NOTES

CLAY DIAGENESIS AND MASS BALANCE—THE FOREST AND THE TREES

The well-profile studies by Weaver and Beck (1971) and Hower *et al.* (1976) documenting smectite diagenesis (also referred to as shale diagenesis by Hower, 1981, and smectite illitization by Bethke and Altaner, 1986, in the U.S. Gulf Coast shales have probably produced more geologic investigations and publications in clay mineralogy in the past two decades than any other single phenomenon in clay science. Although smectite diagenesis documented in well samples is commonly referred to as depth diagenesis, or as a depth-related or depth-dependent phenomenon, it is probably controlled mostly by temperature and potassium availability, among other factors (see Pollastro, 1993).

The most convincing evidence of smectite illitization in the early Gulf Coast well-profile studies came from detailed mineralogical and chemical investigations of shale cuttings in the Gulf Coast Case Western Reserve University 6 (CWRU6) well (Hower *et al.,* 1976). Subsequently, other studies have adapted and applied the mineral and chemical data of Hower *et al.* (1976) in part or whole to perform mass balance equations in sedimentary rocks or basins or to explain the various interpretations concerning the chemical and physical nature of the smectite-to-illite reaction (see Chamley, 1989, and Weaver, 1989). Most recently, the excellent papers by Eberl (1993) and Awwiller (1993) have addressed the data and interpretations of Hower *et al.,* 1976, and provide new insight on the reactions and mechanisms in Gulf Coast shale diagenesis. Here, I briefly describe how the data and interpretations of Gulf Coast shale composition and diagenesis from the study of Hower *et al.* (1976) may represent only part of the smectite illitization picture. Using the Gulf Coast examples, it is intended here to identify and demonstrate how observations in clay petrology may be easily biased from overfocus on fine-grained fractions, often resulting in an unintentional loss of context with the bulk rock and consequent misrepresentative interpretations.

Despite the wealth of excellent data, observations, and interpretations by Hower *et al.* (1976) on the Gulf Coast shales of CWRU6, others needed for a comprehensive understanding of Gulf Coast shale diagenesis and smectite illitization may not have been addressed. Although major constituent bulk chemistry was reported, mineralogical changes that took place with depth

were presented, discussed, and interpreted from size-specific fractions, i.e., the weight percent of a particular mineral phase or group might increase or decrease in a particular size fraction with depth, but how significant was that particular size fraction and its depth-related mineralogic changes to the bulk or whole shale mineralogy? Bulk-rock mineral composition of the shale samples could be pieced together from the tables of data of Hower *et al.* (1976) by performing a few simple calculations. However, nowhere was the whole-rock mineral composition of the shale specifically compiled, displayed, or discussed. Towe (1974) discusses how "quantitative" clay petrology is sometimes unintentionally biased when analyzing a specific clay fraction by XRD. He cautioned how it is possible that "a forest of information can be lost in the trees of experimentation"—more specifically, that a fair representation of the bulk sample deserves at least as much attention as that of the clay fraction. Similarly, it is pointed out here that such great detail was given to mineralogy and chemistry of specific parts (individual size fractions) in the study by Hower *et al.* (1976), that little consideration was given to the whole (the bulk shale). Moreover, although subsequent studies of the smectite-to-illite reaction documenting changes with depth in one or more specific size fractions have monitored corresponding mineralogical changes in the bulk rock (e.g., Boles and Franks, 1979; Pollastro, 1985; Jennings and Thompson, 1986; Awwiller, 1993), others have not (e.g., Shaw and Primmer, 1989).

Boles and Franks (1979) first related bulk-shale composition in CWRU6, in part, to smectite illitization by calculating the weight percent of I/S in the bulk rock for the five samples of cuttings analyzed for particle size distribution by Hower *et al.* (1976). Using this limited bulk-rock data, Boles and Franks (1979) identified an 18 percent weight loss in I/S clay in shale samples over a depth interval from 1850 m to 4600 m and an illite layer content increase in I/S of about 50 percent. They concluded that the illitization of smectite more closely approximated a reaction in which Al and K are conserved and smectite is destroyed (hereafter referred to as Reaction 2), a process they referred to as "cannibalization." This interpretation was different than the original smectite-to-illite reaction defined by Hower *et al.* (1976) (hereafter referred to as

93

Table 1. Particle size distribution of well-cutting samples from Case Western Reserve University Gulf Coast Well 6.

Depth (m)	>10 μm	2–10 μm	0.5–2 μm	0.1–0.5 μm	<0.1 μm	Total
1850	15.6	13.2	8.4	42.0	20.8	100.0
2400	16.4	11.0	14.6	35.1	22.8	99.9
3400	21.2	14.3	12.1	33.4	19.1	100.1
4600	18.1	25.1	18.6	25.8	12.5	100.1
5500	25.0	23.8	23.7	19.0	8.6	100.1

Data from Hower *et al.* (1976) in wt. % of size fraction (air dried).

Reaction 1) for the Gulf Coast shales of CWRU6. Moreover, Reaction 2 of Boles and Franks (1979) was of much greater significance to sandstone cementation because substantially more silica, calcium, iron, and magnesium are released than in Reaction 1 of Hower *et al.* (1976). Hower (1981) briefly discussed the bulk I/S relation presented by Boles and Franks (1979) and concluded that Reaction 2 may be more appropriate. The amount or change in total clay, quartz, feldspar, or calcite in the bulk rock, however, were not calculated or addressed by Boles and Franks (1979).

Here, bulk-mineral composition was calculated for each of the five samples of cuttings that were analyzed by Hower *et al.* (1976, Table 2) for particle-size distribution and integrated and compared with the data, relations, and interpretions from individual size fractions of their report. Eberl (1993, Table 1) recently calculated bulk-mineral composition in a similar fashion for the same five shale samples from CWRU6 to reformulate and reinterpret illite formation in Gulf Coast shales from mass-balance equations. Although Eberl (1993) generally outlined many of the changes in bulk shale mineralogy with depth, discussions and interpretations were specific to his proposed model of illite formation.

The depth-designated samples from CWRU6 were 1850, 2450, 3400, 4600, and 5500 m; the original particle-size data of Hower *et al.* (1976) are shown in Table 1. The wt. % of each mineral phase was calculated here from the semiquantitative XRD data of Hower *et al.* (1976, Tables 3 and 4) for each size fraction of the five samples. For example, the shale sample from 1800 m

contains 93 wt. % total clay (as phyllosilicates, see Schultz, 1964) in the 0.1- to 0.5-μm fraction from Table 3 of Hower *et al.* (1976), and the 0.1- to 0.5-μm fraction comprises 42 wt. % of the sample (Hower *et al.,* 1976, Table 2), thus calculating 39 wt. % (42 × 0.93) of the total clay for this fraction. After calculating the wt. % clay for each of the five fractions, the accumulative total clay from all of the parts is about 69 wt. % for the bulk shale. Calculation of each mineral phase (or mineral group) in a similar way for each of the five shale samples, the bulk-shale XRD mineral composition was determined. The results are summarized in Table 2.

The data of Hower *et al.* (1976) can now be viewed from a changing whole-rock mineral composition with depth and are illustrated here (Figure 1) in a fashion similar to the data presented by Hower *et al.* (1976) for specific size fractions. There is a noticeably significant change in bulk-shale mineralogy from 1850 m to 5500 m in CWRU6. In wt. % of the whole rock, shale sample at 1850 m contains about 68% total clay and 16% quartz, as compared with shale sample at 5500 m having 54% clay and 36% quartz. This is a change in the clay/quartz ratio from about 4.3 to 1.5, respectively, significant to the interpretation of both diagenesis and provenance. Additionally, there is a progressive loss in total feldspar content from 9% at 1850 m to 4% at 4600 m, and then an increase to 10% at 5500 m. The decrease in calcite of about 6% with depth reported by Hower *et al.* (1976), also shown here in Table 2, cannot explain these much larger differences in clay and quartz contents and corresponding clay/quartz ratios simply by the addition of (or by a dilution effect from) calcite.

These data and relations allow comparative analysis of bulk-shale data from other studies and, more importantly, a much broader view for the analysis of Gulf Coast shale deposition and diagenesis. Was starting (detrital) composition of the shales relatively constant throughout deposition? If so, the amount of clay had decreased and/or quartz had increased dramatically per unit weight of shale with increased depth and diagenesis—or could there have been a significant change in source materials with time and depth (particularly

Table 2. Calculated bulk-rock mineralogies, in wt. %, of well-cutting samples in the Case Western Reserve University 6 well, U.S. Gulf Coast from X-ray powder diffraction data of Hower *et al.* (1976).

Depth (m)	Clay	(I/S, C, K, M)	Quartz	Calcite	Plagioclase	K-feldspar	Total
1850	69(68)	(51, 0, 15, 2)	16	7	6	3	101
2450	69	(49, 6, 12, 3)	22	2	2	5	100
3400	65(64)	(46, 6, 12, tr)	30(29)	3	3	<1	102
4600	59(62)	(45, 8, 9, 0)	32(34)	<1	4	0	95
5500	55(54)	(38, 8, 8, 0)	37(36)	<1	10	0	102

Data in parentheses are values normalized to 100%. Clay = total clay as phyllosilicates; I/S = illite/smectite; C = chlorite; K = kaolinite; M = mica.
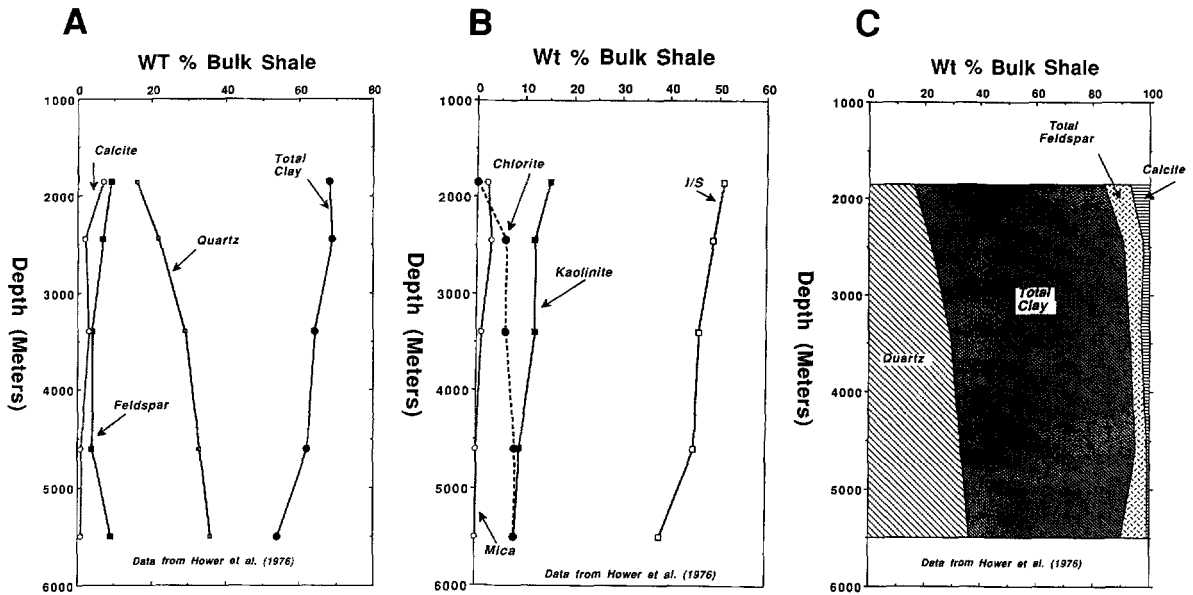
Figure 1. Weight percent (wt. %) mineral or mineral group *vs* depth in bulk shale from X-ray powder diffraction analysis of five well-cutting samples analyzed for particle-size distribution in the Gulf Coast, Case Western Reserve University 6 well. Data calculated and normalized to 100% from Hower *et al.* (1976). A) Line graph showing changes in individual mineral groups and phases in bulk shale. B) Line graph showing changes in individual clay minerals in bulk shale. C) Accumulative area graph showing changes in general bulk composition. I/S = illite/smectite.

a progressive increase in the clay/quartz ratio upsection)? Are potassium feldspar and mica being dissolved, or were these specific mineralogical changes with depth source related?

For example, the data show a progressive decrease in clay with depth, consistent with a cannibalization reaction (Reaction 2), as first suggested by Boles and Franks (1979). If clay was cannibalized (i.e., dissolved and recycled during smectite illitization) with increasing diagenetic reaction extent, a smaller amount of particular chemical components, such as Al and K, would be needed to complete clay reactions in the shale that result in progressively less clay. Reaction 2 also allows for greater amounts of silica to form than Reaction 1. Although Boles and Franks (1979) point out that Reaction 2 creates a greater potential for the exportation of silica for cement in nearby more porous reservoir sandstones, the bulk-shale mineral data calculated here, and in the recent study by Awwiller (1993), suggest that silica, as quartz, may be conserved within the shale.

Particular caution should be taken in extrapolating any interpretation in mineralogy and diagenesis of bulk shale in well profiles when the clay analysis is limited to one specific clay-size fraction—a situation of which I personally need reminding. Because crystal habit and size may inherently vary with different clay minerals, it is of particular concern that the clay fraction studied does not produce a size-selective clay-mineral assemblage misrepresentative of that in the bulk rock. Also,

the contribution of any one size fraction to the bulk rock may vary considerably from sample to sample. In the case of well profiles, if coarser chlorite and illite clays (relative to finer I/S) form in a shale sequence with increasing temperature due to burial, they may be absent or present only in minor amounts in the finest (e.g., <0.5 μm or <0.1 μm) fractions, but more abundant in the coarser (e.g., 0.5–5 μm) fractions.

For example, several interpretations, extrapolations, and comparisons are made to the data from CWRU6 of Hower *et al.* (1976) by Awwiller (1993) using data and assumptions from the Shell Carroll No. 1 well derived from the bulk shale and the <0.5 μm fraction; however, no quantitative data are reported on what wt. % the <0.5-μm fraction contributes to the bulk shale. Cautiously assuming that the clay-mineral abundance of <0.5 μm material is equally representative to that of the bulk shale, Awwiller (1993) presents a case that although the total amount of clay decreases in the Carroll No. 1 well, the total amount of I/S is almost identical in shallow and deep samples. Thus, he concludes that smectitic I/S does not appear to be cannibalized to conserve Al for the production of illitic I/S, a contrasting interpretation to that observed of Boles and Franks (1979) on the CWRU6 data. Applying the wary assumption that clay-mineral abundance of the <0.5 μm fraction is equally representative of the bulk shale, calculating a total I/S(?) for the bulk shale, and then recasting the data of Awwiller (1993) here shows, however, that although I/S appears to increase in the
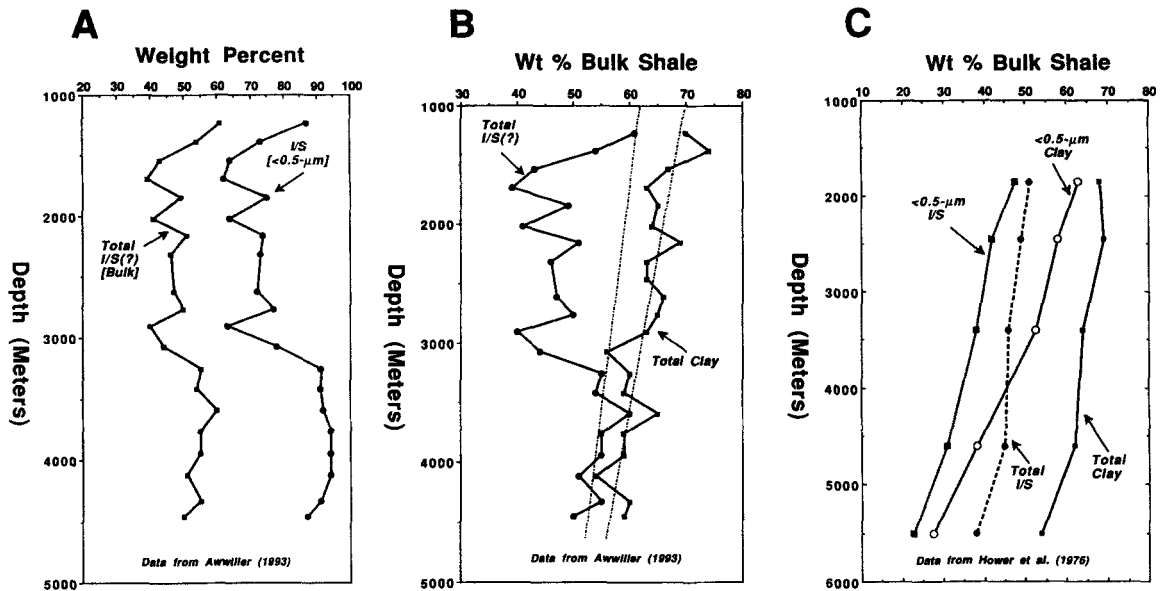
Figure 2.   Weight percent (wt. %) mixed-layer illite/smectite (I/S) and total clay minerals (total clay) *vs* depth in bulk shale and <0.5 μm fraction *vs* depth from X-ray powder diffraction analysis of well cuttings from Gulf Coast. A, B) Data from Awwiller (1993) in the Shell Carroll No. 1 well. Total I/S (?) was calculated assuming that clay abundance for bulk shale is similar to that determined for <0.5 μm fraction. Dashed lines in B indicate possible trends of decreasing total I/S (left) and total clay (right) in bulk shale with increasing depth in well. C) Data calculated from Hower *et al.* (1976) in the Case Western Reserve University 6 well.

<0.5 μm fraction with increasing depth in the well, the assumed total I/S in the bulk shale may actually decrease (Figure 2A). This is particularly shown by those samples below 3200 m (where kaolinite, illite, and chlorite are minimal), a trend very similar to that of the total clay content (Figures 2A and 2B). Moreover, the trend line established by I/S below 3200 m can be projected to the uppermost sample in the well which also contains minimal kaolinite, illite, and chlorite (Figure 2B). These shale samples along the dashed line in Figure 2B could indicate similar source materials and starting composition perhaps suggesting that the increase in kaolinite in the upper half of the well may be related to a change in clay-source material. A selective fractionation of finer I/S relative to illite and chlorite in the <0.5 μm fraction could also explain the I/S distribution.

Moreover, combining the size-fraction data of Hower *et al.* (1976, Table 3) from CWRU6 shows that the <0.5 μm material of Gulf Coast shales may not be representative of the whole. Although the <0.5 μm material from CWRU6 is composed of >90% clay that is >90% I/S, the contribution of the <0.5 μm fraction to the bulk shale decreases progressively from about 63 wt. % at 1850 m to 28 wt. % at 5500 m (Figure 2C). Thus, this size-specific data now related to the bulk shale show a dramatic loss in the <0.5 μm material (Figure 2C). This could indicate a dramatic loss in I/S unless, perhaps, I/S particles are growing progressively larger (>0.5 μm) because total I/S in the rock

is much greater than <0.5 μm I/S in the deepest samples. Alternatively, chlorite (commonly inherent of coarser-size than I/S) increases with depth and is more abundant in the >0.5 μm fractions. Again, these relations of the parts to the whole may be critical to the interpretations of deposition and diagenesis.

These observations and relations from the bulk mineralogy of shale with depth in CWRU6 can also be compared with other studies of deeply-buried Gulf Coast shales. For example, Freed (1979) found in a study of Gulf Coast shale samples an overall increase in total clay content from 65%–70% at about 670 m to 75%–80% at about 4600 m; there was a slight increase in total feldspar content and no significant change in the amount of quartz over this same interval. Similarly, it is shown here that although K-feldspar decreases in CWRU6, total feldspar content (mainly as plagioclase) of the deepest sample at 5500 m increased slightly from that of the shallowest sample at 1800 m (Figure 1C). Freed (1981), in a later study of smectite illitization in two geopressured wells, Hidalgo County, Texas, documented that quartz, total clay, calcite, and K-feldspar contents are constant and plagioclase feldspar content gradually increased with depth. He concluded that Reaction 2 of Boles and Franks (1979) better explained the diagenetic reactions occurring with depth in the shale samples studied. In contrast to CWRU6, Freed and Peacor (1989, 1992) noted the presence of K-feldspar at all depths in shales from the Gulf Coast of Texas, including depths well below the

cessation of the smectite-to-illite transformation, suggesting the K-feldspar was not consumed in the reaction. Inconsistencies such as those noted above could suggest either 1) local variations in deposition and/or diagenesis or 2) that other factors control the resulting composition of Gulf Coast shale.

Many of the mineralogic relations shown in the data presented in specific size fractions by Hower *et al.* (1976) could also be misinterpreted and extrapolated to the bulk shale mineralogy. For example, Hower *et al.* (1976) found a general increase in the abundance of clay minerals with increasing depth within the coarser size fraction and also noted a slight decrease in the amount of clay minerals with depth in the 0.1- to 0.5 μm fraction. They attributed the increase in clay in the coarser fraction to three factors: 1) an increase in lithification with increased burial causing more difficult disaggregation of the sample; 2) a loss of silt-size potassium feldspar into clay-size material; and 3) dissolution of calcite. Without presenting the bulk-mineral composition, one might interpret an overall increase, rather than decrease, in clay content from the data and discussion presented. Similarly, any mineralogic changes or relations in the bulk shale should not be generically applied to explain reactions within any specific size fraction nor should the data from specific size fractions be ignored. Sometimes different overall relations are observed in mineralogy for both bulk shale and specific size fractions (e.g., total clay and feldspar and quartz contents in CWRU6), or similar changes and relations may occur in both, as with K-feldspar, calcite, and mica contents in CWRU6.

In conclusion, this paper cautions how the interpretation of clay diagenesis and mass balance from the details of analytical data in clay petrology studies may sometimes be biased or misleading from unintentional overfocus on specific parts or size fractions of a shale sample. Although the observations and interpretations documented here may be questioned, the clay petrology study of CWRU6 addressing clay diagenesis and mass balance demonstrates the importance in knowing the mineralogy of the bulk shale, or whole rock, as well as that of any of the size-specific fractions—a case of the forest and the trees.

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U.S. Geological Survey   Richard M. Pollastro
MS 960, Box 25046
Denver, Colorado 80225

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