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OXYGEN ISOTOPE COMPOSITIONS OF MIXED-LAYER SERPENTINE-CHLORITE AND ILLITE-SMECTITE IN THE TUSCALOOSA FORMATION (U.S. GULF COAST): IMPLICATIONS FOR PORE FLUIDS AND MINERALOGIC REACTIONS

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Abstract—Oxygen isotopic compositions were determined for coexisting mixed-layer serpentine-chlorite (Sp-Ch) and illite-smectite (I-S) from 5 Tuscaloosa Formation sandstone cores sampled between 1937 and 5470 m burial depth. High gradient magnetic separation (HGMS) was used to concentrate Sp-Ch and I-S from the <0.5 μm fraction of each core sample into fractions with a range in the Sp-Ch : I-S ratio, and end-member $\delta^{18}O$ compositions were determined by extrapolation. The Sp-Ch $\delta^{18}O$ values range from +10.4 to 13.7‰ and increase with burial between 3509 and 5470 m. The only exception is Sp-Ch from 1937 m, which has an anomalously high $\delta^{18}O$ value of +12.6‰. The I-S $\delta^{18}O$ values range from +16.1 to 17.3‰ and do not change significantly between 3509 and 5470 m burial depth.

Pore water $\delta^{18}O$ compositions calculated from Sp-Ch and I-S values and measured borehole temperatures range from −2.6 to +10.3‰. The isotopically light values indicate that Sp-Ch formed at shallow burial depths in the presence of brackish to marine water and/or meteoric water. The depth-related increase in $\delta^{18}O$ of Sp-Ch is attributed to oxygen exchange between mineral and pore water during diagenetic mineral reactions. Increasing $\delta^{18}O$ values, in conjunction with XRD and SEM data, indicate that transformation of serpentine layers to chlorite layers and *Ibb* polytype layers to *Iaa* polytype layers occurred on a layer-by-layer basis when individual layers dissolved and recrystallized within the confines of coherent crystals. Possible explanations for the variation in I-S $\delta^{18}O$ values include depth-related differences in pore water $\delta^{18}O$ values present at the time of I-S crystallization, contamination by detrital $2M_1$ mica and $1M$ polytype rotations that facilitated oxygen exchange.

Key Words—Diagenesis, Illite-Smectite, Oxygen Isotopes, Sandstone, Serpentine-Chlorite, Tuscaloosa Formation.

INTRODUCTION

Mixed-layer Sp-Ch consists of randomly interstratified 7-Å serpentine-like layers and 14-Å chlorite-like layers. In sandstone of the Lower Cretaceous Tuscaloosa Formation, Sp-Ch has an average chemical composition of $(Fe_{3.2}Mg_{0.9}Al_{1.7})(Si_{2.9}Al_{1.1})(O_{10})(OH)_8$, and it occurs as pore-linings, peloids, replacements (of biotite clasts) and infillings (Ryan and Reynolds 1996). The pore-linings occur as 7–10-μm-thick mats of crystals that coat detrital grains except at grain intersections. They are of significant interest because they are believed to inhibit authigenic quartz growth, thus preserving anomalously high primary porosities (>20%) in sandstones buried to depths as great as 6600 m (Heald and Anderegg 1960; Pittman and Lumsden 1968; Thomsen 1982). By analyzing textural relationships, Thomsen (1982) determined that the pore-linings formed soon after deposition, and Ryan and Reynolds (1996) suggested, based on similarities in depositional environment, texture and mineralogic structure, that the Sp-Ch originated as odinite. Odinite is a 7-Å Fe-rich mineral that is known to form in the upper decimeter of sands deposited in Holocene tropical marine environments (Odin et al. 1988; Bailey 1988a) and it may transform to Sp-Ch (Hillier 1994; Ryan and Reynolds 1996; Spotl et al. 1994) and/or berthierine (Hornibrook and Longstaffe 1996) at burial depths as shallow as 30 m (Bailey 1988a; Odin et al. 1988). Determining the origin of pore-lining chlorite minerals is significant because of their importance in preserving porosity in reservoir sands, and also because of their relationships to Fe-Mg-rich 7-Å clay minerals such as odinite and berthierine, mixed-layer 7-Å/14-Å clay minerals and 14-Å chlorite.

X-ray diffraction (XRD) analyses indicate that the amount of serpentine layers in Tuscaloosa Formation Sp-Ch ranges from 21% at 1937 m burial depth to 3% at 5470 m (Ryan and Reynolds 1996). The polytype of the Sp-Ch is pure *Ibb* at burial depths <2000 m. At depths greater than 2000 m, the polytype is randomly interstratified *Ibb/Iaa*, and the proportion of *Ibb* layers in the *Ibb/Iaa* polytype progressively decreases from ~100% at <2000 m to 53% at 5470 m. The decreases in both %Sp layers and %*Ibb* polytype layers with increasing burial indicate that Sp layers transform to Ch layers and *Ibb* layers transform to *Iaa* layers with increasing temperature and possibly time.

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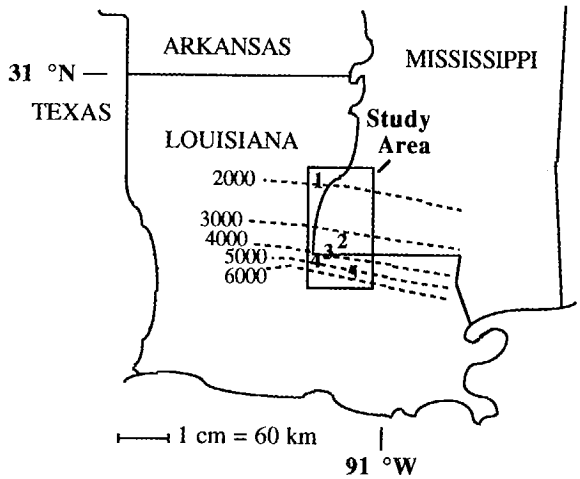

Figure 1. Location map of core samples analyzed in this study. Numbers 1–5 indicate approximate locations and depths of samples as follows: 1 = 1937 m; 2 = 3509 m; 3 = 4054 m; 4 = 4568 m; 5 = 5470 m. Burial depth isopachs (in m) show depth to base of Lower Tuscaloosa Formation sandstone, the interval analyzed in this study.

Ryan and Reynolds (1996, 1997) noted that: 1) the crystallite thickness (c^* direction) of Sp-Ch does not increase with increasing grade, nor does the size of crystals in the *a-b* dimension (Thomsen 1982); and 2) there is essentially no change in Sp-Ch major elements composition with increasing grade. From this they inferred that the Sp to Ch and *Ibb* to *Iaa* reactions occurred via a cell-preserved mechanism, with individual layers reacting within the confines of coherent crystallites, rather than by the commonly observed pathways of changing chemical composition (Hower and Mowatt 1966; Jahren and Aagaard 1992) and Ostwald ripening crystal growth (e.g., Eberl et al. 1990; Jahren and Aagaard 1992).

Scanning electron microscopy (SEM) and thin-section analyses of Tuscaloosa Formation sandstone indicate that authigenic I-S typically occurs as fibrous aggregates on Sp-Ch crystal surfaces, indicating that it formed after the Sp-Ch (Hamlin and Cameron 1987; Wiygul and Young 1987). All of the authigenic I-S analyzed in this study is well ordered ($R \geq 1$ ordered) with 6–9% expandable (smectite) layers (Ryan 1994). I-S expandability and crystallite thickness (along c^*) show essentially no variation with depth, and the only noted structural change in I-S involves an erratic increase in rotational ordering of the *tv*-1*M* polytype (Ryan 1994) consistent with progression from 1*Md* to 1*M* (Eberl and Środoń 1984).

This study seeks to address 2 specific points. The first is the origin of Sp-Ch in Lower Tuscaloosa Formation sandstone. Recent studies (Ehrenberg 1993; Hillier 1994; Ryan and Reynolds 1996) indicate that Sp-Ch originates as odinite, and if this is true, $\delta^{18}O$ values of Sp-Ch should reflect the marine water in which it initially formed. However, Weedman et al. (1996) indicate that diagenetic chlorite formed at 100 to 125 °C in Tuscaloosa sandstone following crystallization of quartz, calcite and dolomite. If so, $\delta^{18}O$ values should reflect deeper basin waters. Diagenetic mineral reactions such as the smectite-to-illite reaction are known to alter oxygen isotopic compositions, particularly when they involve dissolution-precipitation (Yeh and Savin 1977; Whitney and Northrop 1988), indicating that initial $\delta^{18}O$ values of Sp-Ch and I-S may have been modified by diagenetic reactions. Nonetheless, a number of studies have been able to utilize $\delta^{18}O$ values of deeply buried clay minerals to infer pore water composition at the time of initial crystallization in spite of diagenetic modifications to mineral structures (Whitney and Northop 1987; Ayalon and Longstaffe 1988; Lee et al. 1989; Longstaffe 1989; Ziegler et al. 1994; Sheppard and Gilg 1996). In those cases, mineral reactions occurred with only limited exchange of oxygen.

Secondly, this study assesses Sp-Ch and I-S reaction mechanisms by examining $\delta^{18}O$ values of each mineral over a wide range of burial depth (1937 to 5470 m) and temperature (85 to 165 °C). In particular, we document variations in $\delta^{18}O$ values which indicate that Sp-Ch reactions (Sp to Ch and *Ibb* to *Iaa*) occurred by a cell-preserved mechanism involving localized dissolution and precipitation.

The Lower Tuscaloosa Formation is a shallow marine sandstone that was deposited in the Gulf Coast Basin during Late Cretaceous time (Worrall and Snelson 1989). Compositionally, it ranges from sublitharenite (Stancliffe and Adams 1986) to quartz litharenite and quartz arenite (Hamlin and Cameron 1987). It has been exposed to a wide range in diagenetic grade, with burial depth increasing southward from surface exposures in central Alabama and adjacent states to 6800 m in the subsurface of Louisiana (Stancliffe and Adams 1986). This sandstone provides an ideal natural environment for the study of authigenic Sp-Ch and I-S. Authigenic Sp-Ch and I-S coexist throughout the Lower Tuscaloosa Formation, and because detrital grains are sand-sized, the clay-size fraction is dominated by authigenic minerals and is almost entirely free of detrital contamination.

MATERIALS AND METHODS

Samples were collected from 5 drill cores that penetrated the tabular, southward-dipping Lower Tuscaloosa Formation at depths of 1937, 3509, 4054, 4568 and 5470 m (Figure 1). The 3509-m sample is actually a composite of 3 small and essentially identical core chips from 3505, 3509 and 3513 m, but it will be referred to as the "3509-m" sample for brevity. The specimen from 4054 m is a fine-grained sandstone and is well cemented, whereas the others are medium-grained and friable (Ryan 1994). The cores used in

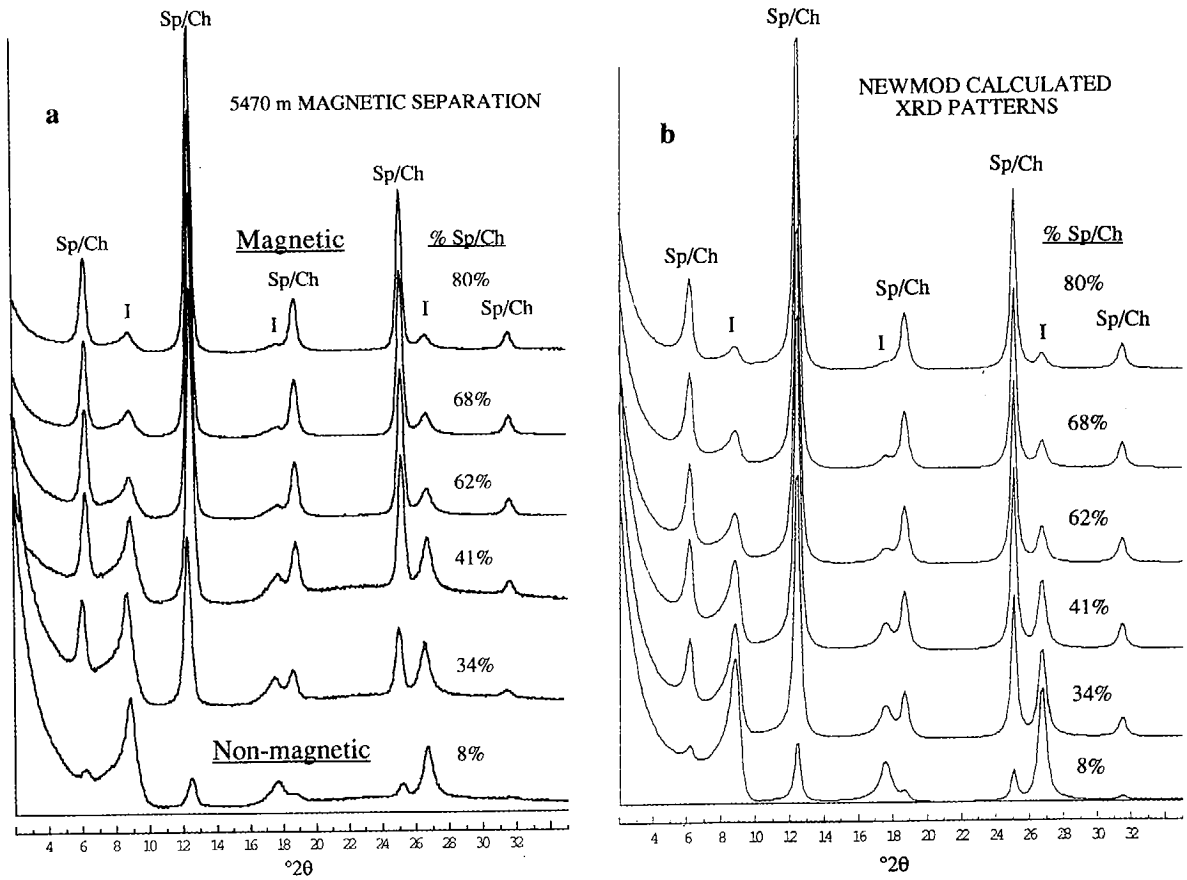

Figure 2. a) Results of HGMS for the 5470-m sample shown as XRD patterns of oriented mounts (<0.5-μm fraction, Cu$K\alpha$). %Sp-Ch represents percentage of Sp-Ch in a 2-component physical mixture of Sp-Ch and I-S. Sp-Ch = randomly interstratified serpentine-chlorite, $I = R \geq 1$ illite-smectite. b) NEWMOD©-calculated XRD patterns (Reynolds 1985) used to estimate %Sp-Ch in analytical HGMS separates. The ratio of the integrated intensities of the Sp Ch (004) and I-S (003) peaks were used to determine %Sp-Ch.

this study were selected based on the range in burial depth mineralogic structure and the fact that they contained sufficient amounts of both Sp-Ch and I-S for analysis. The cores were provided by David R. Pevear of Exxon Production Research Company, Houston, Texas. Surface outcrop samples were found to contain abundant kaolin and no Sp-Ch, and thus were not analyzed in this study.

The cores were washed in distilled water to remove drilling mud, disaggregated with an iron mortar and pestle and centrifuged to separate the <0.5-μm and 0.5–2-μm fractions. Due to the presence of up to 30% kaolin in the 0.5–2-μm fraction, especially at depths <3600 m, we selected the <0.5-μm fraction for this study. The <0.5-μm fraction consisted of Sp-Ch and I-S, but virtually no kaolin as determined by XRD analyses. Accordingly, the <0.5-μm fraction was concentrated in a high-speed centrifuge, and HGMS (Tellier et al. 1988) was used to separate Sp-Ch and I-S for oxygen isotope analyses. It was not possible to completely separate clay suspensions into pure Sp-Ch and I-S end members, so HGMS was used to produce a range in the Sp-Ch:I-S ratio (Figure 2), and end-member Sp-Ch and I-S oxygen isotope compositions were determined by extrapolation (Figure 3) using a method similar to the one used by Whitney and Northrop (1987). HGMS fractions were obtained using a Frantz L-1CN Canister Magnetic Separator manufactured by S. G. Frantz Co. of Trenton, New Jersey. Flow rates of the mineral suspensions ranged from 150 to 300 mL/min, and magnetic field strength was varied between 1 and 14 kilogauss to achieve the necessary range in Sp-Ch:I-S ratio (Ryan 1994). Following magnetic separation, oriented powder mounts of the different fractions were prepared by dropping clay slurries onto glass slides and drying under a heat lamp. The filter peel technique (Drever 1973), which is the preferred method of oriented mount preparation for quantitative XRD analyses (Reynolds 1992), was not used and sonification was kept to a minimum to avoid contamination from glassware and plastic centrifuge vials. Sp-Ch:I-S ratios for the HGMS fractions were

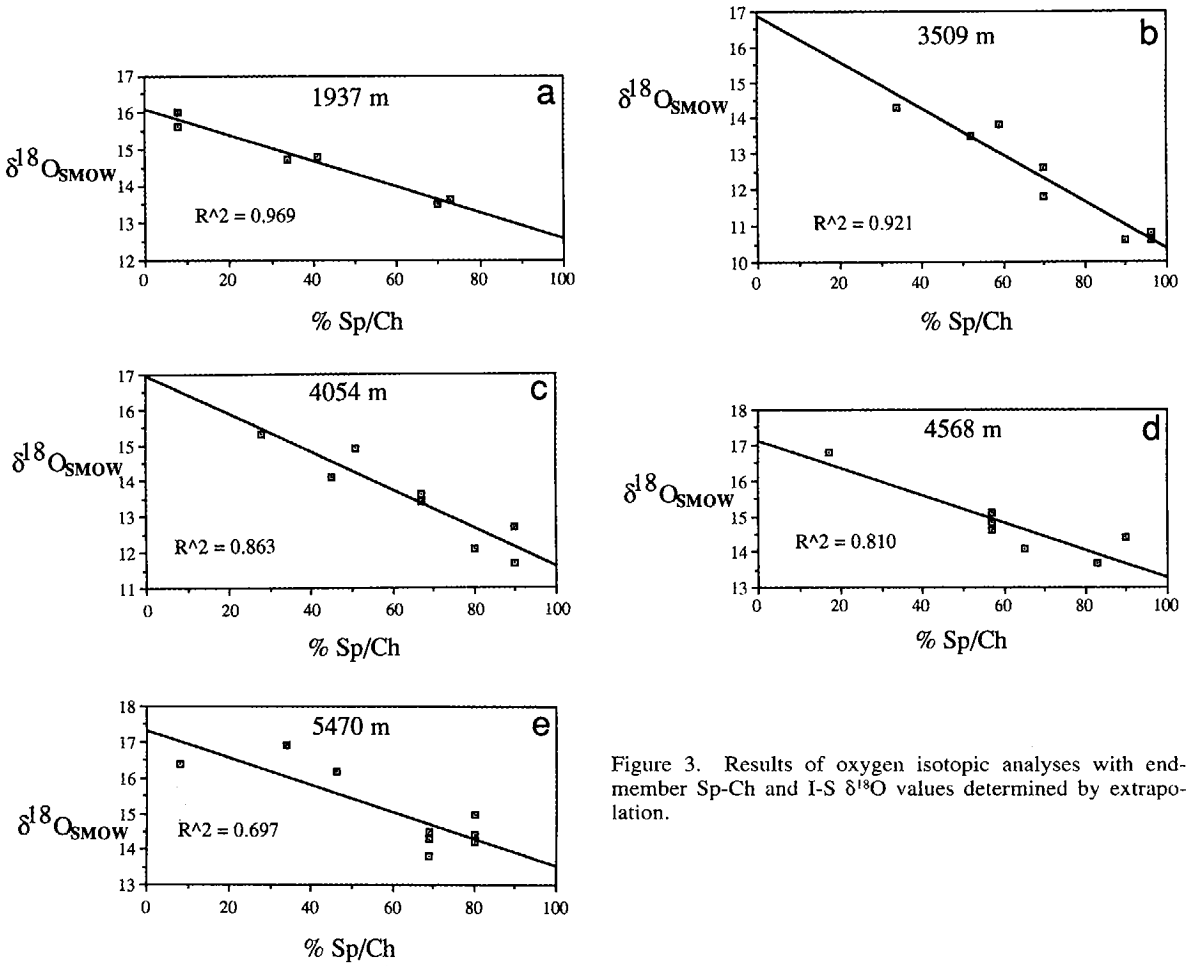

Figure 3. Results of oxygen isotopic analyses with end-member Sp-Ch and I-S $\delta^{18}O$ values determined by extrapolation.

determined using the computer programs NEWMOD© and MIXER© (Reynolds 1985). NEWMOD©-calculated diffraction patterns of Sp-Ch and I-S representative of the Sp-Ch and I-S in each sample were added point-by-point using MIXER©, and the Sp-Ch : I-S ratio in the calculated diffraction pattern was varied until it matched the sample powder (Figure 2). The Sp-Ch : I-S ratio was determined by measuring integrated peak intensities of the Sp-Ch 004 (3.53-Å) and I-S 003 (3.33-Å) peaks. These peaks were used because the effects of X-ray beam absorption and instrumental distortions should be similar for both peaks. Prior to isotope analyses, samples were placed in a drying oven at 60 °C for at least 24 h and then were stored in a dessicator for at least 24 h.

Oxygen isotope extractions were performed according to the methods of Clayton and Mayeda (1963), and data are reported relative to standard mean ocean water (SMOW) in per mill. To liberate oxygen, 7–15 mg of sample were reacted with BrF_5 at 550–600 °C, and the oxygen was converted to CO_2 and measured in a Finnigan MAT Delta E mass spectrometer. Prior to reaction with BrF_5, all samples were preheated to 200–250 °C in the reaction chambers for 1 h to drive off nonstructural water. Each set of 6 analyses included 1 or 2 internal laboratory standards to keep results internally consistent. Four $\delta^{18}O$ values from 4568 m were corrected by adding 1.8‰ to correct for systematically low values in standards, and 2 duplicate analyses of that sample produced values that were 1.5 and 2.0‰ higher than the first run, thus justifying correction of the data. Interestingly, 9 samples (19% of total attempted analyses) produced large amounts of noncondensable gas during reaction with BrF_5 that would not convert to CO_2, and results could not be obtained for these samples. Spotl et al. (1994) observed a similar phenomenon when analyzing pore-lining chlorite from the Spiro sandstone and suggested that it may have been due to residual pyrobitumen in the samples.

Reproducibility was ±0.4% or better for all 5 samples. Percentage yield varied from 70 to 100%, perhaps due to the presence of refractory minerals such as anatase, and possibly due to the inherent difficulty associated with loading very fine-grained powders into

Table 1. Sp-Ch and I-S $\delta^{18}O$ values, calculated temperatures† determined from a fractionation equation based on equations of Wenner and Taylor (1971) and Savin and Lee (1988), measured borehole temperatures (Alford 1983),‡ and variations in Sp-Ch and I-S mineralogy. $P_{0'}$ is the probability of 0° (1*M*) polytype rotations in I-S, with higher $P_{0'}$ values indicating greater rotational order.

Burial depth (m)	$\delta^{18}O_{Sp\text{-}C}$	$\delta^{18}O_{I\text{-}S}$	*T* (°C) ($\Delta_{I\text{-}S\text{-}Sp\text{-}Ch}$)†	*T* (°C) (Burial)‡	%Sp in Sp-Ch	%*lbb* in *lbb*/*laa*	$P_{0'}$
1937	12.6	16.1	353	85	21	~100	0.70
3600	10.5	16.9	102	120	11	83	0.60
4054	11.7	16.9	147	130	17	73	0.60
4568	13.4	17.1	326	140	5	67	0.70
5470	13.7	17.3	349	165	4	53	0.75

reaction chambers. Of the 38 analyses for which $\delta^{18}O$ values were obtained, 12 produced 100% yield, 13 were between 90 and 99% and only 3 were less than 80%. Duplicate analyses indicated that variations in % yield did not produce any significant error.

In order to assess the degree of $\delta^{18}O$ equilibrium between Sp-Ch and I-S, temperatures of formation of coexisting Sp-Ch and I-S were calculated using an illite-chlorite curve derived by combining the chlorite-water curve of Wenner and Taylor (1971) and the illite-water equation of Savin and Lee (1988):

$$2.39 \times 10^6 \times T^{-2} - 4.19 = 10^6 \ln \alpha_{\text{ill-wat}}$$

(Savin and Lee 1988) [1]

$$1.56 \times 10^6 \times T^{-2} - 4.70 = 10^6 \ln \alpha_{\text{chl-wat}}$$

(Wenner and Taylor 1971) [2]

$$0.83 \times 10^6 \times T^{-2} + 0.51 = 10^6 \ln \alpha_{\text{ill-chl}} \quad [3]$$

The chlorite-water curve of Wenner and Taylor (1971) is based on analyses of naturally occurring chlorite and serpentine in low-grade metamorphic rocks, and Savin and Lee (1988) suggested that this curve is the most accurate chlorite-water curve at <150 °C, so we feel it is applicable to the mixed-layer Sp-Ch studied here. Wenner and Taylor indicated that fractionations between chlorite-water and serpentine-water are similar and proposed the same curve for both. Savin and Lee (1988) combined the quartz-illite curve of Eslinger and Savin (1973) with the quartz-water curve of Matsuhisa et al. (1979) to arrive at the illite-water curve. It must be pointed out here that fractionation factors are not particularly well known at diagenetic temperatures and should not be used as geothermometers (Savin and Lee 1988). In this study, calculated temperatures were used to infer the degree of oxygen isotope equilibration between coexisting Sp-Ch and I-S, but not to indicate absolute temperatures of formation of those phases. The equations of Wenner and Taylor (1971) and Savin and Lee (1988) were also used to estimate the oxygen isotope composition of pore water in equilibrium with Sp-Ch and I-S using measured borehole temperatures of Alford (1983).

I-S from 9 samples representing a wide range in burial depth (1702 to 5470 m) was concentrated by HGMS and then dated by the K-Ar method in order to determine timing of I-S crystallization. Prior to K-Ar analysis it was determined by XRD analysis of oriented powder mounts that the <2-μm fraction contained detrital $2M_1$ mica. Oriented mounts of the <0.5-μm fraction revealed no evidence of detrital mica, so it was used in K-Ar analysis. Analyses were performed by Krueger Enterprises, Inc., Geochron Laboratories Division, Cambridge, Massachusetts.

RESULTS

Results of oxygen isotopic analyses are summarized in Table 1 and in Figures 3 and 4. Table 2 shows

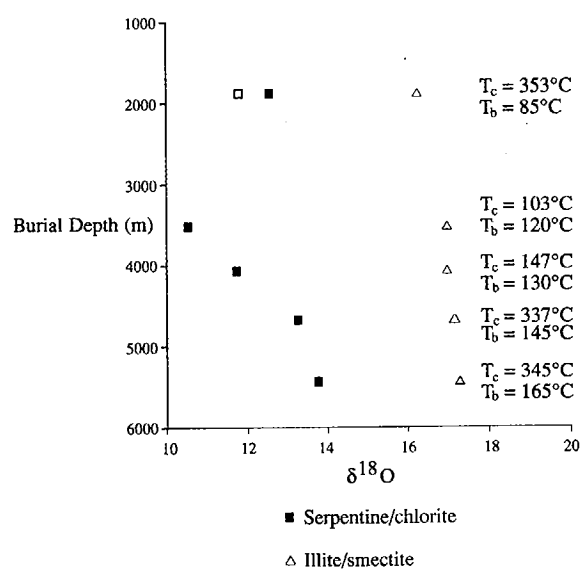

Figure 4. Sp-Ch and I-S $\delta^{18}O$ values plotted against burial depth, with calculated temperatures (T_c) and current burial temperatures (T_b). Calculated temperatures were determined using fractionation equations of Wenner and Taylor (1971) and Savin and Lee (1988) and are used to infer degree of isotopic equilibrium between Sp-Ch and I-S, but not to indicate equilibrium temperatures of Sp-Ch crystallization. The open square at 1937 m refers to a 12.6‰ value corrected to 11.8‰ to account for the presence of 32.8‰ siderite.

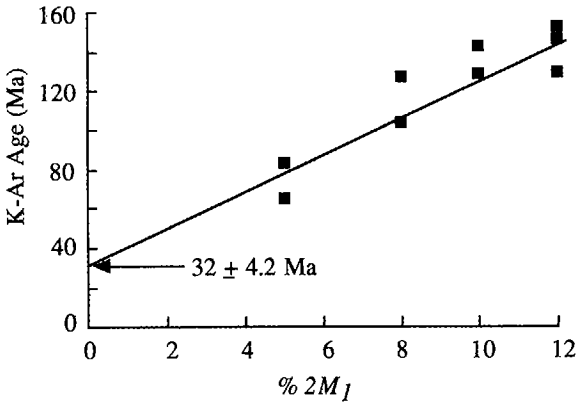

Figure 5. K-Ar dates (in Ma) plotted versus %$2M_1$ mica ($2M_1/1M + 2M_1$). Extrapolation to the $1M$ end-member results in a 32 ± 4.2 Ma date.

calculated pore water values. Regression coefficients (R^2 values as shown on Figure 3) are similar to those obtained by Whitney and Northrop (1987), who also used extrapolation to determine end-member chlorite and illite $\delta^{18}O$ compositions. Duplicate analyses performed on selected samples indicate an uncertainty of ±0.4‰. Although time consuming, the use of HGMS (Tellier et al. 1988) to create a range in mineral proportions of 2-component mixtures appears to be a valid means of determining end-member $\delta^{18}O$ compositions in cases where pure separates cannot be obtained without the use of destructive chemical techniques (Whitney and Northrop 1987; Ryan 1994).

Oxygen isotopic compositions for Sp-Ch range from 10.4 to 13.7‰ and progressively increase with increasing burial, the only exception being Sp-Ch from 1937 m, which seems to have an anomalously high $\delta^{18}O$ value of 12.6‰. The range in composition is similar to values of Tuscaloosa Formation pore-lining Sp-Ch (12.3 to 15.4‰) determined by Suchecki (1983). Values of $\delta^{18}O$ for I-S show a much smaller range than the Sp-Ch, increasing from 16.1 to 17.3 (Figure 4) between 1937 and 5470 m, with the most significant shift occurring at shallow depth between 1937 and 3509 m (16.1 to 16.9).

XRD patterns of the paramagnetic fraction of the 1937-m sample indicated the presence of ~4% siderite (by wt). Siderite was not detected in XRD patterns of any of the other, deeper samples analyzed in this study. In an attempt to correct for the presence of siderite in the 1937-m sample, we determined $\delta^{18}O$ of the siderite using the method of Rosenbaum and Sheppard (1986), attempting to use the mole fraction of CO_2 gas extracted from the paramagnetic fraction of the sample to estimate the amount of siderite originally in the powder. The value of $\delta^{18}O$ for the siderite in that sample was 32.8‰, but only 2 μmol of CO_2 gas were retrieved from the 155-mg sample, indicating that only about 0.15% of the powder was siderite, or reaction was incomplete. Considering the siderite $\delta^{18}O$ value of 32.8‰, the powder would have needed to contain 20% siderite to produce Sp-Ch with a value of 8.5‰, the value that would be predicted by extrapolating the data points from >3500-m depth on Figure 4. Based on quantitative XRD analysis (determined by comparing physical mixtures of siderite and Sp-Ch created from powders), the corrected value for 1937 m Sp-Ch could be 11.8‰.

Seven of the 9 samples dated by the K-Ar method produced dates older than the depositional age of 91 to 97 Ma (Worrall and Snelson 1989). No $2M_1$ mica was detected in oriented powder mounts of the <0.5-μm fraction, but subsequent XRD analyses of randomly oriented <0.5-μm powders revealed the presence of 5–12% $2M_1$ mica (Ryan 1994), underscoring the need for detailed XRD analysis of powders prior to K-Ar analysis. K-Ar dates range from 63 to 150 Ma and are positively correlated with % $2M_1$ mica (Figure 5) determined using the computer programs NEWMOD©, Wildfire© and MIXER© (Reynolds 1985, 1993). Extrapolation to the $1M$ end-member results in a 32 ± 4.2 Ma K-Ar age, with error determined by the sum of the squares for errors method described by Aczel (1995). Extrapolation to the $2M_1$ end-member results in a K-Ar date of ~990 Ma.

DISCUSSION

Stable isotopic compositions of diagenetic clay minerals depend on a number of factors, including 1) the isotopic composition of pore fluid, 2) the temperature of crystallization, 3) diagenetic mineral reactions that can modify initial $\delta^{18}O$ values and 4) the extent of exchange between mineral and pore water after crystallization (Yeh and Savin 1977; Whitney and Northrop 1988; Savin and Lee 1988; Longstaffe 1989; Sheppard and Gilg 1996). Textures determined by SEM and thin-section microscopy indicate that Sp-Ch and I-S are authigenic (Thomsen 1982; Hamlin and Cameron 1987; Wiygul and Young 1987; Reynolds et al. 1992), and XRD analyses indicate that the powders analyzed for $\delta^{18}O$ were relatively free of contamination, so we are confident that the Sp-Ch and I-S values reported here primarily result from the effects of (1) through (4). However, obtaining pure separates of such fine-grained minerals is difficult, and we have identified 3 potential sources of contamination in our analyses, one being siderite in the magnetic fractions from 1937 m. The second is detrital $2M_1$ mica (muscovite) present in the I-S-bearing nonmagnetic fractions. The $2M_1$ mica comprises 5 to 12% of total dioctahedral micas (Ryan 1994), and XRD data show that it erratically decreases with depth (Table 1). Values of $\delta^{18}O$ for the $2M_1$ mica were not determined, but if the $2M_1$ has lower $\delta^{18}O$ values than the authigenic I-S, then the observed increase in $\delta^{18}O$ of I-S may reflect a decrease in the amount of $2M_1$ with increasing depth as deter-

Table 2. Pore water $\delta^{18}O$ compositions calculated from fractionation equations of Wenner and Taylor (1971) and Savin and Lee (1988) at a range of temperatures. Probable temperature of Sp-Ch crystallization is 30 °C, I-S is believed to have formed at a minimum temperature of 50 °C and 165 °C is the maximum temperature to which the deepest sample has been exposed (Alford 1983).

Burial depth (m)	$\delta^{18}O_{pw}$ (30 °C)		$\delta^{18}O_{pw}$ (50 °C)		$\delta^{18}O_{pw}$ (100 °C)		$\delta^{18}O_{pw}$ (165 °C)	
	Sp-Ch	I-S	Sp-Ch	I-S	Sp-Ch	I-S	Sp-Ch	I-S
1937	0.3	−5.7	2.3	−2.6	6.1	3.1	9.2	7.8
3600	−1.8	−4.9	0.2	−1.8	4.0	3.9	7.1	8.6
4054	−0.6	−4.9	1.4	−1.8	5.2	3.9	8.3	8.6
4568	1.1	−4.5	3.1	−1.4	6.9	4.3	10.0	9.0
5470	1.4	−4.4	3.4	−1.3	7.2	4.4	10.3	9.1

mined by XRD analyses (Table 1). The third potential for contamination is anatase, which was present in trace amounts in all samples. SEM analyses reveal that it is intergrown with both Sp-Ch and I-S, and probably because of this it could not be concentrated by HGMS. It is very refractory and could not have been removed without damaging the other minerals. XRD analyses indicate that it is present in approximately equal quantities and did not systematically vary in the powders analyzed (Ryan 1994), indicating that it is not responsible for the systematic increases in $\delta^{18}O$ with depth.

Pore Fluid Composition

In sandstones, where water : rock ratios are high, the $\delta^{18}O$ values of diagenetic minerals are dominantly controlled by pore water composition (Longstaffe 1987). At shallow depths, pore water $\delta^{18}O$ compositions tend to be indicative of depositional environment, whereas waters at greater depths are influenced by water-rock interactions and isotopic exchange with ^{18}O-rich phases (Longstaffe 1989). In the absence of mineralogic changes, $\delta^{18}O$ values of diagenetic minerals should reflect the $\delta^{18}O$ composition of pore water present at the time of crystallization (Yeh and Savin 1977; Longstaffe 1987; Whitney and Northrop 1987). However, mineralogic reactions can significantly modify $\delta^{18}O$ of authigenic clay minerals, with the amount of oxygen exchanged being proportional to the extent of the reaction (Yeh and Savin 1977; Suchecki and Land 1983; Savin and Lee 1988; Whitney and Northrop 1988). The mineralogic changes in Sp-Ch and I-S facilitated oxygen exchange between mineral and pore water, and the current $\delta^{18}O$ values of both Sp-Ch and I-S are thought to reflect a mixture of initial $\delta^{18}O$ values and values inherited during subsequent oxygen isotope exchange. The $\delta^{18}O$ values of the shallowest samples should be closest to the values inherited when the minerals first crystallized.

Sp-Ch formed during the earliest stages of diagenesis (Thomsen 1982). It preceded all other diagenetic phases, with the exception of localized hematite rims, and the Sp-Ch possibly formed within the upper 10 m of sediment (Bailey 1988a; Ryan and Reynolds 1996), indicating an initial crystallization temperature of ~30 °C (Hornibrook and Longstaffe 1996). I-S, on the other hand, likely formed at temperatures of 50 to 100 °C. This estimate is based on 1) I-S formed after Sp-Ch; 2) previous work (Lee et al. 1989) which indicates that I-S in sandstone commonly crystallizes between 50 and 100 °C; and 3) the presence of nearly identical I-S (6–9% exp, $R \geq 1$) in all samples at burial depths >1700 m, which implies that the I-S formed either at depths <1700 m (<75 °C), or it formed over a wide range of depth during an event approximately 32 Ma. In either case crystallization temperature of I-S in the shallowest sample would be <75 °C. The estimated minimum temperatures of Sp-Ch (30 °C) and I-S (50 °C) formation were used to calculate initial pore water compositions (Table 2).

Using fractionation equations of Wenner and Taylor (1971) and Savin and Lee (1988), we estimate that minimum $\delta^{18}O$ value for pore water was −2.6 to −1.8‰ and maximum was +9.1 to +10.3‰ (Table 2). The estimated range in pore water $\delta^{18}O$ values (−2.6 to +10.3‰) is similar to $\delta^{18}O$ pore water values of −5 to +8‰ obtained from Cenozoic Gulf Coast sandstones (Kharaka et al. 1979). The maximum value of 10.3‰ is comparable to a pore water $\delta^{18}O$ value of +8‰ from Tuscaloosa sandstone at 5400 m burial depth (Weedman et al. 1996), and to an estimated value of +10‰ in the Spiro sand of the Arkoma Basin (Spotl et al. 1994). The initial value of ~−2‰ is consistent with Cretaceous $\delta^{18}O$ seawater values of −4 to −1‰ (Karhu and Epstein 1986), and it is also identical to an initial pore water $\delta^{18}O$ value of −2‰ obtained from shallow marine sandstones of the Alberta Basin (Longstaffe 1987). The increase in pore water $\delta^{18}O$ with increasing burial depth is indicative of mixing between isotopically light meteoric/marine water and isotopically heavy formation water during burial diagenesis (Sheppard and Gilg 1996; Longstaffe 1987; Savin and Lee 1988). If the mineralogic reactions occurred progressively with increasing temperature (Ryan and Reynolds 1996), then the distribution of $\delta^{18}O$ within Sp-Ch crystals is probably heterogeneous, with adjacent layers having different oxygen isotope compositions. The progressive and possibly kinetically controlled nature of the mineralogic reactions (Sp →

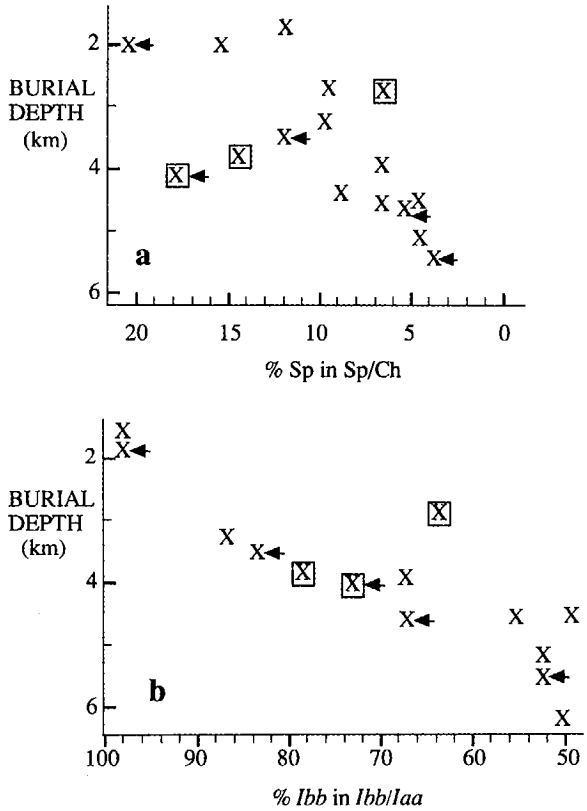

Figure 6. a) Variations in %Sp in mixed-layer Sp-Ch plotted as a function of burial depth (Ryan and Reynolds 1996). Arrows indicate samples analyzed in this study; boxes indicate well-cemented sandstones with poorly formed pore-linings. b) Variations in %*Ibb* layers in randomly interstratified *Ibb*/*Iaa* Sp-Ch polytype plotted as a function of burial depth (Ryan and Reynolds 1996). Arrows indicate samples analyzed in this study; boxes indicate well-cemented sandstones with poorly formed pore-linings.

Ch, *Ibb* → *Iaa*) would likely produce crystals consisting of interstratified *Ibb* Sp layers with low $\delta^{18}O$ values and *Iaa* Ch layers with high $\delta^{18}O$ values. This makes it unlikely that Sp-Ch (and possibly I-S) is in oxygen isotopic equilibrium with current pore waters, and the range in composition given may not represent the full range of pore fluid composition.

Recent studies, citing similarities in texture, mineralogic structure, chemical composition and depositional environment between 7-Å odinite and mixed-layer Sp-Ch (7 Å/14 Å), have concluded that pore-lining Sp-Ch originates as odinite at very shallow burial depths in tropical marine sands (Ehrenberg 1993; Hillier 1994; Ryan and Reynolds 1996, 1997). Odinite has not been found in sediments older than Holocene, nor, apparently, at burial depths >150 m (Bailey 1988c), whereas Sp-Ch has been documented in sandstones at depths >1500 m, thus leaving a gap which has prevented unequivocable determination of the transformation of odinite to Sp-Ch.

The $\delta^{18}O$ values determined for Sp-Ch in this study provide additional evidence that is consistent with a shallow diagenetic origin of Sp-Ch. Initial pore water values of −2‰ indicate that Sp-Ch formed in the presence of brackish-to-marine/meteoric pore water, and when the oxygen isotope data are combined with textural, chemical, sedimentological and mineralogical results (Ryan and Reynolds 1997), there is strong evidence for an early diagenetic transformation of odinite to Sp-Ch. If the odinite → pore-lining Sp-Ch theory proves to be true, it has important implications for predicting occurrences of high porosity and permeability in deeply buried sandstones, namely that such sandstones are likely to be those that were deposited under conditions where odinite forms. Those conditions include a tropical depositional environment characterized by warm water (~25 °C), sandy sediment, often with a significant bioclastic content, pH values of 7.5 to 8.5 (Bailey 1988a) and either Fe-rich river water (Odin et al. 1988) and/or Fe-Mg-rich detritus (Ryan and Reynolds 1997). Typical settings include brackish lagoons, deltas, shallow shelf regions and tidal inlets (Odin et al. 1988).

Implications for Mineralogic Reactions

Values of $\delta^{18}O$ for Tuscaloosa Formation Sp-Ch (+10.4 to 13.7‰) are similar to values for grain coating chlorite from sandstones of the Cretaceous Viking Formation (+10.7 to 13.4‰; Longstaffe 1989) and Pennsylvanian Spiro sandstone (+12.7 to 14.8‰; Spotl et al. 1994), which, like the Tuscaloosa Formation, were deposited on continental shelves in shallow marine environments and have been subsequently diagenetically altered. Tuscaloosa Formation I-S values are similar to those for illite and I-S from sandstones of the Viking Formation (+13.8 to 16.5‰; Longstaffe 1989) and Permian Rotliegendes Formation (+13 to 21‰; Lee et al. 1989), although Tuscaloosa Formation I-S (+16.1 to 17.3‰) shows a smaller range.

Sp-Ch in the Tuscaloosa Formation exhibits a series of mixed-layer serpentine-to-chlorite and *Ibb*-*Iaa* polytype reactions (Figure 6), but unlike other diagenetic chlorites, these transformations do not appear to occur via Ostwald-ripening crystal growth (Ryan and Reynolds 1997), a mechanism which has been observed in chlorite and Sp-Ch reactions elsewhere (Eberl et al. 1990; Jahren and Aagaard 1992; Hillier 1994). During Ostwald-ripening crystal growth, small crystallites dissolve and the dissolution products recrystallize on larger, less reactive crystallites, giving rise to increases in mean crystallite size and, commonly, changes in mixed-layer proportions and chemical compositions with increasing grade (Eberl et al. 1990; Jahren and Aagaard 1992). However, there is no systematic increase in crystallite thickness (along c^*) of Tuscaloosa Formation Sp-Ch, nor is there systematic variation in the *a*-*b* dimension of Sp-Ch crystals (Thomsen 1982),

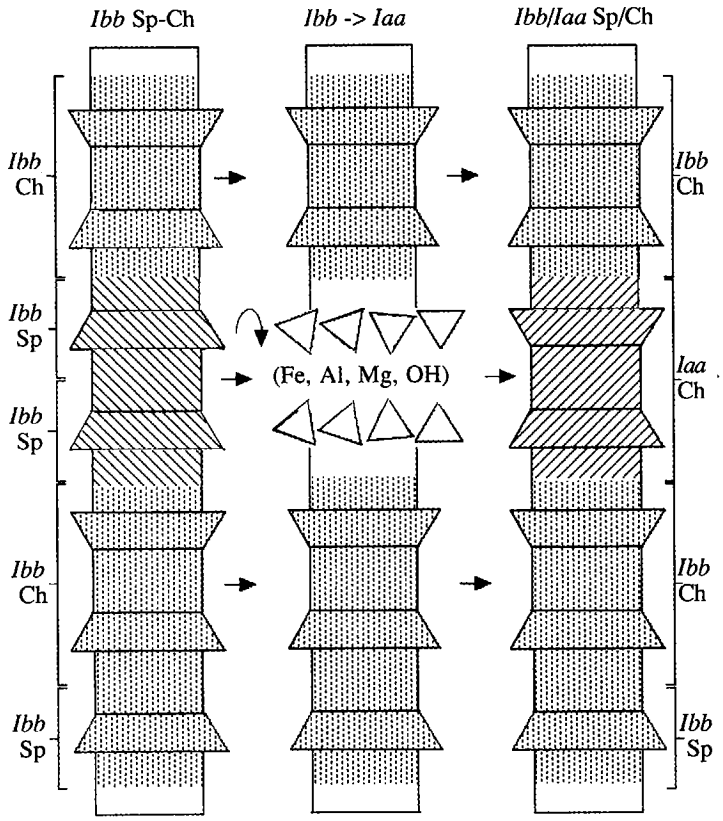

Figure 7. Diagram of the cell-preserved *Ibb* Sp-to-*Iaa* Ch reaction.

indicating that the decreases in proportions of 7-Å serpentine layers and *Ibb* polytype layers do not occur by Ostwald-ripening crystal growth. SEM/energy dispersive X-ray (EDX) determinations of Sp-Ch major element composition show no systematic variation with depth (Ryan and Reynolds 1997), suggesting that no significant cation exchange occurred during the reactions and raising the possibility that the reactions may have occurred in the solid state. However, the depth-related increases in $\delta^{18}O$ of Sp-Ch indicate that oxygen was exchanged between Sp-Ch and pore water during mineralogic reactions. Similar variations in $\delta^{18}O$ observed in conjunction with I-S reactions have been attributed to dissolution-precipitation (e.g., Yeh and Savin 1977; Whitney and Northrop 1988; Ziegler et al. 1994).

We interpret the XRD, SEM/EDX (Ryan and Reynolds 1997) and $\delta^{18}O$ data as indicating that the Sp-Ch reactions occurred via a cell-preserved, layer-by-layer mechanism when serpentine layers dissolved and recrystallized as chlorite layers within the confines of existing crystals (Figure 7). Sp-Ch crystallites were not destroyed during the mixed-layer transformations, and the crystallites appear to have functioned as frameworks within which planar (possibly metastable) serpentine zones dissolved and recrystallized as chlorite. This type of reaction mechanism is similar to those observed in a variety of settings for reactions of Sp to Ch (Ahn and Peacor 1985; Jiang et al. 1992; Li and Peacor 1993; Banfield and Bailey 1996; Xu and Veblin 1996), biotite to chlorite (Eggleton and Banfield 1985; Li and Peacor 1993), and smectite to illite (Altaner and Bethke 1986; Altaner and Ylagin 1993). Furthermore, difference in crystal structure between serpentine and chlorite indicates that the serpentine-to-chlorite reaction must involve at least partial dissolution. The transformation of 2 adjacent 7-Å layers to one 14-Å layer cannot occur in the solid state because it requires inversion of a tetrahedral sheet (Brindley 1961; Reynolds 1988; Banfield and Bailey 1996). The 7 Å–14 Å reaction must involve localized reorganization of atoms that would facilitate exchange of oxygen between mineral and pore water without necessarily changing the bulk chemistry or size of the Sp-Ch crystals.

The *Ibb*-to-*Iaa* polymorphic reaction occurs simultaneously with the serpentine-to-chlorite reaction, indicating that *Iaa* chlorite layers formed from precursor *Ibb serpentine* layers. However, % serpentine decreases from 21% to 3% while %*Ibb* in *Ibb*/*Iaa* decreases from 100% to 53% (Figure 6), indicating that some of the *Iaa* chlorite layers must have also formed from

precursor *Ibb chlorite* layers. While the inversion of a tetrahedral sheet during the serpentine-to-chlorite reaction necessitates dissolution and reprecipitation (at least of the tetrahedral sheet), the *Ibb* chlorite-to-*Iaa* chlorite reaction involves an *a*/3 shift between 2:1 layers and hydroxide interlayers (Bailey 1988b) but not inversion of the tetrahedra, and as such could conceivably occur in the solid state. However, it is probable that transformations of Sp-to-Ch and *Ibb*-to-*Iaa* in Tuscaloosa sandstone occurred simultaneously during inversion of tetrahedral sheets (Ryan and Reynolds 1996), a reaction mechanism that has been observed in the retrograde transformation of chlorite layers to serpentine layers in which *a*/3 shifts accompanied the Sp-Ch reaction (Banfield and Bailey 1996).

Differences in slope of the Sp-Ch and I-S $\delta^{18}O$ trends with respect to depth indicate that they have undergone isotopic exchange at different rates, and the differences can be attributed to the different ways Sp-Ch and I-S have responded to increasing temperature. The large-scale mineralogic changes in serpentine content and *Ibb*/*Iaa* polymorphism are reflected in the 3.3‰ $\delta^{18}O$ increase, whereas the I-S polytype rotations, which exhibit a significantly smaller range in structural variations than Sp-Ch, are consistent with the smaller $\delta^{18}O$ increase of 1.2‰. The shift in $\delta^{18}O$ of I-S may reflect dissolution and reprecipitation of 2:1 layers accompanying the rotation (or translation) of coherently stacked 2:1 layers from 120° to 0° ($P_{0°}$, Table 2). An alternate and perhaps more valid interpretation is that the I-S crystallized during an event approximately 32 Ma, with shallow I-S recording lower $\delta^{18}O$ values characteristic of shallow pore waters. I-S that crystallized in deeper samples did so in the presence of basinal brines with higher $\delta^{18}O$ values. In that case, increasing 1*M* polytype rotational order ($P_{0°}$, Table 2) with depth reflects higher temperatures of crystallization in the deeper samples. Also, the erratic decrease in $2M_1$ mica cannot be ruled out as a possible contributor to the I-S isotopic shift.

Temperatures calculated from Sp-Ch–I-S fractionation for the 3509-m and 4054-m samples are relatively consistent with measured borehole temperatures and temperatures calculated, assuming a 25–33 °C/km geothermal gradient (Alford 1983), indicating that Sp-Ch and I-S from those samples may be in oxygen isotopic equilibrium (Table 2). However, this may be coincidence, especially given differences in the timing of Sp-Ch and I-S crystallization and the differences in the magnitude of Sp-Ch and I-S diagenetic reactions. Calculated temperatures for the 1937-m, 4568-m and 5470-m samples are far higher than current burial temperatures, and assuming that the current temperatures are maximum temperatures (Alford 1983), Sp-Ch and I-S in those samples are well out of equilibrium. The Sp-Ch–I-S disequilibrium at 4568 m and 5470 m is attributed to the different rates of oxygen isotopic exchange related to differences in the magnitudes of the Sp-Ch and I-S mineralogic reactions. Specifically, Sp-Ch has undergone mixed-layer reactions involving a larger proportion of layers than has I-S, thus facilitating the incorporation of greater amounts of $\delta^{18}O$-rich formation water in Sp-Ch. Explaining the disequilibrium at 1937 m is more difficult because it seems to involve an anomalously high Sp-Ch value. While the $\delta^{18}O$ value is typical for Sp-Ch-type minerals (Suchecki 1983; Hornibrook and Longstaffe 1996; Spotl et al. 1994), is within the range of the other 4 samples, and correlates to a pore water value of 0‰, consistent with marine/meteoric waters, it appears anomalous when compared to the trend shown by the 4 deeper samples. The I-S $\delta^{18}O$ value, however, is consistent with the I-S trend. The presence of siderite ($\delta^{18}O$ = 32.8‰) in the paramagnetic fractions of the 1937-m sample suggests that the high Sp-Ch value may have been due to contamination from siderite, but XRD data and the low yield in the siderite $\delta^{18}O$ analysis indicate there was insufficient siderite in the powder to account for the high value. Even based on the XRD analysis showing 4% siderite in the paramagnetic fraction, the corrected value for 1937-m Sp-Ch is 11.8‰, which still appears to be anomalously high and suggests that additional factors may be involved. Other potential explanations for the high Sp-Ch value include: 1) the Sp-Ch crystallized in the presence of localized, anomalously high $\delta^{18}O$ pore water and still records a detrital $\delta^{18}O$ signature; and 2) an undetected isotopically heavy contaminant was present in the magnetic fractions of that sample, which seems unlikely given that no additional phases were detected in XRD analyses.

The best explanation involves retention of the $\delta^{18}O$ value inherited during crystallization at shallow depth combined with limited contamination by 32.8‰ siderite. If Sp-Ch formed from precursor odinite (Ryan and Reynolds 1996) in conjunction with dissolving ultramafic rock fragments (Thomsen 1982), the high $\delta^{18}O$ value could reflect localized pore water produced by dissolution of O^{18}-rich odinite and ultramafic minerals in the presence of marine water. The $\delta^{18}O$ value could also be attributed to difference in depositional environment. The higher value at 1937 m is consistent with crystallization in the presence of marine water (0‰), whereas the lower value at 3509 m indicates more brackish waters of −2‰ (Longstaffe 1989). Under either scenario, the high $\delta^{18}O$ value would likely be preserved at shallow burial depth (<2000 m), where diagenetic mixed-layer reactions have not yet occurred to a significant extent and oxygen exchange between Sp-Ch and pore water has been limited by the lack of reactions (Savin and Lee 1988; Sheppard and Gilg 1996). I-S crystallized later, perhaps at 32 Ma in the presence of higher temperature and different pore waters, and thus records values consistent with the deeper I-S values.

Similar "anomalous" $\delta^{18}O$ values attributable to detrital precursors also have been observed in shallowly buried Gulf Coast shale. Yeh and Savin (1977) found oxygen isotopic disequilibrium at depths <2500 m as indicated by a wide range in $\delta^{18}O$ values of I-S from different particle sizes, whereas at depths >2500 m, I-S $\delta^{18}O$ values for the different size fractions were significantly more homogeneous and more reflective of ambient pore water values due to oxygen exchange facilitated by mixed-layer I-S reactions.

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REFERENCES

Aczel AD. 1995. Statistics: Concepts and applications. Chicago: Irwin. 533 p.

Ahn JH, Peacor DR. 1985. Transmission electron microscopic study of diagenetic chlorite in Gulf Coast argillaceous sediments. Clays Clay Miner 33:228–237.

Alford EV. 1983. Compositional variations of authigenic chlorites in the Tuscaloosa Formation, Upper Cretaceous of the Gulf Coast Basin [M.S. thesis]. New Orleans, LA: Univ of New Orleans.

Altaner SP, Bethke CM. 1986. Layer-by-layer mechanism of smectite illitization and application to a new rate law. Clays Clay Miner 34:136–145.

Altaner SP, Ylagin RF. 1993. Interlayer-by-interlayer dissolution: A new mechanism for smectite illitization. Progr Abstr, 30th Annu Meet Clay Miner Soc; San Diego, CA. p 88.

Ayalon A, Longstaffe FJ. 1988. Oxygen-isotope studies of diagenesis and porewater evolution in the western Canada sedimentary basin: Evidence from the Upper Cretaceous basal Belly River sandstone, Alberta. J Sed Petrol 58:489–505.

Bailey SW. 1988a. Structures and compositions of other 1:1 trioctahedral phyllosilicates. In: Bailey SW, editor. Hydrous phyllosilicates (exclusive of micas), Rev Mineral 19. Washington, DC: Mineral Soc Am. p 169–188.

Bailey SW. 1988b. Chlorites: Structures and crystal chemistry. In: Bailey SW, editor. Hydrous phyllosilicates (exclusive of micas), Rev Mineral 19. Washington, DC: Mineral Soc Am. p 347–403.

Bailey SW. 1988c. Odinite, a new dioctahedral-trioctahedral Fe^{3+}-rich 1:1 clay mineral. Clay Miner 23:237–247.

Banfield JF, Bailey SW. 1996. Formation of regularly interstratified serpentine-chlorite by tetrahedral inversion in long-period serpentine polytypes. Am Mineral 81:79–91.

Brindley GW. 1961. Chlorite minerals. In: Brown G, editor. The X-ray identification and crystal structures of clay minerals. London: Mineral Soc. p 242–296.

Clayton RN, Mayeda TK. 1963. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. Geochim Cosmochim Acta 27: 43–52.

Drever JI. 1973. The preparation of oriented clay mineral specimens for X-ray diffraction analysis by a filter-membrane peel technique. Am Mineral 50:741–751.

Eberl DD, Środoń J. 1984. Illite. In: Micas, Rev Mineral 13. Washington, DC: Mineral Soc Am. p 495–544.

Eberl DD, Środoń J, Kralik M, Taylor BE, Peterman ZE. 1990. Ostwald ripening of clays and metamorphic minerals. Science 248:474–477.

Eggleton RA, Banfield JF. 1985. The alteration of granitic biotite to chlorite. Am Mineral 70:902–910.

Ehrenberg SN. 1993. Preservation of anomolously high porosity in deeply buried sandstones by grain-coating chlorite: Examples from the Norwegian Continental Shelf. Am Assoc Petrol Geol Bull 77:1260–1286.

Eslinger EV, Savin SM. 1973. Oxygen isotope geothermometry of the burial metamorphic rocks of the Precambrian Belt Supergroup, Glacier National Park, Montana. Geol Soc Am Bull 84:2549–2560.

Hamlin KH, Cameron CP. 1987. Sandstone petrology and diagenesis of Lower Tuscaloosa Formation reservoirs in the McComb and Little Creek field areas, southwest Mississippi. Trans Gulf Coast Assoc Geol Soc 37:95–104.

Heald MT, Anderegg RC. 1960. Differential cementation in the Tuscarora sandstone. J Sed Petrol 30:568–577.

Hillier S. 1994. Pore-lining chlorites in siliciclastic reservoir sandstones: Electron microscope, SEM, and XRD data, and implications for their origin. Clay Miner 29:665–679.

Hornibrook ERC, Longstaffe FJ. 1996. Berthierine from the Lower Cretaceous Clearwater Formation, Alberta, Canada. Clays Clay Miner 44:1–21.

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

Jahren JS, Aagaard P. 1992. Diagenetic illite-chlorite assemblages in arenites. I. Chemical evolution. Clays Clay Miner 40:540–546.

Jiang W-T, Peacor DR, Slack JF. 1992. Microstructures, mixed-layering, and polymorphism of chlorite and retrograde berthierine in the Kidd Creek massive sulfide deposit, Ontario. Clays Clay Miner 40:501–514.

Karhu J, Epstein S. 1986. The implication of the oxygen isotopic composition of selected limestones and fossils. Geochim Cosmochim Acta 37:1787–1816.

Kharaka YK, Lico MS, Wirght VA, Carothers WW. 1979. Geochemistry of formation waters from Pleasant Bayou No. 2 well and adjacent areas in coastal Texas. Proc 4th Geopressured-Geothermal Energy Conf; Austin, TX. p 168–193.

Lee M, Aronson JL, Savin SM. 1989. Timing and conditions of Permian Rotliegende sandstone diagenesis, southern North Sea: K/Ar and oxygen isotopic data. Am Assoc Petrol Geol Bull 73:195–215.

Li G, Peacor DR. 1993. Sulfides precipitated in chlorite altered from detrital biotite: A mechanism for local sulfate reduction? Abstr Progr Geol Soc Am Ann Meet 25. p 146–147.

Longstaffe FJ. 1987. Stable isotope studies of diagenetic processes. In: Kyser TK, editor. Stable isotope geochemistry of low temperature fluids, Miner Assoc Canada Short Course 13. p 187–257.

Longstaffe FJ. 1989. Stable isotopes as tracers in clastic diagenesis. In: Hutcheon IE, editor. Short course in burial diagenesis, Miner Assoc Canada Short Course 15. p 201–277.

Matsuhisa Y, Goldsmith JR, Clayton RN. 1979. Oxygen isotope fractionation in the system quartz-albite-anorthite-water. Geochim Cosmochim Acta 43:1131–1140.

Odin GS, Bailey SW, Amouric M, Frohlich F, Waychunas GA. 1988. Mineralogy of the facies verdine. In: Odin GS,

editor. Green marine clays, Devel Sedimentol 45. Amsterdam: Elsevier. p 159–206.

Pittman ED, Lumsden DN. 1968. Relationship between chlorite coatings on quartz grains and porosity, Spiro Sand, Oklahoma. J Sed Petrol 38:668–670.

Reynolds RC Jr. 1985. NEWMOD©—A computer program for the calculation of one-dimensional diffraction profiles of clays. RC Reynolds, Jr: 8 Brook Road, Hanover, NH.

Reynolds RC Jr. 1988. Mixed-layer chlorite minerals. In: Bailey SW, editor. Hydrous phyllosilicates (exclusive of micas), Rev Mineral 19. Washington, DC: Mineral Soc Am. p 601–630.

Reynolds RC Jr. 1992. X-ray diffraction studies of illite/smectite from rocks, <1 μm randomly oriented powders, and <1 μm oriented powder aggregates: The absence of laboratory-induced artifacts. Clays Clay Miner 40:387–398.

Reynolds RC Jr. 1993. WILDFIRE©—A computer program for the calculation of three-dimensional diffraction profiles of clays. RC Reynolds, Jr: 8 Brook Road, Hanover, NH.

Reynolds RC Jr, DiStefano MP, Lahann RW. 1992. Randomly interstratified serpentine/chlorite: Its detection and quantification by powder X-ray diffraction methods. Clays Clay Miner 40:262–267.

Rosenbaum J, Sheppard SMF. 1986. An isotopic study of siderites, dolomites, and ankerites at high temperatures. Geochim Cosmochim Acta 50:1147–1150.

Ryan PC. 1994. Serpentine/chlorite and illite/smectite in the Tuscaloosa Formation: Origins, chemistry, mineralogic structures, and oxygen isotope compositions [Ph.D. thesis]. Hanover, NH: Dartmouth College. 177 p.

Ryan PC, Reynolds RC Jr. 1996. The origin and diagenesis of grain-coating serpentine-chlorite in Tuscaloosa Formation sandstone. U.S. Gulf Coast. Am Mineral 81:213–225.

Ryan PC, Reynolds RC Jr. 1997. The chemical composition of serpentine/chlorite in the Tuscaloosa Formation, U.S. Gulf Coast: EDX vs. XRD determinations, implications for mineralogic reactions, and the origin of anatase. Clays Clay Miner 45:339–352.

Savin SM, Lee M. 1988. Isotopic studies of phyllosilicates. In: Bailey SW, editor. Hydrous phyllosilicates (exclusive of micas), Rev Mineral 19. Washington, DC: Mineral Soc Am. p 189–223.

Sheppard SMF, Gilg HA. 1996. Stable isotope geochemistry of clay minerals. Clay Miner 31:1–24.

Spotl C, Houseknecht DW, Longstaffe FJ. 1994. Authigenic chlorites in sandstones as indicators of high-temperature diagenesis, Arkoma Foreland Basin. USA. J Sed Res A64: 553–566.

Stancliffe RJ, Adams ER. 1986. Lower Tuscaloosa fluvial channel styles at Liberty Field, Amite County, Mississippi. Trans Gulf Coast Assoc Geol Soc 36:305–313.

Suchecki RK, Land LS. 1983. Isotopic geochemistry of burial-metamorphosed volcanogenic sediments, Great Valley sequence, northern California. Geochim Cosmochim Acta 47:1487–1499.

Suchecki RK. 1983. Isotopic evidence for large-scale interaction between formation waters and clastic rocks. Abs Prog Geol Soc Am 15 (96th Annu Meet). p 701.

Tellier KE. Hluchy MM, Walker JR, Reynolds RC Jr. 1988. Application of high-gradient magnetic separation (HGMS) to structural and compositional studies of clay minerals. J Sed Petrol 58:761–763.

Thomsen A. 1982. Preservation of porosity in the Deep Woodbine/Tuscaloosa Trend, Louisiana. J Petrol Tech 34: 1156–1162.

Weedman SD, Brantley SL, Shiraki R, Poulson SR. 1996. Diagenesis, compaction, and fluid chemistry modeling of a sandstone near a pressure seal: Lower Tuscaloosa Formation, Gulf Coast. AAPG Bull 80:1045–1064.

Wenner DB, Taylor HP Jr. 1971. Temperatures of serpentinization of ultramafic rocks based on $^{18}O/^{16}O$ fractionation between coexisting serpentine and magnetite. Contrib Mineral Petrol 32:165–185.

Whitney G, Northrop HR. 1987. Diagenesis and fluid flow in the San Juan basin, New Mexico—Regional zonation in the mineralogy and stable isotope composition of clay minerals in sandstone. Am J Sci 287:353–382.

Whitney G, Northrop HR. 1988. Experimental investigation of the smectite to illite reaction: Dual reaction mechanisms and oxygen isotope systematics. Am Mineral 73:77–90.

Worrall DM, Snelson S. 1989. Evolution of the northern Gulf of Mexico, with emphasis on Cenozoic growth faulting and the role of salt. In: Bally AW, Palmer AR, editors. The geology of North America, an overview: The geology of North America, A. Boulder, CO: Geol Soc Am. p 97–138.

Wiygul GJ, Young LM. 1987. A subsurface study of the Lower Tuscaloosa Formation at Olive Field, Pike and Amity Counties, Mississippi. Trans Gulf Coast Assoc of Geol Soc 37:295–302.

Xu H, Veblen DR. 1996. Interstratification and other microstructures in the chlorite-berthierine series. Contrib Mineral Petrol 124:291–301.

Yeh H-W, Savin SM. 1977. The mechanism of burial metamorphism of argillaceous sediments: Oxygen isotopic evidence. Geol Soc Am Bull 88:1321–1330.

Ziegler K, Sellwood BW, Fallick AE. 1994. Radiogenic and stable isotope evidence for age and origin of authigenic illites in the Rotliegend, southern North Sea. Clay Miner 29:555–565.

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