Characteristics of mixed-layer smectite/illite density separates during burial diagenesis

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ABSTRACT

We report a method to physically separate smectite from illite in natural shale samples. This method is based upon the large contrast in the density of mixed-layer clay minerals reported in the literature. Our objective was to investigate the behavior of separate density fractions of mixed-layer smectite and illite during burial diagenesis.

Samples were obtained from shale cuttings hand-picked from a well drilled offshore Louisiana. Each sample was separated into 5 fractions: “pure” end-member smectite (EMS), smectite-rich mixed-layer clays (SML), illite-rich mixed-layer clays (IML), “pure” end-member illite (EMI), and quartz (FGQ). The mineralogy of each clay-mineral separate as determined by XRD was reasonably consistent at all depths, although the abundance of the mixed-layer separates varied. The illite-rich mixed-layer fraction increased in abundance with depth at the expense of the smectite-rich mixed-layer fraction. The fine-grained quartz fraction showed an increase in abundance, a decrease in average grain size, a loss of K-feldspar, and a heavier isotopic signature with depth. We did not, however, find a correlation with depth in the amount of the end-member clay fractions. The isotopic signature of the end-member smectite shows evidence of equilibration with depth, but the end-member illite does not. We conclude that the discrete illite fraction is detrital in origin and was not involved in the clay-mineral transformation at the depths sampled in our well. It reflects the sediment provenance.

The results of this study illustrate the efficacy of the newly developed density separation technique for physically isolating clay mineral species from one another.

INTRODUCTION

Lynch (2000) considers smectite to illite diagenesis the most important reaction in clastic sedimentary diagenesis. Since the pioneering work of Hower et al. (1976), there have been several excellent studies examining the smectite to illite transition. These works document the decrease in expandability of mixed-layer clays and the increase in illite crystallinity with increasing burial depth. Środoń (1980) developed a method using X-ray diffraction (XRD) peak positions to measure the smectite-illite ratio of the mixed-layer clay fraction. A number of studies have relied on this method or similar methods to verify the smectite to illite transition. Recent studies use the method of matching modeled XRD patterns of various calculated clay mixtures to patterns from actual samples (Reynolds 1989). The ability to physically separate individual clay minerals and X-ray them separately would permit a more-direct approach to the study of the smectite to illite reaction.

The physical separation of clay-mineral species (by differences in chemical, size, magnetic, dielectric, and density properties) has been burdened with difficulties (Towe 1974). Overlapping ranges of properties between different clay minerals are among the primary causes for the inability to separate them physically. Particularly troublesome impediments to separation by density are the extremely small grain size, the platy morphology of clays resulting in large surface areas that can “raft” mineral grains, adsorption of material from separating media, and electrostatic forces that can cause flocculation. In spite of these inherent difficulties, the tangible research benefits that would result from a successful clay-mineral separation method encouraged us to develop this technique.

Density differences of smectite-illite

There has been partial success involving the quantitative separation of clay minerals. Studies of the separation of clay minerals by settling and particle size (Kerns 1967), adsorption by organic heavy liquids (Nelson 1995), dielectric separation (Müller 1967), and magnetic separation (Russel et al. 1984; Schultz and Dixon 1979) have all documented that certain clay minerals can be concentrated given time, patience, and special equipment. However, quantitative clay-mineral separation has not yet been realized for two of the major clay-mineral constituents of non-metamorphosed shales, illite and smectite. It is not uncommon to find fine-grained sedimentary rocks dominated by mixtures of smectite and illite, with variable amounts of quartz, feldspars, kaolinite, chlorite, and heavy minerals in clastic basins world-wide. This mineralogy is particularly evident in the U.S. Gulf Coast section where discrete smectite, discrete illite, and mixed layer illite-smectite with variable proportions of illite interlayers have been reported (Aronson and Hower 1976). In addition, minor amounts of quartz and feldspar are usually present in Gulf Coast shales, particularly in the coarser grain sizes. The ability to physically separate smectite from illite will be of use to the many investigators of these rocks.

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Physical separation of clays using density differences

Published specific gravities of clay minerals span a rather wide range—from 2.0 (low end for smectites) to 3.3 (high end for chlorites) (Deer et al. 1966). As a result of their high surface area and variable inter-layer expandability, determination of the precise density of clay minerals is problematic. Nevertheless, comparisons of the reported clay-mineral density ranges are useful for predicting which clays can be separated physically. Density ranges for the common clay minerals from Deer et al. (1966) are listed in Table 1. As seen in the table, the density of smectite is significantly less than the density of the other major clay minerals. This difference provides the theoretical basis for the physical separation of smectite from other minerals in fine-grained sedimentary rocks. The partial overlap in the ranges of reported density often precludes a complete separation of illite from chlorite and from kaolinite. However, actual density differences among the clay minerals in rocks of interest should be examined, and may be sufficient for producing mineral separates or mineral concentrates, particularly in combination with techniques involving magnetic and other properties of clay minerals.

Strategy

The aim was to develop a density technique for separating the illite-smectite family into fractions with varying proportions of illite. The procedure presented in this paper was developed and proved by recovering the end-members of different clay-mineral standards, after we mixed them together artificially. Separating clay-mineral species within shales recovered from an offshore Louisiana well further tested the method. The relative amounts and the mineralogy (based upon XRD) of density separates with depth were investigated. The “end-member” smectite and illite from each depth were analyzed for their oxygen isotopic signatures. In addition, the fine-grained (<10 μm) quartz fraction was separated and investigated with respect to both depth and the corresponding stage of clay-mineral diagenesis in terms of the progressive illitization of the illite-smectite.

Geologic setting

The well cuttings used in this study belong to a vertical well in Ship Shoal Block 97, offshore Louisiana, Gulf of Mexico, approximately 120 km west of the Mississippi River delta, 16 km offshore, and in a water depth of 80 meters (Fig. 1). The shallowest samples collected from the well are Pleistocene in age. The Lenticulina I foraminifera assemblage was noted at 1563 meters (5090 feet), and approximately marks the Pliocene/Pleistocene boundary. The lower Pliocene is marked by the appearance of Textularia X at 2666 meters (8690 feet).

The total depth penetrated by the well was 4146 meters (13 670 ft), into the Late Miocene as indicated by the presence of the benthic foraminifera, Bolovina thalamannii. Paleontological data and interpretation are from Paleodata, Inc. (unpublished data 1998).

Experimental methods

Shale rock chips were handpicked out of well cuttings collected from 11 shale-rich intervals as indicated by well logs. Sand-rich sections were skipped to avoid the possible local influence of diagenetic reactivants from sandstone bodies within the shales. Shale chips were crushed using a mortar and pestle and passed through a 62 μm sieve. The coarsest-grained material, primarily quartz and feldspar, was removed by ultrasonically wet-sieving with a 10 μm micromesh sieve, the smallest size practical. A 5 μm micromesh sieve was available, but it was found that the suspended samples would not pass through, even under the highest power settings of the ultrasonic probe. The average shale contains over 30% quartz and feldspar, most of which is greater than 10 μm in size (Totten and Blatt 1993). The coarser than 10 μm fraction of shales is primarily detrital in origin, and is not a major reactant in the I-S reaction. We refer to this fraction as the coarse-grained quartz and feldspar fraction (CGQ).

The material that passed through the 10 μm sieve is the focus of this study. Although this size boundary is not common in clay-mineral studies, it is compatible with our goal of including fine-grained quartz in the investigation. Although the standard less than 2 μm size definition for clay is based upon equivalent spherical diameter (e.s.d.), the actual maximum diameter for such platy shaped grains is a good deal larger (Moore and Reynolds 1997). We assume that, for these shales, the clay mineralogy of the less than 10 μm size fraction produced by micro-sieving is similar to the clay mineralogy of a less than 2 μm e.s.d. fraction that would have been produced by centrifuging. We also assume that any mineralogical variation between the less than 10 μm size fraction of our study and the less than 2 μm size fraction of most XRD studies is primarily

<table>
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<th>TABLE 1. Density range of clay minerals</th>
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<td>Clay mineral group</td>
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<td>Smectites</td>
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<td>Chlorites</td>
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<td>Muscovites</td>
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* Deer et al. (1966).
controlled by the amount of quartz and feldspar present, and not by any variation in clay mineralogy.

The final preparation for the density separations consisted of filtering the less than 10 \mu m pan fraction with a 0.45 \mu m acetate filter, then washing the material off the filter into a 50 mL centrifuge tube with heavy liquid of the beginning density. It is possible that a portion of the <0.45 \mu m material was lost during this procedure, and other investigators may wish to recover the pan fraction using a different method. More detailed descriptions of sample preparation may be found in Mack (1999) and Borges (1999).

**Density separation method**

Until recently, the favored liquids used for mineralogical density separations were halogenated hydrocarbons such as tetra-bromoethane and bromoform. These liquids are not suited to separating clay minerals because of their tendency to strongly adsorb to the mineral surfaces. It is virtually impossible to wash these adsorbed molecules from the clays after exposure. To further limit their suitability, the smectite preferentially adsorbs these organic heavy liquids, which reduces the effective density difference between the clays. In addition, these organic solvents are established carcinogens and require following proper protocols for handling, use, and disposal.

These problems are solved with lithium metatungstate (LMT), an inorganic, water-based, non-toxic salt. We discovered the properties of LMT with respect to clays during our experience in separating heavy-minerals from shale (Hanan and Totten 1996). The specific gravity \( G \) of LMT solutions can be adjusted using distilled water to between 1.0 and 3.4. At room temperature (25 °C), the reported characteristic viscosity of LMT solutions used in this study varied from 4 centipoises at \( G = 2.3 \) to 20 centipoises at \( G = 2.7 \) (LMT and AMT, 1992). After mineral separation, LMT may be recovered by evaporation at low temperatures (less than 100 °C) and reused. It is important not to allow the LMT to crystallize into the solid form, as it is extremely difficult to dissolve. LMT is available from Commercial Testing & Engineering Co. (4665 Paris St., Suite B-200, Denver, CO 80239).

To obtain an LMT solution of specific density, a stock solution having \( G = 3.1 \) was diluted by adding sufficient distilled water. The amount of distilled water to add was calculated using the simple formula: \( V_o = (V_i \rho_i - V_o \rho_o)/(\rho_o - \rho_i) \), where \( V_o \) is the volume of distilled water, \( V_i \) is the volume of stock solution, \( \rho_i \) is final density required, and \( \rho_o \) is the density of the stock solution (3.1), and \( \rho_o \) is the density of water at lab temperature. The precise density of the working solution was determined by weighing the LMT needed to fill a calibrated 25 mL pycnometer. The working LMT solutions were stored in air-tight flasks.

Approximately 1 g of dried and disaggregated sample was placed in 50 mL polycarbonate centrifuge tubes with screw-capped lids. LMT with \( G = 2.3 \) was added to fill and balance the weight of the tubes. The mixture was suspended by shaking the tubes vigorously. All of the suspensions easily dispersed in LMT. The tubes were centrifuged at 3000 rpm for one hour at constant temperature. To minimize rafting (dense sink material trapped in a lighter fraction) the float at the top of the tubes was resuspended without disturbing the sink portion using a paddle made from a paper clip and spun with an electric drill. The tubes were then centrifuged for an additional hour.

The test tube containing the LMT solution was frozen using a liquid N\(_2\) bath (Fig. 2). The thin layer of float material at the top of the tube was removed carefully by washing with distilled water into a 0.45 \mu m acetate filtering apparatus and recovered. The thin float layer includes most of the material with a density less than 2.3 of all size fractions (some of the finest-sized material with a density close to 2.3 has not had time to float to the top of the tube, but all of the material greater than 2.3 has had time to sink through the small distance at the top of the tube). The remaining LMT was then allowed to melt, and the liquid above the layer of sink material was slowly withdrawn with a micro-pipette and set aside. The purpose for this step was to minimize the amount of LMT remaining in the tube to dilute the next suspension. The liquid LMT between the sink and the float layers appeared to be clear and free of any solids. However, calculations based upon Stoke’s Law suggest that this liquid will still contain ultra-fine material, especially of particles with a density near that of the LMT. The thin layer in the bottom of the test tube only contained material denser than 2.3, of all size fractions.

For the next separation LMT with \( G = 2.4 \) was added to the tube and the sink material denser than 2.3 was resuspended in this fluid using an ultrasonic probe. The tube was centrifuged as before to isolate the material denser than 2.4. The float layer

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1We considered recovering the sink material each time by washing onto a filter, which would require transferring material off the filter and back into the centrifuge tube. The result of trials convinced us that the quantity of material stuck on the filter and hence lost was significant. In our method, almost 50 mL of the next density fluid was added to the sink and approximately 0.5 mL of the previous density fluid remained during each separation. The effect on the density was negligible. For example 45 mL of LMT at 2.400 gm/cc added to 0.5 mL of LMT at 2.300 gm/cc results in 45.5 mL of LMT with a density of 2.399 (0.04% error in density).

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**Figure 2.** Weight percentages of the clay-mineral standards with densities greater than LMT solutions (portion of clay standard that sunk) after one hour of centrifuge time. Also shown are the amounts of SAz-1 and SWy-1 that sank after 18 hours in LMT having \( \rho = 2.1 \).
after this separation contains material lighter than 2.4 and denser than 2.3. The sink layer contains material denser than 2.4.

This process was repeated using LMT with \( G = 2.7 \) and 2.85. The final sink layer was recovered by filtering in a similar manner. This fraction contains the heavy mineral fraction. The result of the density separations is four clay-mineral bearing density fractions: (a) less than 2.3, (b) 2.3 to 2.4, (c) 2.4 to 2.7, and (d) 2.7 to 2.85.

**X-ray diffraction analyses**

The mineralogy of the density separates was determined by X-ray diffraction (XRD) at the Microbeam Laboratory in the Department of Geology and Geophysics at the University of New Orleans. Oriented sample mounts were prepared after the method of Moore and Reynolds (1997). Air-dried and glycolated analyses of the same preparation were made on a Scintag XDS-2000 diffractometer using CuK\( \alpha \) radiation, at 40 kV and 20 mA, scan range 2–40°, step-size 0.02°, and scan time of 2 seconds per step. Glycolation was achieved by placing samples in a glycol-saturated atmosphere for 24 hours at room temperature.

**Fine-grained quartz and feldspar fraction**

The <10 μm quartz and feldspar fraction was recovered from an aliquot of the fraction with a density between 2.4 and 2.7 by the sodium bisulfate fusion technique outlined in Totten and Blatt (1996). The quartz and feldspar grains were examined using a digital Amray 1820 scanning electron microscope, also housed at the Microbeam Laboratory at UNO. Back-scattered electron images were collected and converted to binary images. Image analysis software was used to calculate the mean grain-size within this fraction for each sample. Energy dispersive spectra were collected to determine the distribution of quartz and feldspar in this fraction.

**Oxygen isotope analyses**

The fine-grained quartz (and feldspar), the <2.3g/cm\(^3\) density clay ("end-member" smectite), and the >2.7g/cm\(^3\) density ("end-member" illite) clay fractions were analyzed for their oxygen isotopic signature at the Stable Isotope Lab at Southern Methodist University. The >2.7g/cm\(^3\) density fraction was treated in warm, dilute sulfuric acid before analysis to remove impurities. Analyses were performed by Ian Richards using the methods of Clayton and Mayeda (1963) for quartz and Savin and Epstein (1970) for clay minerals.

**RESULTS**

Test of the density separation method

Prior to the development of the method used and described above, tests of clay mineral behavior in LMT solutions of variable densities were performed. To determine the particular density of LMT at which the various clay mineral species would sink, a series of LMT solutions were prepared, ranging in density from 1.9 to 2.9 g/cm\(^3\) in increments of 0.1 g/cm\(^3\). Approximately 0.5 g aliquots of sample were placed in each of the various density solutions. The amount of sink was determined at each density by centrifuging for one hour followed by freezing the sink and some of the LMT in the bottom portion of the tube. The remaining unfrozen LMT solution and floating material was decanted. The clay mineral standards chosen for this test were SAz-1 (Ca montmorillonite), SWy-1 (Na montmorillonite), SWa-1 (ferrigenous mont-morillonite), IMt-1 (illite), and KGA-1 (kaolinite). These standards were obtained from the Source Clays Program of the Clay Minerals Society. Descriptions of the geology of the source area, as well as considerable additional information regarding these clays, may be found in van Olphen and Fripiat (1979) and Costanzo and Guggenheim (2001).

Figure 2 shows the percentage of sinks for each clay standard at each LMT density after one hour at 3000 rpm. Because mineral standards are largely mono-mineralic, we expected a sharp break between sink and float for the entire sample at a single density. This behavior was observed in the illite, kaolinite, and the SAz-1 (Ca-smectite) standard. The standards SWy-1 (Na-smectite) and SWa-1 (ferrigenous smectite), however, show a gradual change in the proportion that sink over a wider range in density after only one hour. Filtering the LMT between the float layer and the sink layer of these samples revealed a small amount of material remaining (although too fine and too sparse to see in the LMT). The amount that remained in suspension in LMT with \( \rho = 2.1 \) was 10.5% of the original total for sample SWa-1, and 11.9% for sample SWy-1. The amount that remained in suspension in LMT with \( \rho = 2.5 \) was 2.3% for sample SWa-1 and 3.8% for sample SWy-1. The behavior of the suspended grains that do not make it into either the sink or float layers is controlled by a combination of their particle size and their amount of density contrast with the LMT solution. Given particles with a density contrast of 0.1 or greater with LMT, calculations based upon Stokes’s Law indicate that only some of the particles <0.6 μm in diameter would remain in the middle of the column after one hour centrifuge time. Removal of the material less than 0.6 μm in diameter that remains in the column requires much longer centrifuge times.

Test of separation method using an artificial mixture of clay mineral standards

Artificial mixtures were prepared by combining different amounts of a smectite clay standard with an illite standard. The LMT method was then performed on these mixtures to test its ability to “unmix” the mixture of the two standards. Two separate artificial mixtures were made with different standards; the smectite standard, SAz-1 and the illite standard, IMt-1; followed by the smectite standard, SWy-1 and the illite standard, Beaver’s Bend. Table 2 contains a comparison of the ratios by
Variation in density behavior with depth in GOM well

The mineral separates from the Gulf of Mexico well are defined in the following manner:

- **EMS**: The <2.3 g/cm³ density fraction is termed *end-member smectite*.
- **SML**: The fraction with a density between 2.3 and 2.4 g/cm³ is termed *smectite-rich mixed layer*.
- **IML**: The fraction with density between 2.4 and 2.7 g/cm³ (exclusive of the fine-grained quartz) is termed *illite-rich mixed layer*.
- **EMI**: The fraction with density >2.7 g/cm³ is termed *end-member illite*.
- **FGQ**: The non-clay fraction finer than 10 μm is termed *fine-grained quartz and feldspar*.
- **CGQ**: The fraction coarser than 10 μm is termed *coarse-grained quartz and feldspar*.

Table 3 shows the results of the mineral separations reported as relative wt%. The following trends are observed in the tabulated data. The EMS and EMI are both minor fractions by weight. The SML is the most abundant component of the shallow samples. The IML is a minor component of shallow samples and becomes the major component as depth increases. The FGQ and CGQ are also minor fractions; however, they both tend to increase slightly with depth.

Table 4 contains the results of the oxygen isotope analyses of aliquots of the FGQ, EMS, and EMI mineral separates. Also included in Table 4 are the mean grain-size, and the amount of feldspar within the FGQ fraction.

**DISCUSSION**

**Amounts of EMS, SML, IML, and EMI density separates**

The dominant density separates in terms of wt% are the smectite-rich mixed layer (SML) and the illite-rich mixed layer (IML) fractions. These two intermediate density fractions combined (SML + IML) comprise between 59 and 90% of the total rock in the 11 samples. The relative abundance of the SML and IML mixed-layer fractions vary with depth in a manner consistent with previous studies using XRD methods. Illite grows at the expense of smectite, as demonstrated by the increase in the amount of IML and the decrease of SML with depth. The variation between the IML and SML is displayed in a plot of the ratio of the IML relative to the total mixed-layer clay (IML + SML) fractions. These two intermediate density fractions combined (SML + IML) comprise between 59 and 90% of the total rock in the 11 samples. The relative abundance of the SML and IML mixed-layer fractions vary with depth in a manner consistent with previous studies using XRD methods. Illite grows at the expense of smectite, as demonstrated by the increase in the amount of IML and the decrease of SML with depth. The variation between the IML and SML is displayed in a plot of the ratio of the IML relative to the total mixed-layer clay (IML + SML) fractions.
SML) fractions with depth (Fig. 4). The increase in abundance of the higher density IML at the expense of the lower density SML is not unlike the increase in illite layers of the mixed-layer I-S determined in previous XRD studies of shale burial diagenesis.

The EMS and EMI fractions have minor abundances relative to the SML and IML separates. Although the amounts of EMI are somewhat lower in the deepest samples, unlike the SML and IML, there is no significant correlation of EMI or EMS abundances in the samples with depth. The EMI fraction is the densest fraction separated and varies between 1 and 10 wt% of the shales. EMS is analogous to the “discrete” illite reported in the coarser (0.5–2 μm size ranges of previous studies (Hower et al. 1976). Although illite is reasonably stable under the conditions encountered in the well, the abundances of EMI do not support an increase in discrete illite as a result of illitization. The lack of any significant systematic variation of the EMI is probably due to the variable contribution of detrital illite over time.

The least dense EMS fraction varies from 2 to 12 wt% of the shales. The persistence of the less-stable EMS is more problematic. The EMS was expected to decrease in abundance (as observed in the SML fraction) and even disappear from the deepest samples during the smectite-illite transformation reaction. The abundance of the EMS fraction, however, did not decrease with depth, and was still present in even the deepest samples.

XRD patterns of density separates

XRD patterns of the oriented EMS, SML, IML, and EMS fractions from all depths are shown, respectively, in Figures 5, 6, 7, and 8. The 001 smectite and smectite-rich mixed-layer peaks broaden and diminish with increasing density, and disappear almost entirely, in the densest EMI fraction. Corresponding to the loss of smectite peaks from the denser separates, there is an increase in the illite 001 (and kaolinite 001) peaks. Based on the distinctly narrow density range of each separate, the mineralogy and the resulting XRD patterns should be fairly consistent for the same density fractions from separate depths.

Indeed, Figures 5–8 reveal how similar the XRD patterns are for the same density fraction from separate depths.

As predicted, the XRD patterns of the eight EMS samples above 3697 meters in Figure 5 are remarkably consistent. The 001 peak positions for the smectite fall between 5.15 and 5.55 °2θ, and indicate that this density fraction consists of...
Figure 7. XRD patterns of the IML fractions from all samples. Samples are arranged in order of increasing depth toward the bottom of the graph. The XRD pattern above the shallowest sample is the NEWMOD-calculated pattern for a mixture of 80% I-S [65% dimica, Fe = 0.2, K = 0.7, 35%, di-smectite 1 gly, Fe = 0.2, R = 2.5], 10% illite [dimica, Fe = 0.2, K = 0.7], and 10% kaolinite.

Figure 8. XRD patterns of the EMI fractions from all samples. Samples are arranged in order of increasing depth toward the bottom of the graph. The XRD pattern above the shallowest sample is the Newmod calculated pattern for a mixture of 90% illite [dimica, Fe = 0.2, K = 0.7] and 10% kaolinite.

dioctahedral smectite expanded to include two ethylene glycol layers (Gly-2). However, the XRD patterns of the three deepest samples demonstrate a shift in the 001 smectite peak position to $7.32-7.52\,^\circ 2\theta$, and indicate these samples are expanded to only one ethylene glycol layer (Gly-1).

These deep EMS samples represent a transitional form of smectite that has not undergone sufficient mineralogical change to increase its density significantly over the shallower samples (or they would have been separated out in the denser fractions). The Gly-2 to Gly-1 transition depth between 3455 and 3697 meters is similar to the depth where Gier (1998) observed a shift in non-density separated samples. The decreasing ethylene glycol expandability of smectites is attributed to increasing layer-charge density (Moore and Reynolds 1997 and Gillot et al. 2001). It would appear that the end-member smectite in the EMS separates achieves an increase in layer charge density somewhat abruptly below 3500 meters. The deep EMS density separates have undergone enough tetrahedral substitution to alter their layer charge, but not enough substitution to alter their density sufficiently for them to separate with the SML fraction.

A similar trend is observed for the XRD patterns of the SML fractions. Figure 6 shows the SML fractions to have broader smectite peaks than the EMS. The SML density range is 2.3–2.4 and the increase in density is attributed to mixed layering with illite. As modeled by Newmod, the SML samples contain 50% illite layers and an ordering of $R = 0$. As expected from the narrow range of densities for all these SML separates, the XRD patterns of the eight samples above 3697 m are remarkably consistent. The 001 peak positions for the mixed-layer I-S fall between 5.50 and 5.75 $^\circ 2\theta$. The three deepest samples in Figure 6 demonstrate a shift in the glycolated I-S 001 peak position to $7.36-7.82\,^\circ 2\theta$. As in the EMS fraction, we interpret this loss of expandability to be an effect of the increased layer charge density of the smectite layers in the deepest samples. The SML sample at 3697 m is noteworthy because its XRD pattern has two distinct peaks associated with both the GLY-1 and GLY-2 dioctahedral smectites. This double-peaked pattern flags the transition between these “species,” and represents a transitional I-S that has not undergone sufficient mineralogical change to increase their density.

The IML patterns shown in Figure 7 also exhibit very little variation with increasing depth. As modeled by NEWMOD, the IML samples contain 65% illite layers and an ordering increase to $R = 2.5$. There is a slight decrease in the height of the smectite peak with increasing depth.

The XRD patterns of the EMI fraction are shown in Figure 8. The overall mineralogy of this fraction is the most consistent with depth of all of the density fractions. The degradation of the smectite peak is complete except for three of the samples that display a very low intensity peak in this region. The peak at $9.8\,^\circ 2\theta$ is consistent with an 001 reflection from pure illite.

O-isotope ratios of end-member clays

The O-isotope ratios of EMS and EMI were determined to assess their involvement in the smectite-illite transformation. The isotopic signature of EMS becomes lighter with depth (Fig. 9). The values for EMS and EMI plot overlap the range reported by Yeh and Savin (1977) for the smectite-rich 0.1–0.5 mm fraction. These authors interpreted this trend as O-isotope exchange between this clay fraction and the pore waters as temperature increased with depth. In the present study, the shallowest EMS samples have an isotopic signature consistent with a low-temperature formation inherited from their source(s), which is modified by isotopic exchange with pore waters as temperature (and depth) increase. The isotopic exchange implies that the deeper samples are somewhat reactive, which is consistent with the increase in layer charge in the same samples.

The lack of any trend with depth in the O-isotope signature
of EMI confirms that this end-member is not reacting during burial diagenesis. The isotopic signature of EMI should vary with depth if this fraction was crystallizing under escalating temperature and increasing burial depth. The small but persistent abundance of EMI, and its non-diagenetic O-isotope signature can best be explained if EMI is detrital, with a lack of production of new high-density end-member illite by diagenesis of I-S.

The trends in the density separates of the clay-mineral fraction of these shales are strong evidence that the smectite to illite transition is occurring within the mixed-layer fractions of these rocks. The pure “end-member” clays appear to be involved minimally in this reaction within the conditions encountered in our well.

Growth of fine-grained quartz

The <10 µm, non-clay mineral fraction (FGQ) is primarily quartz, with some feldspar in the shallower samples. Below 2500 m, K-feldspar shows a dramatic decline in abundance, and is absent below 3500 m. Hower et al. (1976) observed an identical trend at the same depths in a well from the Texas Gulf Coast. The FGQ fraction exhibits a steady increase with depth (Fig. 10), similar to that seen by Hower et al. (1976). In addition, the mean grain-size of this fraction decreases with depth. Authigenic growth of very fine-grained quartz during burial diagenesis is the reason for these two trends. The addition of authigenic fine-grained material to the existing detrital quartz within this fraction decreases the mean grain size. This finding confirms the authigenic growth of quartz during shale diagenesis as reported by Land et al. (1997), Lynch (2000), and Totten and Blatt (1996).

The heavy O-isotopic signature of the fine-grained quartz fraction (FGQ) correlates with the mean grain size, which supports an authigenic origin for the finest material. The range of values is within the range reported for authigenic, silt-sized quartz by Blatt (1989). The isotopic signature becomes heavier with increasing depth (Fig. 11). The trend is very similar to the one reported by Yeh and Savin (1977) in the >2 µm fraction.

The slight shift of our trend to heavier values compared with Yeh and Savin (1977) is probably because our samples were all finer than 10 µm in size, whereas theirs included the entire >2 µm fraction.

CONCLUDING REMARKS

Numerous methods have been employed since the landmark study by Hower et al. (1976) on the smectite to illite transition to examine the chemical and mineralogical changes in shales during burial diagenesis. The most widely used method for evaluating the clay-mineralogical change has been use of XRD to measure the relative peak changes, combined with numerical modeling to predict XRD patterns due to the presence of mixed-layer clays. The present study permits the examination of physically separate, individual components involved in the clay-mineral transformations during burial diagenesis. This study outlines a new method to isolate mixed-layer clays of...
differing S/I content based upon density. The results of the technique presented in this paper broaden our understanding of I-S diagenesis in shales. Heretofore, most researchers have concluded (or implied) that during the burial diagenesis of shale, the whole assemblage of mixed layer I-S grains “marches in step” toward achieving progressively higher proportions of illite interlayers with depth of burial. Our results suggest that a continuously varying population of I-S exists that is not “marching in step” toward an appropriate end-point of illitization. Even as that end-point is reached during advanced burial diagenesis, an SML smectite-rich I-S subpopulation is still present, which we have been able to detect because of its low density. This research supports a population view of the shale diagenesis reaction in which the demography of the I-S population shifts away from a SML-dominated population toward an IML-dominated one with increased burial.

A further unexpected result of this study was the persistence of the “end-member” clays (EMI and EMS) over the depth range of the sample well. A low-density phase (EMS) occurs in samples over the entire sample range (to a depth of 4100 m). This phase shows an expandable smectite peak to at least a depth of 3500 meters. However, below 3500 m, we noted the crystallographic evidence that diagenesis is affecting this fraction by a decrease in the expandability of the 001 smectite peak. This finding is consistent with depths where Burst (1969) observed the onset of more advanced illitization and dewatering. The lack of any decrease in the weight proportion of this density fraction suggests that diagenetic change is not sufficient to shift this smectite out of the low-density range. This study also confirms the growth of authigenic quartz (FGQ) during illitization of shales. This quartz is formed from the silica released during this reaction. The ability to physically separate clays based upon their density differences should be a valuable tool to many investigators of fine-grained rocks. After using LMT density separations to isolate the SML and IML fractions, the continuous change of their relative amounts with depth confirms that the illitization is a continuous transformation. It is interesting that although a significant change in the overall mineralogy of the rock occurs with depth, only minor changes in mineralogy are observed within each of the density fractions.

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