

AUTHIGENESIS OF KAOLINITE AND CHLORITE IN TEXAS GULF COAST SEDIMENTS

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Abstract—Core cuttings from numerous wells traversing Oligocene through Recent sediments of the Texas Gulf Coast were examined with a scanning electron microscope using the back-scattered electron imaging mode (BSE) to ascertain diagenetic changes in clays and associated minerals of mudrocks and of adjacent sandstones. Several occurrences of authigenic kaolinite and chlorite were noted, each characterized by a specific texture and a specific diagenetic microenvironment. In all occurrences kaolinite appears to have formed before chlorite, and in some the kaolinite appears to have precipitated directly from solution. Chlorite, ubiquitously an iron-rich variety, appears to have precipitated in some places directly from solution. It has also been noted pseudomorphous after kaolinite. A progressive decrease in the iron content of mixed-layer illite/smectite with increasing depth is believed to have released the necessary iron and to have driven the kaolinite-to-chlorite reaction.

Key Words—Authigenesis, Back-scattered electron imaging, Chlorite, Illite/smectite, Iron, Kaolinite.

INTRODUCTION

A back-scattered electron imaging study of Texas Gulf Coast sediments was undertaken to provide information on the diagenetic phases and reactions occurring in mudrocks and in the pore spaces of adjacent sandstones. For this purpose core cuttings were examined from numerous wells traversing Tertiary and Quaternary sediments. Back-scattered electron imaging (BSE) was chosen rather than conventional scanning electron microscopic analysis to distinguish minerals by compositional differences. Phase identification using a combination of BSE and energy-dispersive X-ray analysis (EDX) has proved to be a rapid and effective method for determining crystal morphologies, mineral compositions, and textural relationships among phases (Krinsley *et al.*, 1983; Pye and Krinsley, 1983). These methods permit direct examination of petrologic and paragenetic relationships among the fine-grained phyllosilicates.

This study focuses on chlorite and kaolinite as authigenic phases. Earlier diagenetic studies (e.g., Muffler and White, 1969; Perry and Hower, 1970; Weaver and Beck, 1971) noted increases in chlorite abundance and decreases in kaolinite abundance with depth. These depth-dependent changes in abundance, determined by X-ray powder diffraction and bulk chemical analyses and attributed to diagenesis, suggested transformation of kaolinite to chlorite. Hower *et al.* (1976) detected no corresponding decrease in kaolinite with depth, but related chlorite development to the transformation of smectite to illite. Subsequent detailed

chemical analyses and transmission electron microscope investigations (Curtis *et al.*, 1985; Ahn and Peacor, 1985) indicated the development of chlorite from smectite, along with the transformation of smectite to illite. Data presented in the present report indicate, however, that a large part of the authigenic chlorite comes from kaolinite, although some is also formed as a result of the smectite-to-illite transformation.

SAMPLING AND METHODOLOGY

Core cuttings were obtained from wells in Harris and Brazoria Counties, upper Texas Gulf Coast, and Hidalgo and Cameron Counties, lower Texas Gulf Coast. The sediments penetrated by these wells comprise numerous, relatively undeformed wedges of marine shales and coastal sandstones that dip and thicken toward the coast. These rocks are dominated by mixed progradational and aggradational deltaic facies (Galloway *et al.*, 1982). Samples from Recent to Oligocene were examined at 100-m intervals over the entire depth of most wells, ranging from 100 to 5700 m. The wells studied and intervals sampled are listed in Table 1.

Small chips (<1 cm), representative of each depth interval, were oven dried for 24 hr at 100°C, impregnated with epoxy resin, and then mounted on glass discs. A flat surface was obtained by lightly grinding for a few seconds with 600 grit. The chips were again impregnated with epoxy and polished on a Buehler Minimet using nylon laps and 1- μ m diamond abrasive. The discs were then coated with 100 Å of carbon and mounted on aluminum stubs.

An ISI SS-40 scanning electron microscope equipped with an annular, four-element backscattered-electron detector and a Si-Li solid-state EDX detector with Kevex "QUANTEX" software were used. Working

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Table 1. Wells and sample intervals.

Well	Operator and lease	County	Depth range/interval
R34637	Shell Oil, State Tract #139-1	Galveston	150–4050 m/200 m
R37879	Texas Eastern Corp., Sadie Hencke #1	Galveston	2300–4800 m/300 m
R37097	La Gloria Corp., S. Weslaco #1	Hidalgo	300–2600 m/100 m
R36762	Stanolin, Sweeny #2	Hidalgo	1700–3400 m/100 m
R46971	Magnolia, Kerlin #1	Cameron	100–5200 m/100 m
R36811	Union of California, Esperson #1	Cameron	2300–3900 m/100 m
R36866	Texas Gulf Products, Wentz #1	Cameron	800–3000 m/100 m
R35881	Shell Oil, P. Hulsey #1	Hidalgo	1300–2300 m/100 m
	Case Western Reserve University #6	Brazoria	1350–3600 m/varies
	Mobil Oil, Hall's Bayou Ranch #1	Galveston	1000–5700 m/varies

Wells prefaced with R were provided by the Texas Bureau of Economic Geology and are identified by their numbers.

distance (focal length), specimen current, and spot size varied depending upon the information desired; an accelerating potential of 20 keV was routinely used.

Phases were identified on the basis of crystal morphology and by their brightness (“Z-contrast”) on the BSE images. Phase identifications were confirmed by qualitative EDX analysis (Figure 1). To distinguish chlorite from compositionally similar berthierine, electron diffraction patterns were obtained using a transmission electron microscope, revealing the 14-Å spacing of chlorite (Figure 2). Because of limited sample availability and the inability to isolate sufficient phyllosilicate material, XRD of oriented mounts was not attempted.

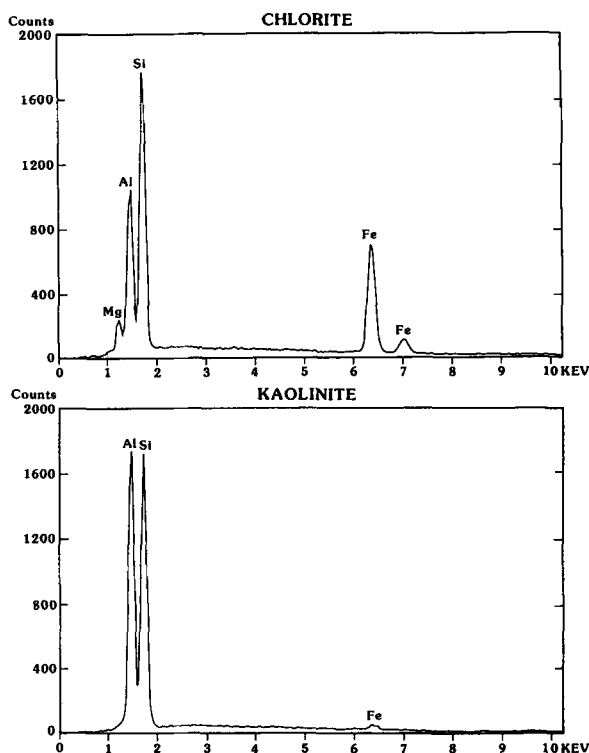


Figure 1. Energy-dispersive X-ray spectra of kaolinite and chlorite.

RESULTS AND DISCUSSION

The authigenic chlorite-kaolinite assemblages occur as: (1) polycrystalline filling in foraminiferal tests in mudrocks; (2) replacement of framework grains in sandstones; and (3) precipitates in sandstone pores. In all assemblages chlorite appears to succeed kaolinite paragenetically.

In the more argillaceous facies, zones occur containing numerous foraminiferal tests composed of calcite. The tests typically contain infillings of calcite and po-

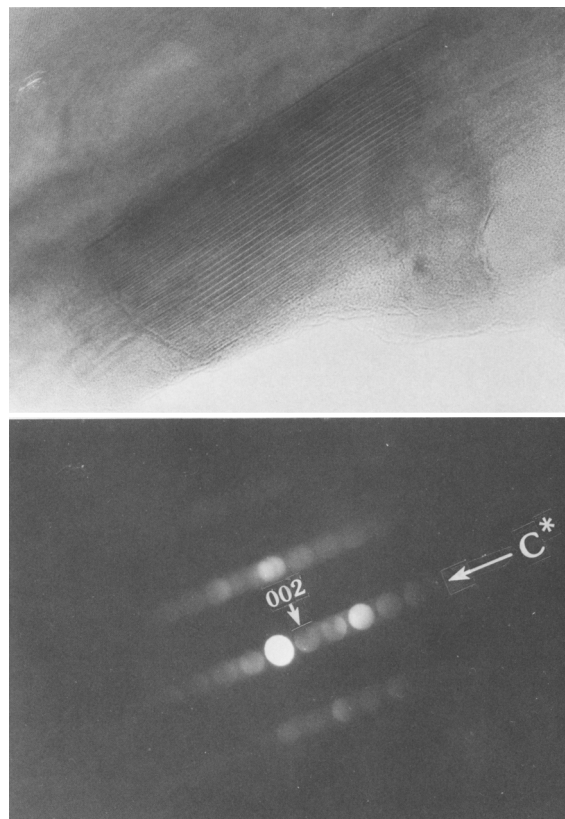


Figure 2. (Upper) Convergent-beam transmission electron microscope image (field of view = 13 μ m) and (lower) selected-area electron diffraction pattern of chlorite.

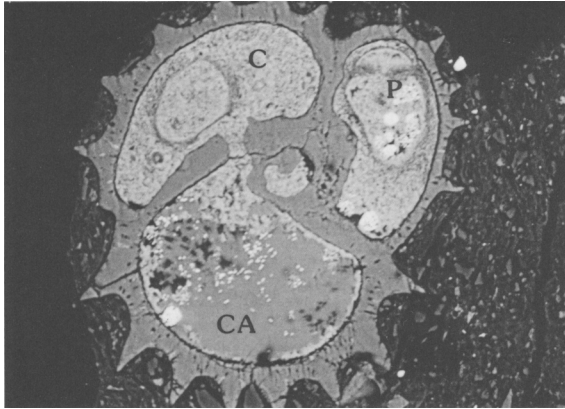


Figure 3. Back-scattered electron image of foraminiferal test filled with chlorite (C), pyrite (P), and calcite (CA). Well 37879, 2565 m. Field of view = 200 μm .

lyframboidal pyrite with or without chlorite and kaolinite (Figure 3). The tests characteristically do not contain mixed-layer illite/smectite (I/S) that comprise the mudrock matrix. The only phyllosilicates found in the foraminiferal tests were kaolinite and chlorite, and their distribution appears to be depth-related. Only kaolinite was found at shallow depths (<1000 m). At greater depths kaolinite coexists with chlorite (Figure 4) and chlorite is typically more abundant. In most of the deep samples no kaolinite was found. Where kaolinite coexists with chlorite, the kaolinite is surrounded by chlorite. The textural and depth relationships suggest a replacement origin for chlorite of an earlier kaolinite infilling. Pollastro (1981) reported similar authigenic kaolinite in foraminiferal tests, occurring as spherical, polycrystalline aggregates coexisting with framboidal pyrite. Similar assemblages were reported by Ehlman *et al.* (1963) and Borst (1973). These authors concluded that the kaolinite-pyrite association

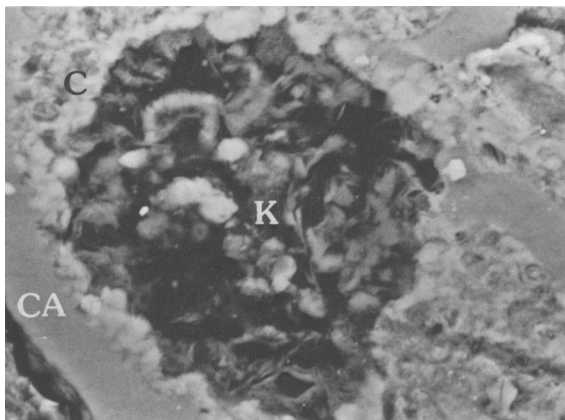


Figure 4. Back-scattered electron image of kaolinite (K) and chlorite (C) within a calcite (CA) test. Well R34637, 2860 m. Field of view = 60 μm .

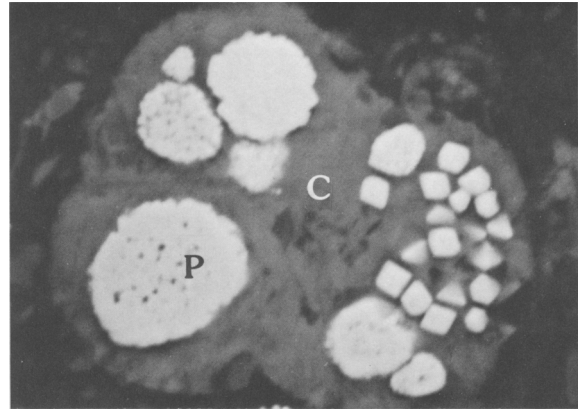


Figure 5. Back-scattered electron image of pyrite (P) and chlorite (C) preserving globular form of original calcite test. Mobil Hall's Bayou Ranch #1, 4320 m. Field of view = 35 μm .

developed authigenically from a colloidal aluminosilicate gel or from solution during early diagenesis. Our observations, described below, suggest that the kaolinite later converted to chlorite in the foraminiferal tests at depth.

In the deepest samples (>4000 m), calcite tests are poorly preserved, but the moldic shapes of the chlorite and ubiquitous association with framboidal pyrite (Figure 5) indicate that they originated as test-fillings even though original tests might now be absent. These relationships support the formation of chlorite in Gulf Coast mudrocks from a kaolinite precursor. The precursor kaolinite was likely related to early, biogenic processes (Pollastro, 1981).

Chlorite was also observed in these mudrocks as a replacement phase after ankerite, as detrital flakes, and as pseudomorphs after precursor detrital phyllosilicates. These modes of occurrence, however, are rare and volumetrically insignificant. Ahn and Peacor

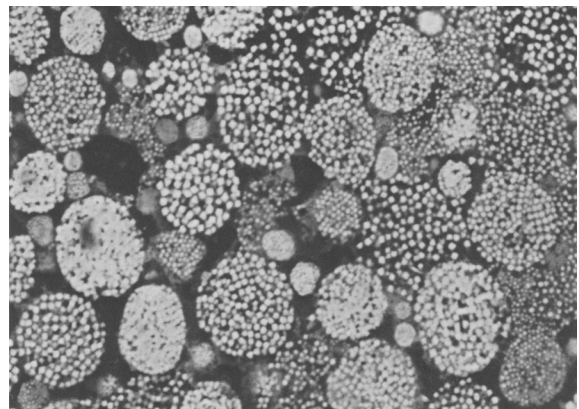


Figure 6. Back-scattered electron image of polyframboidal pyrite. Well R36866, 2100 m. Field of view = 100 μm .

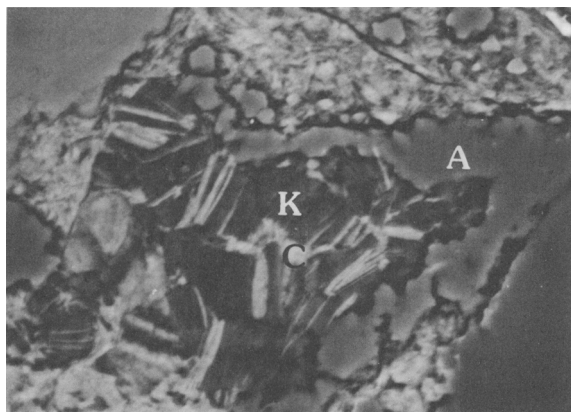


Figure 7. Back-scattered electron image of kaolinite (K) with lamellar chlorite (C) and albite (A). Well R37879, 4570 m. Field of view = 85 μm .



Figure 8. Back-scattered electron image of lamellar chlorite (C) pseudomorphous after blocky kaolinite (K). Well R37879, 4570 m. Field of view = 45 μm . A = albite.

(1985), using transmission electron microscopy, found chlorite in well C.W.R.U. #6 intergrown with the I/S matrix. Such chlorite was not observed in the present study, probably because its particle size is beyond the resolution limits of BSE imaging.

The coexistence in the tests of chlorite and pyrite suggests that the iron required for the kaolinite-to-chlorite reaction may have been derived from the pyrite. The pyrite, however, shows original textures with no evidence of dissolution (Figure 6). Even in the deepest samples pyrite is abundant and coexists with the chlorite. Moreover, the polyframboidal habit of the pyrite within foraminiferal tests indicates that it formed by the reduction of sulfate to sulfide *in situ*, with sulfide, not iron, as the pyrite-limiting species (Bernier, 1969). This apparent non-reactivity of the pyrite implies that iron in the chlorite was not derived from pyrite but from a fluid phase that was oversaturated in iron with respect to pyrite precipitation.

In the coarser-grained clastic sediments, authigenic chlorite and kaolinite coexist as replacements of framework grains and as interstitial pore fillings. These assemblages were found at depths >3000 m beneath a zone of enhanced, secondary porosity.

The kaolinite replacing framework grains has a dense, blocky texture (Figure 7); chlorite occurs around the kaolinite as plates and as face-to-face lamellae within, and pseudomorphous after, the kaolinite (Figure 8). Grains of calcic plagioclase and albite are common and typically contain areas of calcite or kaolinite. The blocky kaolinite, commonly found within albite, appears to replace the feldspar. The lamellar intermixture of chlorite and kaolinite, chlorite being pseudomorphous after kaolinite, suggests replacement of kaolinite by chlorite. Although chlorite can not isostructurally replace kaolinite by solid-state substitution, the reaction might have proceeded through a berthierine intermediary, i.e., increasing iron activity transformed kaolinite to

berthierine which then isochemically transformed to the chlorite polymorph. The transformation of kaolinite to berthierine was documented by Iijima and Matsumoto (1982); the polymorphic transformation of berthierine to chlorite has been documented by Nelson and Roy (1958), Velde (1973), and Ahn and Peacor (1985), among others.

A third, distinct chlorite-kaolinite association in the Texas Gulf Coast occurs as interstitial pore fillings in coarser clastic rocks. Kaolinite occurs interstitially in pores as loose, microporous, randomly arranged booklets (Figure 9). Keller (1978) indicated that this particular habit for kaolinite is characteristic of direct precipitation from aqueous solution. This texture suggests that interstitial fluids contained enough aluminum to form kaolinite. Although kaolinite precipitation does not require a large quantity of aluminum, it does imply amounts sufficient to affect clay diagenesis.

Chlorite in this type of occurrence is found as radiating and face-to-edge clusters of hexagonal plates

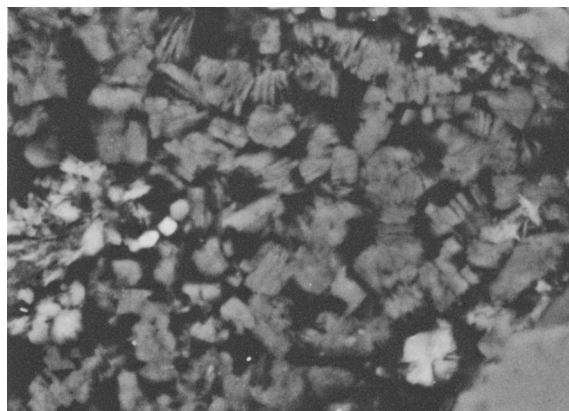


Figure 9. Back-scattered electron image of pore-filing kaolinite books. Well R37879, 3070 m. Field of view = 70 μm .

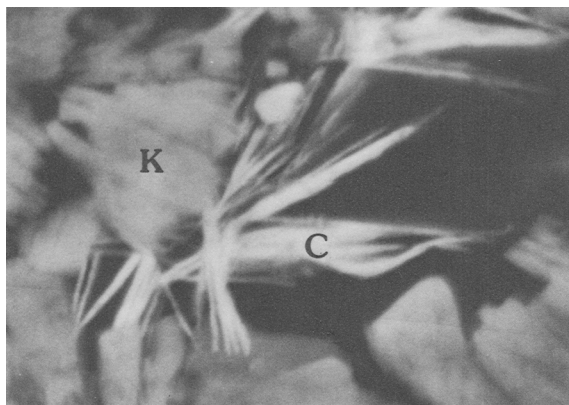


Figure 10. Back-scattered electron image of chlorite (C) nucleating upon interstitial kaolinite (K). Well R37879, 4570 m. Field of view = 20 μm .

(Figure 10) within the micropores of the kaolinite. These textures clearly show the authigenic nature of both kaolinite and chlorite and suggest the precipitation of chlorite directly from a fluid phase. Chlorite in this occurrence appears to have formed later than the kaolinite, but as a later pore-filling precipitate, rather than as a replacement of the kaolinite.

The paragenetic relationships in all three assemblages indicate that authigenic kaolinite was succeeded by authigenic iron-rich chlorite, suggesting an increase of the pore-fluid Fe/Al ratio with depth. The only potential sources of iron in these wells are pyrite, iron oxides, and the I/S matrix of the mudstones. Pyrite appears to be stable at all depths, to be more abundant with increasing depth, and thus not to be the source of iron to a fluid phase. Iron oxides appear to decrease in abundance with increasing depth but are probably volumetrically insignificant as iron sources. The decrease of the iron oxide/sulfide ratio with depth probably reflects the fluid $f\text{O}_2/f\text{S}_2$ values.

The I/S clay matrix of the mudstones, however, is volumetrically significant. Hower *et al.* (1976) found a decrease in the iron and magnesium content of I/S with increasing depth for one of the wells of this study (C.W.R.U. #6) and proposed that the smectite-to-illite reaction could be a source of cations for the formation of the chlorite. TEM data of Ahn *et al.* (1983) and Ahn and Peacor (1984) confirm this decrease in iron and magnesium during the transformation of smectite to illite. We believe that the smectite-to-illite transformation is the chief source of iron and is the driving mechanism for chlorite development. Although, as Ahn and Peacor (1985) demonstrated, submicrometer-size chlorite may form from smectite, the present data indicate that chlorite also developed authigenically as a precipitate in pores and replaced kaolinite. With sufficiently high activity of iron, iron-rich chlorite became stable relative to either kaolinite or smectite.

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REFERENCES

- Ahn, J. H., Lee, J. H., and Peacor, D. R. (1983) Mineralogical and textural transition in phyllosilicates during burial diagenesis of Gulf Coast shales: *Geol. Soc. Amer. Abstr. Prog.* **15**, p. 512.
- Ahn, J. H. and Peacor, D. R. (1984) The smectite-to-illite transformation in Gulf Coast argillaceous sediments based on microstructure by TEM/AEM: in *Program with Abstracts, 21st Annual Meeting of The Clay Minerals Society, Baton Rouge, Louisiana, 1984*, p. 22.
- Ahn, J. H. and Peacor, D. R. (1985) Transmission electron microscopic study of diagenetic chlorite in Gulf Coast argillaceous sediments: *Clays & Clay Minerals* **33**, 228–236.
- Berner, R. A. (1969) Migration of iron and sulfur within anaerobic sediments during diagenesis: *Amer. J. Sci.* **267**, 19–42.
- Borst, R. L. (1973) Authigenic kaolinite crystals within microfossils of the Danian Limestone, North Sea: in *Proc. Int. Clay Conf., Madrid, 1972*, J. M. Serratos, ed., Div. Ciencias C.S.I.C., Madrid, 41–48.
- Curtis, C. D., Hughes, C. R., Whiteman, J. A., and Whittle, C. K. (1985) Compositional variation within some sedimentary chlorites and some comments on their origin: *Mineral. Mag.* **49**, 375–386.
- Ehlman, A. J., Hulings, N. C., and Glover, E. D. (1963) Stages of glauconite formation in foraminiferal sediments: *J. Sed. Petrol.* **33**, 87–96.
- Galloway, W. E., Hobday, D. K., and Magara, K. (1982) Frio Formation of the Texas Gulf Coast basin: Depositional systems, structural framework, and hydrocarbon origin, migration, distribution, and exploration potential: *Texas Bur. Econ. Geol. Rept. Invest.* **122**, 78 pp.
- Hower, J., Eslinger, E., Hower, M. E., and Perry, E. A. (1976) Mechanism of burial metamorphism of argillaceous sediments: 1. Mineralogical and chemical evidence: *Geol. Soc. Amer. Bull.* **87**, 725–737.
- Iijima, A. and Matsumoto, R. (1982) Berthierine and chamosite in coal measures of Japan: *Clays & Clay Minerals* **30**, 264–274.
- Keller, W. D. (1978) Classification of kaolins exemplified by their textures in scan electron micrographs: *Clays & Clay Minerals* **26**, 1–20.
- Krinsley, D. H., Pye, K., and Kearsley, A. T. (1983) Application of backscattered electron microscopy in shale petrology: *Geol. Mag.* **120**, 109–114.
- Muffler, L. J. P. and White, D. E. (1969) Active metamorphism of upper Cenozoic sediments in the Salton Sea geothermal field and the Salton Trough, southeastern California: *Geol. Soc. Amer. Bull.* **80**, 157–182.
- Nelson, B. W. and Roy, R. (1958) Synthesis of chlorites and

- their structural and chemical constitution: *Amer. Mineral.* **43**, 707–725.
- Perry, E. and Hower, J. (1970) Burial diagenesis in Gulf Coast pelitic sediments: *Clays & Clay Minerals* **18**, 165–177.
- Pollastro, R. M. (1981) Authigenic kaolinite and associated pyrite in chalk of the Cretaceous Niobrara Formation, eastern Colorado: *J. Sed. Petrol.* **51**, 553–562.
- Pye, K. and Krinsley, D. H. (1983) Mudrocks examined by backscattered electron microscopy: *Nature* **301**, 412–413.
- Velde, B. (1973) Phase equilibria studies in the system MgO-Al₂O₃-SiO₂-H₂O: Chlorite and associated minerals: *Mineral. Mag.* **39**, 297–312.
- Weaver, C. E. and Beck, K. C. (1971) Clay-water diagenesis during burial: How mud becomes gneiss: *Geol. Soc. Amer. Spec. Pap.* **134**, 96 pp.

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