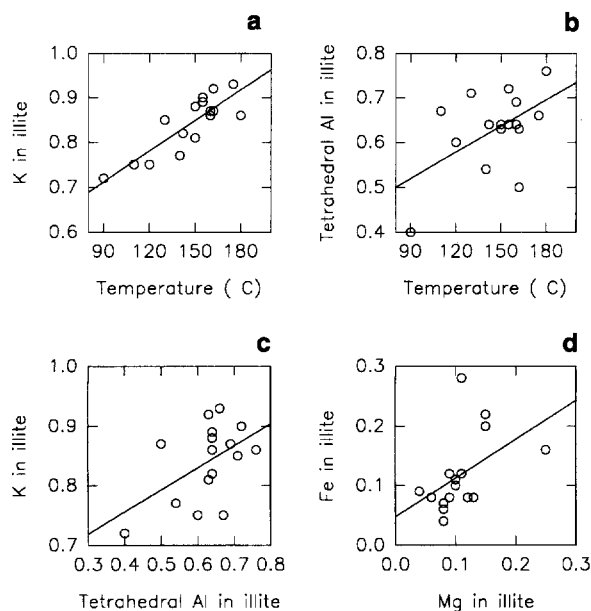


Figure 6. Illite compositional trends: (a) potassium vs temperature; (b) tetrahedral Al vs temperature; (c) relationship between K and tetrahedral Al; (d) relation between Fe and Mg in the illite structure.

function of temperature (Figure 6a). From Figures 6b and 6c it is evident that no simple relation among tetrahedral Al and temperature and K content exists in illites. The reason for this is the variable amounts of Fe, Mg, and Al in illites (Figure 6d) which account for charge differences in the octahedral layer of the illite structure.

DISCUSSION

The increase in tetrahedral Al in chlorites (Figure 4e) is similar to the trends found by Cathelineau and Neiva (1985) and Cathelineau (1988) for hydrothermal chlorites, and by Jahren and Aagaard (1989) and Hillier and Velde (1991) for sedimentary chlorites. Cathelineau (1988) has suggested that the tetrahedral Al content can be used as a geothermometer in hydrothermal systems. In sedimentary systems the tetrahedral Al content in chlorites is a function of formation temperature, ripening history and host rock composition (Jahren, 1991) and can therefore not be used as more than an indication of the formation temperature. In hydrothermal systems the composition of the host rock and the hydrothermal solution will play a part in making a tetrahedral Al geothermometer valid only in calibrated individual systems.

In many of the shallower samples buried to less than about 4000 m, illite coexists with kaolinite or dickite. Some workers have proposed that illite does not form in the Haltenbanken area of offshore Norway, for kinetic reasons, before around 130°–140°C, and then with kaolinite as a precursor (Bjørlykke *et al.*, 1986; Ehren-

berg and Nadeau, 1989). Porewater composition studies, on the other hand, have shown no significant change in porewater composition and pH in the temperature interval where the kaolinite-illite transition takes place (Aagaard *et al.*, 1990). This result indicates that illite buffers the porewater composition at lower temperatures than the kaolinite-to-illite transition temperature. Petrographic evidence for the presence of illite before the massive illitization event in these rocks is scant but Ehrenberg and Nadeau (1989) reported some incipient illitization at about 125°C based on SEM observations, possibly with a more unstable precursor than the kaolinite-K-feldspar assemblage.

In this study illite is found in minor amounts between 90° and 130°C as tiny filamentous crystals not easily detectable by methods other than TEM. Illite is widespread at higher temperatures. The appearance of massive illite in wells with present day burial temperatures of more than 130°–140°C in both the Haltenbanken and North Sea areas is interesting because these wells are at their maximum burial. The Haltenbanken sandbodies have undergone 0.5 to 1 km of subsidence in the Pleistocene, which means that the illitization is mainly temperature dependent and very recent. On the other hand, K-Ar ages from virtually all dated illite populations from this area give ages between 30 and 55 my (Ehrenberg and Nadeau, 1989). This dilemma, old ages on one side and a dynamical illite system continuously recrystallizing on the other side giving younger and younger ages as recrystallization proceeds, cannot be harmonized. In view of the evidence presented by Eberl and Srodon (1988) on sericites, K-Ar dating of clay-sized particles in complicated systems like sedimentary environments is an unreliable method. The reason for this could be contamination problems; e.g., 1% contamination by a 1500-my-old sericite would give a recent illite population an age of 15 my.

Indirect evidence for an ongoing dynamical grain coarsening dependent upon time and temperature is found in the K increase in illites shown in Figure 6a interpreted to reflect an increase in crystal thickness supporting an Ostwald ripening-related recrystallization. The amount of K in illites can be viewed as a function of the number of 2:1 layers in each crystallite. If the illite crystals are fundamental particles (Nadeau, 1985), that is 2 nm, or two 2:1 layers thick, only one K layer is required to hold the two 2:1 layers together. This means that only 0.5 formula unit of K is necessary, theoretically. For 10 2:1 layers 0.9 formula unit of K is necessary, etc. Ideally this would give a 1:1 correlation between K and tetrahedral Al to maintain particle neutrality. A K increase from 0.7 per formula unit at 100°C to 0.9 per formula unit at 160°C would, if all interlayer positions are filled, represent an increase in illite size of about three times (from about three 2:1 layers to about ten 2:1 layers). This would theoretically, in a closed system, require that 85% of the total volume

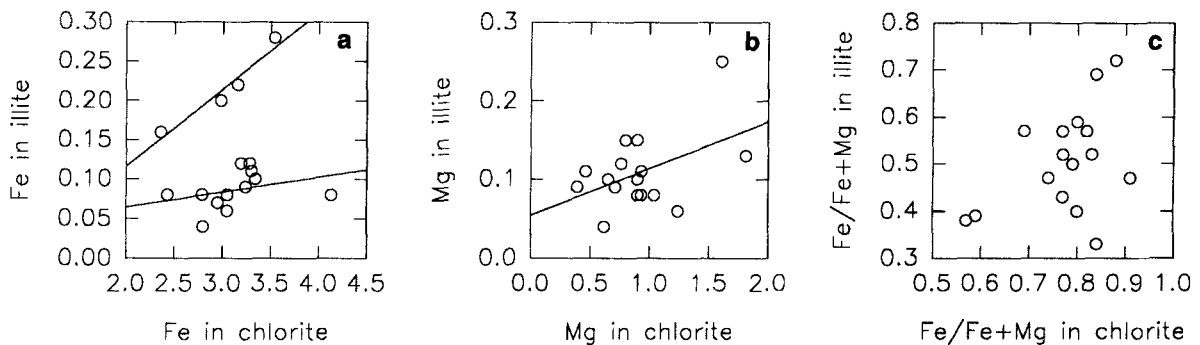


Figure 7. Illite-chlorite relations: (a) Fe in chlorite vs Fe in illite, (1) represents pure illite and (2) represents illite with probable intercalation of Fe-layer silicate; (b) Mg in chlorite vs Mg in illite; (c) Fe/Fe+Mg in chlorite vs Fe/Fe+Mg in illite.

of illite have reequilibrated ages and oxygen isotopes during dissolution-reprecipitation reactions.

Ostwald ripening theory is, however, difficult to apply directly to the coarsening of illite near the massive illitization temperature because the theory is not valid where mineral reactions take place. The kaolinite plus K-feldspar reaction ends when one of them is totally consumed by the illite formation reaction, usually taking place around 140°C. After the completion of the kaolinite conversion, illite is expected to follow closed system grain coarsening kinetics again because of its small crystal size. Before the massive illitization event at around 140°C, illite is always supersaturated in the porewater (Aagaard *et al.*, 1990). But from TEM observations, only a few small crystals nucleate early and then grow very slowly until, for kinetic reasons, a new nucleation event takes place. This nucleation event is a result of a build-up of illite supersaturation as the kaolinite + K-feldspar assemblage becomes unstable. This increase in supersaturation apparently cannot be compensated by growth of the few existing illite crystals in the system.

In this study the kaolinite is generally absent in the deeper samples where illitization has taken place, indicating excess K-feldspar. In some wells, however, kaolinite is present because of insufficient internal K supply (no K-feldspar left in the rock) for the kaolinite-to-illite mineral reaction to go to completion. This is the case for the deepest sample studied, where fresh kaolinite crystals are encountered at almost 5000 m burial and 180°C. The last observation is important, and indicates that neither the amount of mass transfer as a result of advective fluid flow, convective fluid flow, or ion diffusion through a static porewater are very effective mass transfer processes in deeply buried sandstones (Bjørlykke *et al.*, 1988).

There is a positive correlation between the amount of Fe in coexisting chlorites and illites (Figure 7a) with a higher Fe/Mg ratio in chlorites relative to the coexisting illites, as expected from a thermodynamic point of view (Velde, 1985). But Figure 7a seems to indicate two separate trends (1 and 2). These trends suggest that

the illite crystal populations with slightly higher Fe content (2) relative to the main illite-chlorite trend (1) could incorporate either a trioctahedral illite component or that a "chloritic" or "smectitic" component is present and intercalated in the illite structure. Except for one Mg+Fe-rich sample (sample I) with a substantial higher Mg content than Fe in the illite structure (Figure 6d), the Fe vs Mg trend indicates that the last explanation is the correct one. The octahedral totals analyzed in illite range between 1.94 and 2.04 with a mean value of 2.00, which is the theoretical value for dioctahedral illites. This fact indicates that eventual pure chlorite or trioctahedral illitic component intercalated in illite is unimportant because chlorite and trioctahedral illite would lead to higher octahedral totals. The Mg in illite vs Mg in chlorite plot depicted in Figure 7b does not show two distinct trends as in the Fe case because of the statistical problems inherent in the analyses. This problem makes it impossible to delineate a reciprocal relationship between the Fe/Fe+Mg ratios in illite and chlorite (Figure 7c) expected in a co-precipitation case.

CONCLUSION

Compositional trends in chlorites and illites as a function of temperature have been delineated and formation relations between the two minerals have been established. The range in chemical composition of authigenic chlorite populations agrees with earlier findings (Curtis *et al.*, 1985; Velde, 1985; Hillier and Velde, 1991).

The illite compositions reported from sandstones are characterized by potassium values between 0.75 and 1, and low Fe and Mg (Srodon and Eberl, 1984) which are in accordance with the results in this study. The temperature-dependent Al/Si compositional variations found in chlorites are interpreted as the result of Ostwald ripening-related recrystallization for all temperatures through dissolution and reprecipitation reactions. The apparent temperature-dependent Fe/Mg chlorite trend present in these analyses and contradic-

tory to earlier findings (Jahren and Aagaard, 1989; Jahren, 1991) is interpreted to be source related.

Grain coarsening in the illite case consists of grain growth with material supplied from outside the illite population (kaolin minerals + K-feldspar) at shallow depth and Ostwald ripening later in the diagenesis. Only minor amounts of illite are necessary to buffer the porewater composition in siliciclastic rocks. This could explain the lack of change in porewater composition (Aagaard *et al.*, 1990) when the time and temperature-dependent kaolinite-to-illite reaction becomes petrographically observable. The reactions take place in a porewater where the pH is buffered by silicate hydrolysis (Hutcheon and Abercrombie, 1989). The kaolin conversion in the Haltenbanken samples is mainly a function of temperature because the sedimentary rocks in the area have undergone more than 1000 m subsidence in the Pleistocene only, implying massive illitization has taken place in the last 3 my only. Co-precipitation of illite and chlorite is indicated, but more reliable data on Fe/Mg ratios in illites are needed to confirm this behaviour.

In some reservoirs fresh kaolin minerals persist in the system down to present day temperatures of 180°C, indicating that mass transfer from K-rich environments like shales is not a very rapid process. This supports isochemical diagenesis (Ehrenberg, 1991) as a general rule where the burial depths have exceeded the maximum depth for meteoric water recharge (Bjørlykke *et al.*, 1988).

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