COMPARISON OF THE MINERALOGICAL AND CHEMICAL COMPOSITION OF 2 SHALES FROM THE WESTERN CANADA SEDIMENTARY BASIN AND THE UNITED STATES GULF COAST

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Abstract—The mineralogy and geochemistry of shales reflect the composition of the initially deposited precursor mud, subsequently modified by diagenetic processes. To see if significant geochemical differences exist between shales that mainly owe their present-day composition to either deposition or diagenesis, we compare the published mineralogical, bulk and clay-fraction geochemical, and clay-fraction O-isotopic compositions of 2 shales. One shale is from the Western Canada Sedimentary Basin (WCSB), and its composition mainly reflects primary (depositional) chemical and mineralogical variations (smectitic to illitic illite/smectite) within this unit. The other shale is from the United States Gulf Coast (USGC), and its composition mainly reflects mixed-layer illite/smectite (I/S) diagenesis of deposited smectitic clay material. The chemical and mineralogical trends of WCSB and USGC shales, including one of increasing illite content in I/S with depth or maturity, are essentially indistinguishable, in both bulk shale and clay fraction, despite the contrasting genetic interpretations for the origin of the contained I/S. Thus, similar mineralogical and chemical trends with depth or temperature can result either from inherited depositional compositional heterogeneity of the sediment, from burial metamorphism of shale or a combination of both. Interestingly, the O-isotopic compositions of the clay fractions from the WCSB and USGC are significantly different, a fact that reflects original clay formation from source material and water of quite different isotopic compositions. The discrimination between depositional and diagenetic contributions to shale composition continues to pose challenges, but a combination of bentonite, illite polytype, clay isotopic and trace and rare earth elemental analyses together with illite age analysis holds promise for future work.

Key Words—Deposition, Diagenesis, Geochemistry, Mineralogy, Mixed-Layer Illite/Smectite, Oxygen Isotopes.

INTRODUCTION

In a recently published study of a shale interval in the WCSB, trends of bulk shale, shale matrix (clay fraction) and bentonite geochemistry and mineralogy with depth and thermal maturity were attributed mainly to inherited, depositional mixing of material originating from 2 contrasting sources, namely, detrital and volcanic (Caritat, Bloch, Hutcheon and Longstaffe 1994). A mineralogical trend of increasing illite in mixed-layer illite/smectite (I/S) with depth/maturity was observed, similar in many respects to what is commonly reported from the study of argillaceous sediments in other basins and attributed to I/S diagenesis. Given, then, that such similarity can arise from 2 contrasting genetic concepts (depositional mixing vs. diagenetic reactions), the question of how similar or different the geochemical and isotopic patterns in shales having undergone mostly one or the other evolutionary

path might be, began to puzzle us. Can the relative influences of depositional inheritance and diagenetic modification upon shale composition be discriminated? Are there recognizable, possibly diagnostic, geochemical or mineralogical signatures that can be of assistance?

To gain insight into these questions, we presently offer a comparison of our previous work in the WCSB with studies of the USGC by Hower et al. (1976) and Yeh and Savin (1977). These studies, and the seminal work of Burst (1969) they followed, have led to the supreme concept of argillaceous sediment metamorphism or clay diagenesis in sedimentary basins. The aim of the present contribution is not to question the correctness of either interpretation in the 2 case studies compared, nor to claim the prevalence of either genetic pathway over the other, but rather: 1) to point out that the processes of deposition and diagenesis both contribute to the composition of shales, and can yield similar geochemical characteristics; 2) to caution that distinguishing the relative importance of deposition and

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diagenesis in any particular investigation is tremendously intricate, yet crucially important; and, finally, 3) to urge mudrock sedimentologists and geochemists to work more closely together when attempting to reconstruct the physico-chemical evolution of a shale package.

BACKGROUND AND APPROACH

Studies of shale diagenesis traditionally have relied heavily upon the careful description of geochemical and mineralogical changes in the clay-sized fractions, as shown from chemical and X-ray diffraction (XRD) data (Burst 1959; Perry and Hower 1970; Hower et al. 1976). More recently, diagenetic changes in fine-grained sediments have been documented, most strikingly in the case of mixed-layer I/S, at the single crystal structure or clay package scale by transmission/analytical electron microscopy (Ahn and Peacor 1986; Yau et al. 1987; Freed and Peacor 1992) or nuclear magnetic resonance spectroscopy (Lindgreen et al. 1991; Schroeder 1993). Differences in shale mineralogy or clay mineral composition either downhole or within a given stratigraphic unit commonly are interpreted as indicating that a diagenetic reaction has taken place.

The formation of illite from smectite with increasing depth generally is perceived to be the most important diagenetic reaction in buried mudrocks. It has been correlated in many studies with the processes of hydrocarbon maturation and expulsion (Burst 1976), and has been suggested to be a primary control of overpressure development in shales (Powers 1967). For these reasons, the processes resulting in the formation of illite in shales have been the focus of considerable research for over 3 decades. In many studies, the fundamental assumption of primary (initial) compositional (i.e., mineralogical and geochemical) homogeneity within the studied unit or interval is made from the beginning, or following some more or less convincing justification. Further, bulk-rock chemical composition and mineralogy are rarely considered in the evaluation of controls on the specific mineral reaction of smectite to illite. Finally, the chemical properties of porewater, with which the clays interact, seldom can be characterized fully. Yet, if mineral reaction mechanisms and controls are to be unraveled, the whole bulk-rock system must be documented and the variables within the system assessed for their contribution to the control on mineral reaction mechanisms (Abercrombie et al. 1994; Pollastro 1994).

From the comparison of the 2 data sets (WCSB and USGC) below, we draw conclusions regarding the diagenetic and depositional controls on shale diagenesis and the intrinsic susceptibility of shales to undergo diagenetic alteration in the 2 different tectonic settings. In the USGC, Oligocene-Miocene age shales from the onset consisted of a reactive assemblage rich in smec-

tite, whereas in the western part of the WCSB, Cenomanian shales were deposited as a less reactive, detrital, illite-rich assemblage. We stress that any study of shale diagenetic processes must first evaluate what the initial chemical and mineralogical variability of the shale may have been at the time of deposition, recognizing that chemical and mineralogical homogeneity rarely is a large-scale characteristic of argillaceous sediments.

MATERIALS AND METHODS

The Western Canada Sedimentary Basin Shale

The Cenomanian Belle Fourche Formation of the WCSB has been the subject of a recent geochemical, mineralogical and isotopic investigation (Caritat, Bloch, Hutcheon and Longstaffe 1994). This unit is the uppermost of 6 dominantly marine shale units that comprise the Lower Colorado Group, which represents a significant part of the Cretaceous foreland basin fill in the Western Interior Seaway (Bloch et al. 1993). From west to east across the study area (a distance of approximately 1300 km), the Belle Fourche Formation thins from about 150 to 20 m, and ranges from >3000 to <300 m in present-day burial depth. Fifty-four shale and bentonite core samples were collected from the Belle Fourche across the basin, targeting a range of depositional environments and thermal maturities. Westernmost samples are pro-deltaic to middle shelf siltstones and mudstones that grade eastward into outer shelf, slope and basinal mudstones and claystones. Petrographic and textural information was obtained by back-scattered electron microscopy supplemented by energy-dispersive X-ray analysis. The samples were analyzed by Rock-Eval pyrolysis to determine the amount (total organic carbon, TOC) and type (hydrogen index, HI) of organic matter as well as level of thermal maturity (T_{max}). X-ray diffraction was performed on whole-rock powders and on oriented <2 μm and <0.2 μm separates using standard treatments (Moore and Reynolds 1989). Bulk-rock and clay-separate (<0.2 μm) chemical compositions were determined by X-ray fluorescence (XRF), and total carbon and sulfur contents by combustion. Seventeen O-isotope determinations of 15 shale clay-fractions (<0.2 or <0.05 μm) and 1 bentonite sample were performed using standard techniques and the results reported in conventional δ notation relative to standard mean ocean water (SMOW) (Craig 1961). Detailed sample location and methods are given in Caritat, Bloch, Hutcheon and Longstaffe 1994.

The Belle Fourche Formation shows no significant bulk-rock geochemical changes with either depth, thermal maturity or depositional environment (Caritat, Bloch, Hutcheon and Longstaffe 1994). In contrast, the mineral assemblage varies significantly. The matrix of immature, basinal Belle Fourche samples is
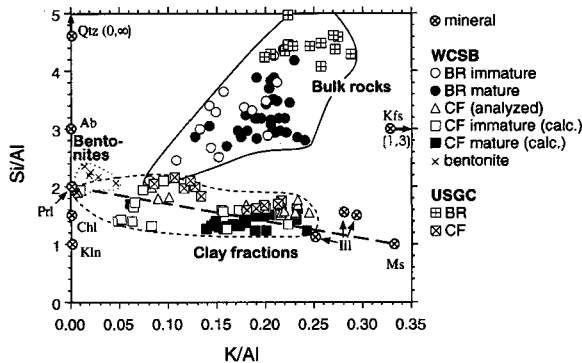
Figure 1. Si/Al vs. K/Al diagram illustrating the geochemical-mineralogical relationships of the Belle Fourche Formation (WCSB) bulk shales (○, ●; 2 samples with Si/Al > 7 not shown here; see Caritat, Bloch, Hutcheon and Longstaffe 1994), bentonites (×), analyzed clay fractions (△) and calculated clay fractions (□, ■) (data from Caritat, Bloch, Hutcheon and Longstaffe 1994), and of the USGC bulk shales (⊞) and analyzed clay fractions (⊠) (data from Hower et al. 1976). Open symbols represent thermally immature ($T_{max} \le 435$ °C) samples, while solid ones represent mature ($T_{max} > 435$ °C) samples. BR = bulk rock; CF = clay fraction. Quartz = Qtz; albite = Ab; pyrophyllite = Prl; chlorite = Chl; kaolinite = Kln; 3 different illites = Ill; muscovite = Ms and K-feldspar = Kfs compositions are indicated by ⊗. The mixing line between muscovite and pyrophyllite is indicated by – – –.

Figure 2. Si/K vs. Al/K diagram for Belle Fourche Formation (WCSB) clay fractions (△) and associated linear regression (slope ≅ 2; $r^2 = 0.99$), which intersects the bentonite field (×) from the WCSB (inset; the WCSB sample represented by ▲ was not used to calculate the regression line). US Gulf Coast (USGC) clay fractions (⊠) (Hower et al. 1976) plot very close to the WCSB linear regression. The regression line is nearly parallel to the mixing line between muscovite and pyrophyllite (– – –); the difference in the y-intercept could be caused by approximately 10% Mg substitution in octahedral sites (R. Ferrell, personal communication 1996).

composed dominantly of smectitic I/S and kaolinite, whereas that of more proximal, pro-deltaic to mid-shelf sediments from the west comprises mainly illitic I/S, kaolinite, mica and minor amounts of chlorite. Thus, one of the mineralogical trends observed to occur with depth in the WCSB shale is an increase in illite content of I/S.

The geochemical-mineralogical relationships of the Belle Fourche Formation shales can be illustrated on an Si/Al vs. K/Al diagram (Figure 1). In terms of bulk chemical composition, the shales are composed essentially of quartz, K-feldspar, kaolinite and illite/muscovite, as shown by XRD data and reflected in the bulk-rock chemistry (Figure 1, ○, ●).

Bulk-rock bentonite samples (×) and shale clay fractions (△) are also plotted on Figure 1. These are aligned along a trend extending from bentonitic (pyrophyllite + ?quartz) to illitic compositions. Again, this is consistent with the mineralogical composition of these samples as determined by XRD.

Calculated clay-fraction compositions were obtained by subtracting SiO_2, Al_2O_3 and K_2O from the bulk shale composition in amounts reflecting the normative abundances of quartz and feldspar (Caritat, Bloch, Hutcheon and Longstaffe 1994). Calculated clay-fraction compositions (□, ■) are similar to the analyzed clay fractions. The higher Si/Al values in the analyzed samples result from clay-sized quartz. These "impurities" are difficult to eliminate, as detrital quartz may persist to size fractions as small as 0.05
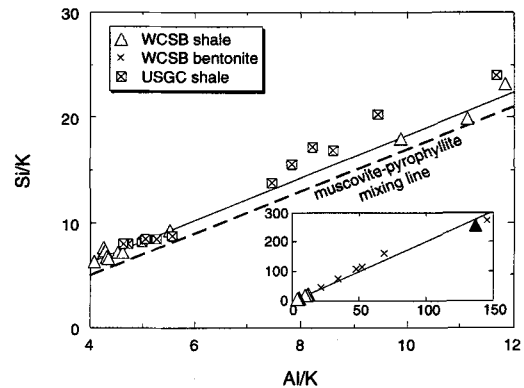
μm (or may even be of diagenetic origin). Nevertheless, the close agreement between the calculated and separated clay-fraction compositions illustrates the utility and accuracy of the normative calculations (method described in Caritat, Bloch and Hutcheon 1994).

To better assess the relationship between the bentonite and the matrix I/S compositions, a plot that widely separates the 2 sample populations is used. Figure 2 shows the linear regression through the Belle Fourche Formation clay fraction population (△) in a plot of Si/K vs. Al/K. The intersection of the clay fraction regression with the bentonite data (Figure 2, inset) is interpreted to indicate that the shale matrix composition results from the mixing of variable proportions of ashfall-derived material with detrital mica and illite, and that the bulk chemistry of the system is not affected by significant mass transport of soluble species (Caritat, Bloch, Hutcheon and Longstaffe 1994).

The O-isotopic composition of the clay fractions (<0.2 and <0.1 μm) separated from Belle Fourche Formation shales and 1 bentonite (<2 μm) varies between +14.06 and +18.16‰. It is plotted in Figure 3 as a function of K/Al of the clay fraction, a number which semi-quantitatively relates to the illite content in I/S.

The USGC Shale

The USGC shale compositions from the Oligocene-Miocene Frio and Anahuac Formations published by Hower et al. (1976) and O-isotopic compositions published by Yeh and Savin (1977), based on analyses
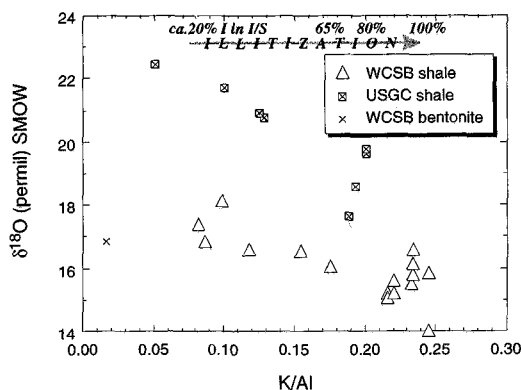
Figure 3. The $\delta^{18}O$ vs. K/Al value for Belle Fourche Formation (WCSB) clay fractions (<0.2 and <0.1 μm) ($\triangle$) and 1 bentonite (<2 μm) ($\times$) and USGC clay fractions (<0.1 μm) ($\boxtimes$) (isotopic data from Yeh and Savin 1977; K/Al values derived from data in Hower et al. 1976). Note the large difference in absolute $\delta^{18}O$ values between these 2 populations. Degree of illitization is indicated by increasing K/Al values.

of cuttings from well CWRU6, are used herein as a comparison with the Belle Fourche Formation shale data. Because these studies have been widely referred to in the clay literature, background information about the USGC shale is not duplicated here in detail. A description of geological setting, sample origin and analytical methods for the USGC data can be found in the original papers. Of importance, however, is the fact that the sampled interval was reported to be continuous and relatively homogeneous. The Frio-Anahuac boundary is intersected at about 2500 m depth. The Frio Formation consists of thick (>2000 m) slope and basinal mudstones overlain by interbedded terrestrial and marginal marine sandstone and shale units, whereas the Anahuac Formation is interpreted as a transgressive, predominantly marine shale wedge that onlaps the Frio (Pye et al. 1986).

The data collected from the USGC by Burst (1969) and subsequently by Hower and coworkers were the basis for the concept of smectite illitization. This fundamental concept was laid down first by the original authors themselves, and was subsequently refined by many clay scientists on the basis of the same central data set or new data from the same area (Awwiller 1993; Eberl 1993; Pollastro 1994). However, a consensus on the governing parameters and the detailed reaction mechanism(s) is yet to be reached (for example, replacement vs. dissolution-precipitation; importance of K, Si and Al in porewater; open vs. closed system diagenesis; and channelized vs. pervasive vs. minor porewater flow).

Bulk-rock USGC shale data (Hower et al. 1976, Table 6) are overlain on Figure 1 (⊞). Overall, these samples are marginally more siliceous and, especially, less aluminous than Belle Fourche Formation shales,

and therefore plot towards the higher end of the Si/Al and K/Al ranges characteristic of the Belle Fourche Formation samples.

In Figure 1, the clay-fraction (<0.1 μm) chemical compositions reported in Hower et al. (1976, Table 7) are superimposed ($\boxtimes$) on the Belle Fourche Formation clay compositions. They are surprisingly similar to the Belle Fourche Formation trend described earlier, and are particularly close to the analyzed clay separates ($\triangle$) from the Belle Fourche Formation.

In Figure 2, the USGC data ($\boxtimes$) are superimposed on the Belle Fourche Formation clay-separate composition and its derived linear regression. The USGC clay fractions fit this WCSB regression remarkably well, given the geographical and genetic differences between these 2 clay populations.

In terms of O-isotopes, a major and significant difference between the WCSB and the USGC shale clay fraction emerges (Figure 3). The USGC clay fractions (<0.1 μm, $\boxtimes$) are more enriched in ^{18}O by 2 to 4‰ with respect to the Belle Fourche Formation clay fractions (<0.2 and <0.1 μm). A trend of decreasing $\delta^{18}O$ with increasing K/Al values (that is, illitization) is apparent for the USGC shales, and to some extent also in the WCSB data.

DISCUSSION AND CONCLUSIONS

The major element chemistry of bulk shales and clay fractions from the WCSB and USGC, as compared herein, are remarkably similar, yet their O-isotopic compositions are clearly distinct. The Belle Fourche samples are bimodal (Figure 3): basinal (distal) shales have higher $\delta^{18}O$ ($\geq 16.6‰$) and lower K/Al values (<0.16) relative to the pro-deltaic (proximal) shales ($\delta^{18}O < 16.6‰$ and K/Al>0.17) (Caritat, Bloch, Hutcheon and Longstaffe 1994). The basinal shales are interpreted to contain smectite and I/S formed by low-temperature alteration of volcanic detritus during early diagenesis. Pro-deltaic shales contain a significant amount of detrital illitic clay formed from the alteration of high-temperature cratonic precursors, and thus have lower $\delta^{18}O$ values and higher K contents (Caritat, Bloch, Hutcheon and Longstaffe 1994). There is no well-defined change in the isotopic composition of I/S with either depth or thermal maturity. In contrast, USGC O-isotopic values do show a depth-related trend and are interpreted to represent significant illitization of I/S, and resulting porewater and clay exchange with increasing temperature during diagenesis (Yeh and Savin 1977). The significant difference in $\delta^{18}O$ values between the 2 data sets most likely reflects differences in source of precursor material, weathering effects and the isotopic composition of surface and pore fluids attending weathering and diagenesis. The 2 clearly different trends indicate the disparate conditions, and perhaps mechanisms, of I/S formation.

The clay fractions from WCSB and USGC are chemically indistinguishable (Figures 1 and 2). Mineralogical similarities are also observed, with trends from smectitic I/S to illitic I/S reported in both cases (Hower et al. 1976; Caritat, Bloch, Hutcheon and Longstaffe 1994). However, the modes of origin of the clays in these 2 settings are interpreted to be widely different. In the case of the WCSB, Caritat, Bloch, Hutcheon and Longstaffe (1994) considered that preservation of depositional heterogeneities in chemical and mineralogical composition was the main cause of the observed geochemical and mineralogical trends. The composition of the USGC clay fractions was interpreted to result from illitization of smectite during burial diagenesis (metamorphism) of an initially homogeneous shale unit (Hower et al. 1976). Thus, accepting the genetic interpretations for clays in these 2 shales as argued in the original papers, the observed similarity in the geochemical and mineralogical characters of these 2 shales implies that both 1) inheritance of depositional chemical and mineralogical variability and 2) smectite illitization during burial can impart similar major element composition and clay mineral assemblages to shales. This similarity is a result of the mixing, regardless of its genetic origin, of muscovite and pyrophyllite, which imposes a slope of 2 on the diagram of Si/K vs. Al/K, for instance (the intercept of the mixing line will depend on the degree of Mg substitution in the octahedral sites of the minerals).

As a consequence, identification of an increase with depth in the illite content of I/S separated from shales does not necessarily indicate that smectite-illite reaction has taken place in the sediment. A detailed investigation of the initial compositional (chemical, mineralogical and isotopic) variability of any shale under investigation should be undertaken, by taking a much greater number of samples of the unit than commonly done today (ideally, compositional homogeneity has to be investigated at different scales, vertically and laterally). Only when this has been done can the relative significance of the depositional and diagenetic signals be assessed. From the comparison of these data sets, it is possible that the importance of initial chemical and mineralogical heterogeneity may have been largely underestimated in previous studies of shale diagenesis.

Finally, it may be appropriate to comment on the difference in tectonic setting between the WCSB and the USGC. In a foreland basin such as the WCSB, the composition of sediments contained within any given stratigraphic unit will reflect depositional setting, particularly proximity to the main source of detritus, the deformation front. Therefore, clay minerals such as muscovite and illite, derived directly or indirectly from high-temperature precursors, are expected to be more abundant in proximal environments, and progressively less abundant basinwards. Ashfall-derived volcanic material, which is deposited more homogeneously over the whole basin, is overwhelmed in proximal environments by the quantity of clastic material shed off the deformation front. We believe that tectonic setting and depositional environment are the primary controls on the observed compositional trends in the Belle Fourche Formation.

The Cenozoic of the USGS is characterized by high, but greatly variable, depositional rates (Yeh and Savin 1977), and sedimentation patterns complicated by salt diapirism or growth faults (Culotta et al. 1992). Detailed stratigraphic analysis of vertical sections is therefore requisite to the interpretation of compositional trends. The depositional setting of the USGC (shallowing-upward within the initially smectitic Frio between 5800 and 2500 m, overlain by predominantly marine Anahuac) will not, *a priori,* result in a marked initial compositional trend of increasing illite content with depth (indeed, shallowing upward sequences may even produce an increase in illite content upward). In contrast, argillaceous sediments derived from the Cordillera and deposited in the western part of the WCSB would have contained less smectitic material, and constituted an illite-rich assemblage from the onset.

If bulk-rock geochemistry can yield similar signatures for shales having undergone contrasting evolutions, as shown here, how then can the depositional and diagenetic signals be distinguished? Specifically, can detrital illite be differentiated from authigenic illite? One promising possibility is the oxygen-isotopic composition of clay fractions. It appears that the environment in which I/S formed can leave a durable and diagnostic O-isotopic signature in the clay fraction. Other procedures might include the analysis of bentonite beds (Hoffman and Hower 1979), illite polytypes (Velde and Hower 1963; Hower and Mowatt 1966), trace and rare earth elements in clays (Awwiller 1994; Cullers 1994; Fagel et al. 1994; Ohr et al. 1994) and illite dating (Mossmann 1991; Roden et al. 1993), together with facies/paleogeographic analysis. Most likely, only a combination of several of these strategies will yield unambiguous answers to these questions.

There is a need for improving our understanding of the initial, depositional composition and clay mineral assemblage(s) of shales as a function of depositional environment and tectonic setting. Mudrock sedimentologists and geochemists must work together toward this goal, if we are to discriminate the effects that depositional and diagenetic processes impart to shale composition. Only then can we expect to unravel the details of the smectite-illite and concurrent reactions in argillaceous sediments.

ACKNOWLEDGMENTS

REFERENCES

Abercrombie HJ, Hutcheon IE, Bloch JD, Caritat P de. 1994. Silica activity and the smectite-illite reaction. Geology 22:539–542.

Ahn JH, Peacor DR. 1986. Transmission and analytical electron microscopy of the smectite-to-illite transition. Clays Clay Miner 34:165–179.

Awwiller DN. 1993. Illite/smectite formation and potassium mass transfer during burial diagenesis of mudrocks: A study from the Texas Gulf Coast Paleocene-Eocene. J Sed Petrol 63:501–512.

Awwiller DN. 1994. Geochronology and mass transfer in Gulf Coast mudrocks (south-central Texas, U.S.A.): Rb-Sr, Sm-Nd and REE systematics. Chem Geol 116:61–84.

Bloch J, Schröder-Adams C, Leckie DA, McIntyre DJ, Craig J, Staniland M. 1993. Revised stratigraphy of the lower Colorado Group (Albian to Turonian), western Canada. Bull Cana Petrol Geol 41:325–348.

Burst JF. 1959. Post-diagenetic clay mineral environmental relationships in the Gulf Coast Eocene. Clays Clay Miner 6:327–341.

Burst JF. 1969. Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration. Am Assoc Petrol Geol Bull 53:73–93.

Burst JF. 1976. Argillaceous sediment dewatering. Ann Rev Earth Planet Sci 4:293–318.

Caritat P de, Bloch J, Hutcheon I. 1994. LPNORM: A linear programming normative analysis code. Comput Geosci 20:313–347.

Caritat P de, Bloch J, Hutcheon I, Longstaffe FJ. 1994. Compositional trends of a Cretaceous foreland basin shale (Belle Fourche Formation, Western Canada Sedimentary Basin): Diagenetic and depositional controls. Clay Miner 29:503–526.

Craig H. 1961. Standards for reporting concentrations of deuterium and oxygen-18 in natural waters. Science 133:1833–1834.

Cullers RL. 1994. The controls on the major and trace element variation of shales, siltstones, and sandstones of Pennsylvanian-Permian age from uplifted continental blocks in Colorado to platform sediment in Kansas, USA. Geochim Cosmochim Acta 58:4955–4972.

Culotta R, Latham T, Sydow M, Oliver J, Brown L, Kaufman S. 1992. Deep structure of the Texas Gulf passive margin and its Ouachita-Precambrian basement; results of the CO-CORP San Marcos Arch survey. Am Assoc Petrol Geol Bull 76:270–283.

Eberl DD. 1993. Three zones for illite formation during burial diagenesis and metamorphism. Clays Clay Miner 41:26–37.

Fagel N, Andre L, Debrabant P. 1994. Geochemical tools useful in order to discriminate the distinct sedimentary components of deep-sea clays (Neogene Equatorial Indian Ocean). Mineral Mag 58A:259–260.

Freed RL, Peacor DR. 1992. Diagenesis and the formation of authigenic illite-rich I/S crystals in Gulf Coast shales: TEM study of clay separates. J Sed Petrol 62:220–234.

Hoffman J, Hower J. 1979. Clay mineral assemblages as low grade metamorphic geothermometers: Application to the thrust faulted disturbed belt of Montana, U.S.A. Soc Econ Paleontol Mineral Spec Publ 26:55–79.

Hower J, Eslinger EV, Hower ME, Perry EA. 1976. Mechanism of burial metamorphism of argillaceous sediments: 1. Mineralogical and chemical evidence. Geol Soc Am Bull 87:725–737.

Hower J, Mowatt TC. 1966. The mineralogy of illites and mixed-layer illite/montmorillonites. Am Mineral 51:825–854.

Lindgreen H, Jacobsen H, Jakobsen HJ. 1991. Diagenetic structural transformations in North Sea Jurassic illite/smectite. Clays Clay Miner 39:54–69.

Moore DM, Reynolds RC. 1989. X-ray diffraction and the identification and analysis of clay minerals. New York: Oxford Univ Pr. 332 p.

Mossmann JR. 1991. K-Ar dating of authigenic illite-smectite clay material: Application to complex mixtures of mixed-layer assemblages. Clay Miner 26:189–198.

Ohr M, Halliday AN, Peacor DR. 1994. Mobility and fractionation of rare earth elements in argillaceous sediments: Implications for dating diagenesis and low-grade metamorphism. Geochim Cosmochim Acta 58:289–312.

Perry EA, Hower J. 1970. Burial diagenesis in Gulf Coast pelitic sediments. Clays Clay Miner 18:165–177.

Pollastro RM. 1994. Clay diagenesis and mass balance—The forest and the trees. Clays Clay Miner 42:93–97.

Powers MC. 1967. Fluid-release mechanisms in compacting marine mudrocks and their importance in oil exploration. Am Assoc Petrol Geol Bull 51:1240–1254.

Pye K, Krinsley DH, Burton JH. 1986. Diagenesis of US Gulf Coast shales. Nature 324:557–559.

Roden MK, Elliott WC, Aronson JL, Miller DS. 1993. A comparison of fission-track ages of apatite and zircon to the K/Ar ages of illite-smectite (I/S) from Ordovician K-bentonites, southern Appalachian basin. J Geol 101:633–641.

Schroeder PA. 1993. A chemical, XRD, and ^{27}Al MAS NMR investigation of Miocene Gulf Coast shales with applications to understanding illite/smectite crystal-chemistry. Clays Clay Miner 41:668–679.

Velde B, Hower J. 1963. Petrographical significance of illite polymorphism in Paleozoic sedimentary rocks. Am Mineral 48:1239–1254.

Yau YC, Peacor DR, McDowell SD. 1987. Smectite-to-illite reactions in Salton Sea shales: A transmission and analytical electron microscopy study. J Sed Petrol 57:335–342.

Yeh HW, Savin SM. 1977. Mechanism of burial metamorphism of argillaceous sediments: 3. O-isotope evidence. Geol Soc Am Bull 88:1321–1330.