

CHARACTERIZATION OF OVERGROWTH STRUCTURES FORMED AROUND INDIVIDUAL CLAY PARTICLES DURING EARLY DIAGENESIS

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Abstract—The coarse (0.4–2 μm) clay fraction of an Albian black shale collected in the Atlantic Ocean (Deep Sea Drilling Project leg 11) consists chiefly (90–95%) of smectite and 5–10% illite. Both minerals are locally surrounded by overgrowth structures, such as fine laths about 0.05–0.4 μm long and 0.02–0.1 μm wide. Individual laths or assemblages of laths protrude from the center of smectite flakes at angles of about 60° to each other. Laths occur around illite crystals in a similar manner or coalesce into a rim that consists of 0.05–0.1- μm -size particles. On the basis of scanning transmission electron microscopy: (1) the center of individual illite crystals consists of a dioctahedral mineral, but the overgrowth structures are Al-Fe beidellites; and (2) the smectite flakes have highly variable compositions, but correspond chiefly to Fe-Al-beidellite, whereas the overgrowths are compositionally close to montmorillonite.

The overgrowth structures seem to have formed during early diagenesis. The chemical composition of overgrowths around illite and smectite tend to be similar in response to the new environment, implying an addition of silica to both materials.

Key Words—Beidellite, Diagenesis, Illite, Montmorillonite, Overgrowths, Scanning electron microscopy.

Resumé—La fraction argileuse (0,4–2 μm) d'un échantillon de black shale albien de l'Atlantique (Deep Sea Drilling Project leg 11) surtout formée de smectite (90–95%) et d'illite (5–10%) a été étudiée. L'étude morphologique des particules en microscopie électronique montre qu'elles sont souvent entourées de sur-croissances généralement formées de lattes très fines longues de 0,05 à 0,4 μm et larges de 0,02 à 0,1 μm . Autour des flocons de smectite, les lattes peuvent être isolées ou former des assemblages de 4 ou 5 lattes formant fréquemment des angles de 60° entre eux. Des faciès identiques se rencontrent autour des illites mais ces minéraux peuvent aussi être entourés de lattes courtes (0,05 à 0,1 μm) et coalescentes formant une auréole plus ou moins continue autour du cristal.

L'analyse de ces argiles par microscopie électronique analytique montre: (1) que la composition du centre des particules d'illite correspond à des minéraux dioctaédriques mais les lattes qui les entourent sont des beidellites Al-Fe; (2) que la composition du centre des smectites, beaucoup plus variable d'une particule à l'autre, correspond à des beidellites Fe-Al et les lattes qui les entourent à des montmorillonites.

Ces sur-croissances semblent se former au cours de la diagenèse précoce. Le fait que la composition des lattes poussant autour des illites converge vers celle des lattes entourant les smectites constitue une indication de la réponse des minéraux à un changement de milieu. Du point de vue chimique, ces modifications nécessitent toute deux un apport de silice.

INTRODUCTION

Due to physical and chemical changes in the environment, clay minerals may be modified during weathering, sedimentation, and diagenesis. These modifications may be minor; for example, they may concern only the nature or the proportion of the exchangeable cations. They may be more drastic, however, and affect the nature and/or proportions of tetrahedral and/or octahedral cations, thereby leading to true mineralogical neoformations. The replacement of smectite by illite during diagenesis is probably the best documented example of such modifications (Dunoyer de Segonzac, 1970; Weaver and Beck, 1971; Hower *et al.*, 1976).

Usually such modifications have been studied by

X-ray powder diffraction and chemical analysis of the clay fraction, i.e., by analytical methods that require at least a few milligrams of sample and thus yield average information on millions or billions of individual clay particles. During recent years, the heterogeneity of clays at various scales has been demonstrated by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and analytical methods, such as electron microprobe or analytical spectroscopy fitted on TEM or scanning electron microscopes (SEM). Consequently, the chemical composition of individual clay particles in so-called "pure clays" (i.e., pure, insofar as can be estimated from an X-ray powder diffraction pattern) show large composition ranges (Paquet *et al.*, 1982; Tardy *et al.*,

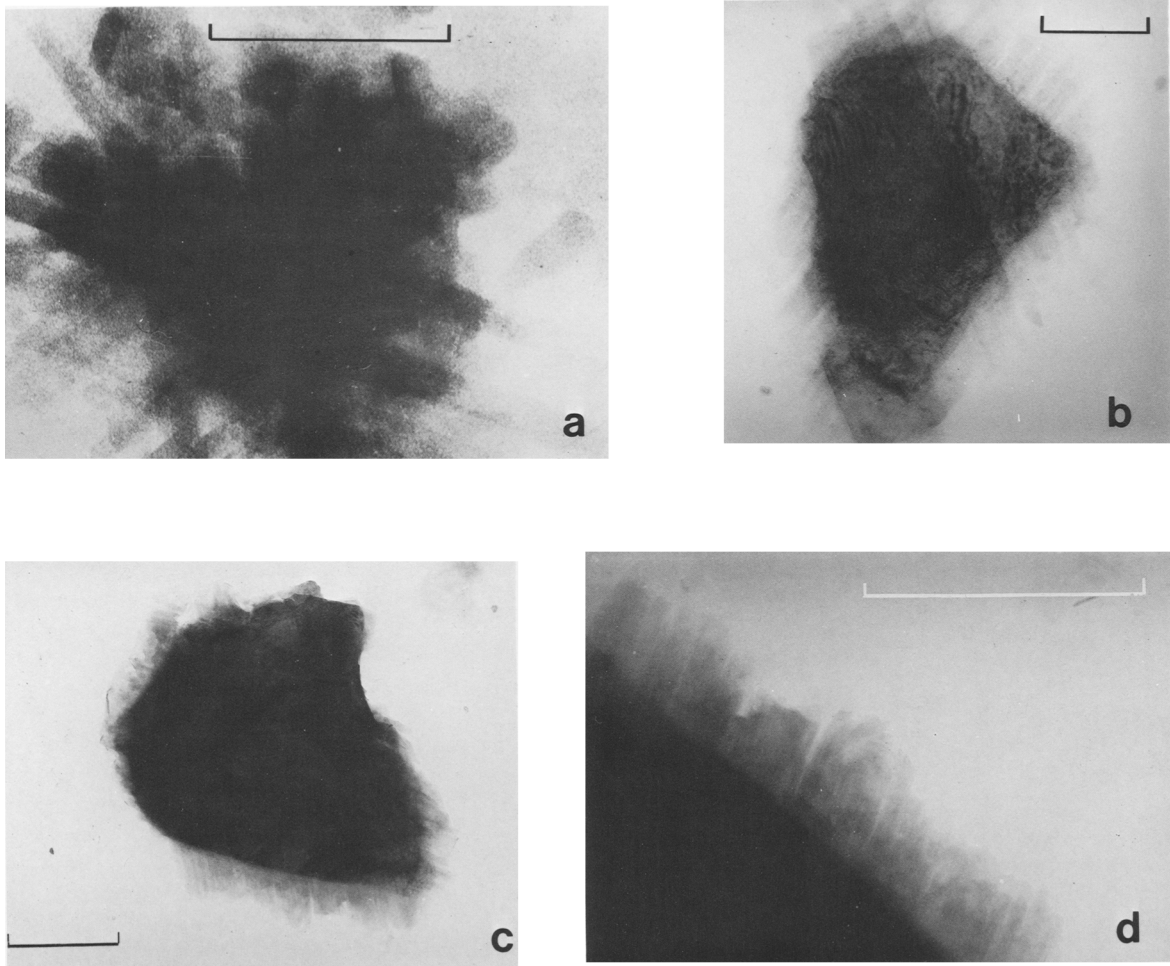


Figure 1. Transmission electron micrographs of overgrowth structures on illite and smectite. Scale bar = 1 μm . (a) bundle of smectite laths. (b) illite crystal surrounded by overgrowth oriented laths. (c) illite crystal rimmed by short and coalescent laths. (d) detailed view of the rim.

1982; Duplay, 1982; Steinberg *et al.*, 1984). Interlayer slips and intergrowth structures have also been observed in various phyllosilicates by HRTEM (Buseck and Cowley, 1983; Banos *et al.*, 1983; Banos and Amouric, 1984; Veblen and Ferry, 1983), and octahedral cations may be irregularly distributed within a single layer (Manceau and Calas, 1985). In addition, various types of overgrowth structures (rims, radiating laths or fibers) have been observed on many clay particles (Trauth, 1977; Hoffert, 1980; Holtzapfel, 1983; Steinberg *et al.*, 1984; Robert *et al.*, 1986).

Overgrowths on clay particles are of particular interest because they suggest a modification of clays in response to environmental change. It is not clear, however, whether such morphological modifications have been accompanied by chemical changes. In the present investigation, scanning transmission electron micros-

copy (STEM) was used to analyze centers and overgrowth structures on illitic and smectitic particles separated from an Albian oceanic sediment.

MATERIALS AND METHODS

Samples

The sample examined was the clay fraction separated from an Albian black shale collected in the Atlantic Ocean (34°54'N, 69°10'W) during leg 11 of the Deep Sea Drilling Project (hole 105.15-3-100; Hollister and Ewing, 1972). The clay fraction comprised 50% of the sediment and consisted chiefly (90–95%) of a ferruginous beidellite and 5–10% illite, chlorite, and interlayered illite/smectite. Small amounts of clinoptilolite, quartz, opal, iron sulfide, and siderite were also present (Holtzapfel, 1983; Holtzapfel *et al.*, 1985). Three

Table 1. Chemical analysis (wt. %) of two size fractions of the studied sample.¹

Size fraction (μm)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	CaO
<0.4	62.8	20.9	9.01	3.4	2.8	0.59
0.4–2	64.1	20.6	7.45	3.2	3.2	0.63

¹ By X-ray fluorescence and atomic absorption spectroscopy.

morphological types of smectite were distinguished: (1) flakes having diffuse borders, 0.05–0.1 μm in size; (2) bundles of laths, 0.01–1 μm long and about 0.1 μm thick, oriented at angles of 60° or 120° to each other (Figure 1a); and (3) flakes surrounded by laths. The laths constituted about 25% of the coarser fraction (0.4 to 2 μm) and as much as 60% of the <0.4- μm fraction. Flakes containing overgrowth laths were less abundant in the fine fraction (15%) than in the coarser fraction (45%) (Holtzapffel, 1983; Holtzapffel *et al.*, 1985). The sample also contained illite crystals surrounded by similar laths (Figure 1b) or rimmed by coalescent, short (0.05–0.1 μm) laths (Figure 1c). Chemical analysis of two size fractions (0.4–2 μm and <0.4 μm) are almost identical (Table 1) despite the fact that the fine fraction contained more laths. The distribution of rare earth elements in the two size fractions is also similar; no cerium anomaly was noted (Holtzapffel *et al.*, 1985), and, thus, the distribution was comparable to that of detrital clays (Haskin *et al.*, 1968; Piper, 1974; Chamley and Bonnot-Courtois, 1981). From Rb/Sr isotope analyses, the lath-shaped smectites appeared to be authigenic, but were apparently formed by the recrystallization of the flakes in an almost closed system shortly after sedimentation (Clauer *et al.*, 1984; Holtzapffel *et al.*, 1985).

Analytical procedure

The scanning-transmission electron microscope (STEM) used (Laboratoire de Physique des Solides, Orsay) was a model VG HB 501 described by Colliex and Treacy (1983). Due to its field emission source, currents of a few picoamperes could be focused onto a 10- \AA diameter area. The composition of the sample could therefore be determined at this scale by energy-dispersive X-ray analysis. The samples had to be trans-

Table 2. Change of the composition (wt. %) of a smectite during three consecutive analyses performed on the same spot (200–300 \AA diameter).

Counting time (s)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	CaO	Na ₂ O
421	67.7	20.6	6.2	4.1	(0.2)	0.8	(0.4)
381	67.2	21.0	6.6	3.7	(0.3)	0.5	0.7
397	66.0	21.3	7.4	3.6	0.4	0.7	0.6

Due to statistical errors, data in parentheses are not significant.

Table 3. Change of the computed composition (wt. %) of a smectite using different absorption coefficients (i.e., different thickness).

Thickness (μm)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	CaO
0.02	61.8	22.4	7.4	3.3	3.9	1.2
0.1	62.4	22.2	7.0	3.3	3.8	1.3
None ¹	61.6	22.4	7.5	3.3	3.9	1.3

¹ None = no absorption correction.

parent to electrons and, depending on their composition, <300–1000 \AA thick, a condition met by most natural clays. A drop of a very dilute suspension of the clay was air-dried on a grid previously coated with a thin film of carbon. During the examination, the electron beam was kept on a fixed spot or allowed to scan over a small area. Radiation damage was more significant during the fixed-spot mode of examination, although it varied from one clay to another. Rautureau and Steinberg (1985) observed that kaolinite is highly unstable under these conditions, compared with illite and smectite. Table 2 shows that three analyses of a smectite performed consecutively on the same spot showed only a minor change of the composition. The scanning mode, however, was used, and the duration of counting was usually 100–200 s.

Measured data were computed using the method proposed by Cliff and Lorimer (1975). Using a least squares fitting (McCarthy and Schamber, 1979), each characteristic peak was compared to data obtained on pure compounds. A reference element was then chosen (here Si), and apparent relative concentrations were computed. The results were then corrected to take into account ionization, fluorescence, counting efficiencies, interelement interactions (ZAF), and absorption (i.e., sample thickness) (Trebbia, 1984). The thickness had only a slight effect on the results (Table 3).

RESULTS

The chemical composition of the center and overgrowth laths and rims of particles of smectite and illite in the coarser fraction (0.4–2 μm) were systematically compared, and cation proportions were recalculated on the basis of 22 oxygens (anhydrous) (Table 4). The oxidation state of Fe was presumed to be Fe³⁺. The percentages of the three main octahedral cations are plotted in Figure 2, and tetrahedral and total Al are plotted in Figure 3. The percentage of K among the exchangeable cations is compared with tetrahedral Al in Figure 4.

Composition of particles

The centers of illite particles are rich in Al, and tetrahedral substitution is high (> 1.2 Al/22 oxygens) (Figure 3). These materials do not appear to be true dioctahedral illite because they contain some Mg. The smectite appears to be an Fe-Al-beidellite containing

Table 4. Analytical data (wt. %) of coarse clay fraction (0.4–2 μm) recalculated on the basis of 22 oxygens.

Sample	Si	Al ^{IV}	Al ^{VI}	Fe	Mg	K	Ca	Na
Illite centers								
16-405	6.67	1.33	3.36	0.38	0.4	1.15	0.07	—
24-405	6.57	1.43	3.32	0.36	0.28	1.74	0.05	—
28-405	6.66	1.34	3.55	0.29	0.19	1.37	0.03	—
10-411	6.44	1.56	3.61	0.23	—	2.06	—	—
13-411	6.8	1.2	3.47	0.28	0.17	1.59	—	—
25-411	6.53	1.47	3.46	0.32	0.14	1.55	0.04	0.23
Overgrowth structures on illite								
18-405	7.52	0.48	2.76	0.69	0.6	0.62	0.16	—
25-405	7.65	0.35	2.2	1.41	0.5	0.3	0.1	—
29-405	8.08	—	2.8	0.54	0.62	0.13	0.8	—
11-411	7.18	0.82	3.3	0.24	0.28	1.38	0.06	0.09
12-411	7.74	0.26	2.99	0.32	0.56	0.82	0.19	—
14-411	8.14	—	2.99	0.32	0.22	0.97	0.06	—
26-411	7.37	0.63	3.16	0.43	0.43	0.75	0.07	0.13
Smectite centers								
20-405	7.4	0.6	2.2	1.28	0.54	0.72	0.17	—
22-405	7.41	0.59	2.48	1.07	0.52	0.63	0.13	—
3-411	7.73	0.27	1.99	1.62	0.5	0.38	0.03	0.02
4-411	7.63	0.37	1.62	2.0	0.53	0.31	0.03	0.09
8-411	7.82	0.18	1.72	1.96	0.36	0.4	0.01	—
15-411	7.83	0.17	2.13	1.38	0.54	0.54	—	—
18-411	7.6	0.4	2.27	1.3	0.32	0.85	0.06	0.06
19-411	7.55	0.45	2.37	1.08	0.49	0.73	0.1	0.19
22-411	7.74	0.26	2.13	1.14	0.75	0.75	0.09	—
31-411	7.89	0.11	2.22	1.19	0.6	0.5	0.08	—
Overgrowth structures on smectite								
21-405	7.9	0.1	2.42	0.88	0.77	0.2	0.23	—
23-405	8.02	—	2.74	0.69	0.64	0.1	0.12	—
5-411	7.9	0.1	2.56	0.91	0.59	0.32	0.05	0.07
6-411	7.85	0.15	2.66	0.92	0.51	0.33	0.03	—
9-411	7.96	0.04	2.45	1.1	0.51	0.3	0.03	—
16-411	7.84	0.16	2.58	0.94	0.45	0.66	0.03	—
17-411	7.97	0.03	2.34	1.13	0.53	0.52	—	—
20-411	7.73	0.27	2.64	0.74	0.52	0.91	0.1	—
21-411	7.8	0.2	2.17	1.22	0.56	0.57	0.1	0.15
32-411	7.97	0.03	2.51	0.98	0.57	0.27	0.08	—
Bulk sample								
0.4–2 μm	7.81	0.19	2.77	0.68	0.58	0.50	0.08	—
0.4 μm	7.67	0.33	2.67	0.83	0.62	0.44	0.08	—

minor Mg (Figure 2). Tetrahedral substitution is low (0.11 to 0.45 atom/22 oxygens) (Figure 3). The chief exchangeable cation of this material is K (Figure 4).

Composition of overgrowths

Overgrowths on illite crystals appear to be smectites that are richer in SiO₂ and Fe₂O₃ and poorer in Al₂O₃ and K₂O than the illite (Figures 2–4). Overgrowths on beidellite flakes appear to be montmorillonite that is richer in SiO₂ and Al₂O₃ and poorer in Fe₂O₃ than the beidellite (Figures 2–4).

DISCUSSION

Composition variability of clay particles

As mentioned above, the chemical composition of individual particles of so-called pure clays may vary

widely. This range in composition was interpreted by Fritz *et al.* (1985) as inhomogeneous equilibrium between clay mineral particles and the aqueous solutions present when the clay was formed. Table 4 and Figures 2–4 show similar results for illite and beidellite; here the minerals were not formed in the sediment, but were of detrital origin. Their diversity may thus be related to a diversity of their sources. Furthermore, the data in Table 4 and Figure 2 show that the composition range of beidellite is broader than that of illite. This difference may be related to the overgrowth structures, because although they can be observed on the edges of the particles, how far they extend into the particle is unknown. Morphological examination of beidellite shows large differences between flakes devoid of overgrowths and authigenic lath assemblages. Intermediate particles show a few remnants (10–20%) of flakes that

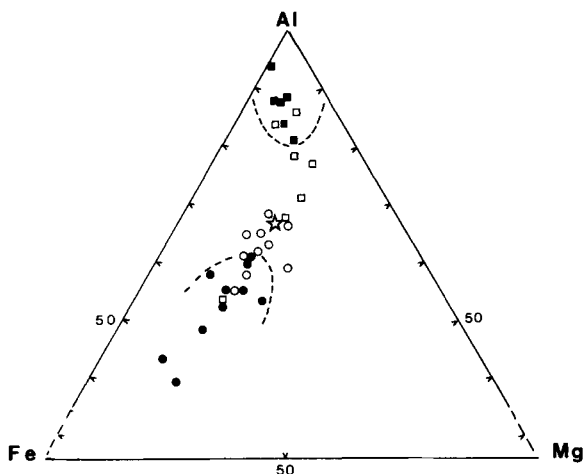


Figure 2. Atom percentages of octahedral cations. Solid squares = central part of illite crystals; open squares = overgrowth structures surrounding illite; solid circles = central part of smectite flakes; open circles = overgrowth structures surrounding smectite; star = conventional analysis of the <0.4- μ m size fraction.

were not modified by the growth of the laths (Holtzapfel, 1983). Such particles are uncommon for illite, the overgrowths of which make up only 10–20% of the observed surface. Thus, overgrowth structures probably continue further into the beidellite flakes than into illite crystals. Therefore, the analysis of the centers of beidellite particles, which involve the thickness of the

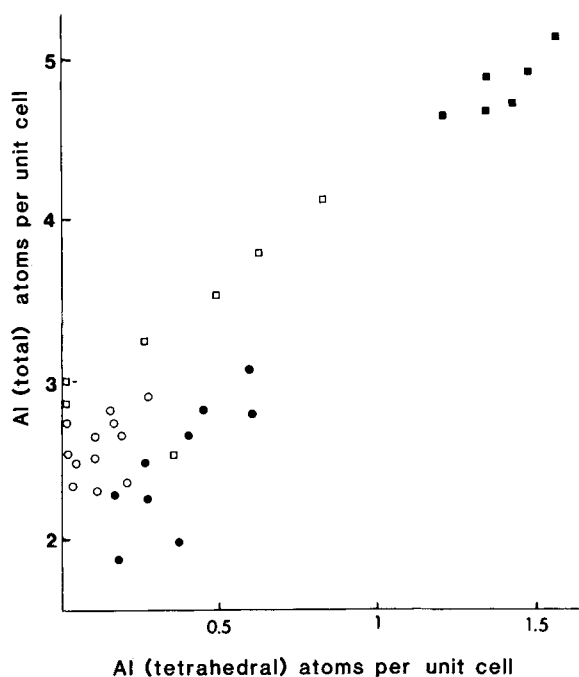


Figure 3. Variations of total atom and tetrahedral atom of aluminum. Symbols are the same as in Figure 2.

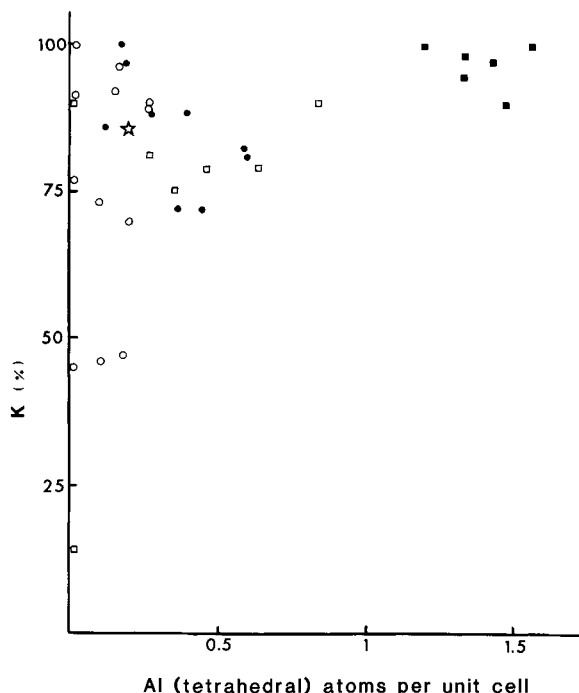


Figure 4. Comparison of the atom percentage of K among exchangeable cations with tetrahedral aluminum. Symbols are the same as Figure 2.

whole particle, may be more influenced by the composition of the overgrowths than are the analyses of illite.

Comparison of particle centers with overgrowth

The centers and overgrowth structures cannot be compared by means of an actual geochemical budget because of the lack of information on which elements were mobilized and which were not. Therefore, only apparent gains and losses with respect to the central part of the particles may be calculated (Table 5).

Concerning octahedral cations, Table 5 shows that compared to the centers, overgrowth structures on illite are poorer and overgrowth structures on beidellite richer in Al. The reverse trend was observed for Fe. Both types of overgrowths are richer in Si and Mg than their supporting material. Thus, the chemical composition

Table 5. Apparent gain or loss of elements in overgrowth structures compared with the particle centers.

Wt. %	Overgrowth structures on illite	Overgrowth structures on smectite
SiO ₂	gain	gain
Al ₂ O ₃	loss	gain
Fe ₂ O ₃	gain	loss
MgO	gain	gain
K ₂ O	loss	?

? = variations are not significant.

of the two types of overgrowth structures on very different minerals (illite and beidellite) tend to be similar (Figure 2). The overgrowth structures may therefore be the result of a re-equilibration of detrital clays with their new diagenetic environment. Particles containing radiating laths probably correspond to the beginning of the process, whereas bundles of laths probably correspond to the end. The model proposed by Fritz *et al.* (1985) may still be valid: equilibrium between each lath and its immediate environment was reached, but equilibrium between each particle and its surrounding solution was not reached, except for particles completely replaced by laths.

Silicification of clays

From the chemical gains and losses noted in Table 5, silicification of the illites and beidellites appears to be obvious. The kind and extent of reactions of clay minerals with dissolved silica has been extensively discussed by many authors (Siffert, 1962; Mackenzie and Garrels, 1965; Siever and Woodford, 1973; Maynard, 1975). According to Siever and Woodford (1973), data on the distribution of clay minerals in sediments are apparently contradictory; in some places some diagenetic effects appear to be present, but in others, few effects have been noted. Siever (1968), Siever and Woodford (1973), and Maynard (1975) showed experimentally that clay mineral silicification is doubtful in normal seawater, but possible in silica-rich interstitial waters. The present data show that silicification does indeed take place in nature, but normal XRD and chemical analysis are unable to demonstrate such discrete modifications.

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