

## **Diagenesis 4. Stable Isotope Studies of Diagenesis in Clastic Rocks**

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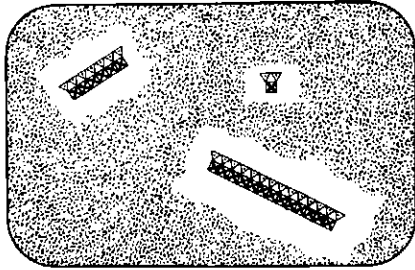
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# Articles



## Diagenesis 4. Stable Isotope Studies of Diagenesis in Clastic Rocks

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### Introduction

The stable isotopes of oxygen ( $^{18}\text{O}/^{16}\text{O}$ ), hydrogen (D/H), carbon ( $^{13}\text{C}/^{12}\text{C}$ ) and sulphur ( $^{34}\text{S}/^{32}\text{S}$ ) are extremely valuable tracers of low temperature water-rock interaction. These geochemical tools can be profitably applied to the study of diagenesis.

The main intent of this paper is to illustrate how oxygen- and hydrogen-isotope methods can be used to deduce the physicochemical conditions that existed during various stages of diagenesis in sandstones and shales. This goal is approached first by discussions of (i) the principles of stable isotope geochemistry, (ii) the oxygen- and hydrogen-isotope variations of waters that may be involved in clastic diagenesis (ocean water, meteoric water, formation fluids, etc.) and (iii) the whole-rock oxygen-isotope geochemistry of clastic rocks. This introduction is followed by a limited number of case studies, each of which illustrates a particular concept concerning the application of stable isotopes to research in clastic diagenesis.

In the first example (the Milk River Formation, southeastern Alberta), two main ideas are presented:

1. Oxygen- and hydrogen-isotope measurements of authigenic minerals in sandstones can be used to identify phases precipitated in response to the introduction of meteoric water into the system, and to show that such phases can form at very low temperatures.

2. The stable isotope signatures of authigenic minerals precipitated from an isotopically-characteristic fluid may provide a method by which the paleohydrology of a sandstone can be inferred.

If some authigenic minerals in sandstones retain isotopic records of previous fluid regimes, it may become possible to identify ancient zones of fluid mixing. Such activity can cause changes in the type and abundance of authigenic minerals in a sandstone and could result in the formation of diagenetic hydrocarbon traps. The ability to recognize such trends from stable isotope measurements may become of real importance to exploration.

The second set of case studies (the "Gray" sandstone, Texas; the Belly River sandstone, Alberta and the Frio Formation, Texas) treat the concept that the  $\delta^{18}\text{O}$  values of individual diagenetic minerals in sandstones can be used in conjunction with experimentally determined oxygen-isotope mineral-water fractionations to estimate crystallization temperatures. These isotopic temperatures can be used to create models for the sequence of authigenic mineral formation during burial diagenesis. From such data, one can estimate geothermal gradients and maximum depths of burial experienced by a sandstone. It may also be possible to model the geochemical evolution of formation fluids and to determine from carbon-isotope measurements whether  $\text{CO}_2$  derived from organic matter has been incorporated into diagenetic carbonates. To predict whether or not thermal conditions necessary for hydrocarbon production existed in argillaceous units adjacent to the sandstones is but one potentially important application of such studies.

The final group of examples concerns stable isotope studies of shale diagenesis. One idea to emerge is that oxygen-isotope geothermometry using mineral pairs (e.g., quartz-illite/smectite) can provide estimates of the maximum temperature to which the shale has been heated. Naturally, such information is of importance when evaluating source rock potential for hydrocarbon generation. The stable isotope results also demonstrate that illite/smectite reactions during burial can, in some cases, control the geochemical evolution of formation fluids.

In summary, the oxygen- and hydrogen-isotope compositions of formation fluids provide a diagnostic signature both of source (e.g., seawater, meteoric water) and of important chemical and physical processes by which the water may have been modified (e.g., mixing, evaporation). The oxygen- and hydrogen-isotope compositions of minerals precipitated during lithification and diagenesis may preserve a record of the fluids with which these phases have equilibrated. Furthermore, under appropriate conditions the oxygen-isotope compositions of authigenic minerals can be used to estimate temperature(s) of crystallization.

The mineral separation and analytical techniques required to perform this type of investigation are complicated. No attempt is made to review this methodology here. However, a reading list is appended at the end of the paper.

A separate paper would be required to elaborate upon the possible applications of carbon- and sulphur-isotopes in studies of clastic diagenesis. The carbon-isotope ratios of carbonate cements can help characterize the source of the C involved in their precipitation and perhaps reveal the passage or presence of hydrocarbons. The sulphur-isotope compositions of authigenic S-bearing minerals can provide information concerning the evolution of pore waters during diagenesis. An initial appreciation of their usefulness as tracers can be gained from Coleman and Raiswell's (1981) study of a concretion-rich shale. They demonstrated that the variation in pyrite morphol-

ogy from early-formed framboids to abundant, later-crystallized euhedra correlated with a marked enrichment in  $^{34}\text{S}$ . Such behaviour can be explained by open system bacterial reduction of seawater sulphate during the formation of the synsedimentary framboids followed by sulphate reduction in a partially closed system (e.g., the loss of sulphate by reduction exceeds replenishment of sulphate) during shallow burial. The sulphate-reduction process can also produce characteristically  $^{13}\text{C}$ -depleted  $\text{CO}_2$  which then may be incorporated into diagenetic carbonates (Curtis, 1977; Coleman and Raiswell, 1981; Wigley et al., 1978). This process generally occurs within the upper few metres of sediment. The  $^{13}\text{C}$ -depleted compositions of such carbonates contrast with  $^{13}\text{C}$ -rich carbonates sometimes formed from  $\text{CO}_2$  produced by fermentation reactions at greater depths (Coleman and Raiswell, 1981; Rosenfield and Silverman, 1959).

As the preceding example shows, the interpretation of carbon- and sulphur-isotope ratios in clastic sedimentary and diagenetic environments, especially those containing hydrocarbons, can become complex. An introduction to carbon- and sulphur-isotopes can be obtained from the papers listed at the end of this article.

### Principles

An introduction to some fundamental aspects of stable isotope geochemistry is a necessary precursor to any discussions concerning diagenesis. Stable isotope values are reported in the  $\delta$ -notation in parts per thousand (permil, ‰). The  $\delta$ -value is defined as:

$$\delta(\text{‰}) = \frac{R(\text{sample}) - R(\text{standard})}{R(\text{standard})} \times 1000 \quad (1)$$

where  $R = {}^{18}\text{O}/{}^{16}\text{O}$ ,  $\text{D}/\text{H}$ ,  ${}^{13}\text{C}/{}^{12}\text{C}$ , etc.

The internationally accepted standard for oxygen- and hydrogen-isotopes is Standard Mean Ocean Water (SMOW) (Craig, 1961a). For carbon-isotopes the *Belleme-tella americana* from the PeeDee formation (PDB) (Craig, 1957) is most commonly employed. The  $\delta$   $^{18}\text{O}$  values for carbonate minerals can also be reported relative to PDB. In this paper all isotope data for oxygen (including carbonates) will be referred to SMOW. All carbon-isotope data will be reported with respect to PDB.

The stable isotope equilibrium fractionation factor for two phases, A and B, is defined as:

$$\alpha_{A-B} = \frac{R_A}{R_B} \quad (2)$$

Experimentally determined oxygen-isotope fractionation factors for mineral pairs or mineral-water pairs ( $\alpha_{A-B}$ ) usually fall

on smooth curves when  $10^3 \ln \alpha_{A-B}$  is plotted versus  $1/T^2$  ( $^{\circ}\text{K}$ ). The temperature dependence of  $\alpha$  forms the basis of oxygen-isotope geothermometry (Urey, 1947; Bigeleisen and Mayer, 1947). The quantity called permil fractionation,  $10^3 \ln \alpha_{A-B}$  (O'Neil, 1979), can be estimated by the  $\Delta$ -value where:

$$\Delta_{A-B} = 10^3 \ln \alpha_{A-B} \approx (\alpha - 1)10^3 \approx \delta_A - \delta_B \quad (3)$$

(Schwarcz, 1981). When dealing with large values of the permil fractionation ( $>10$ ), a common occurrence for minerals formed in low temperature environments, the approximation  $\delta_A - \delta_B$  becomes inaccurate and it is advisable to calculate  $\Delta_{A-B}$  precisely.

The oxygen- and hydrogen-isotope composition of a mineral formed during lithification or diagenesis is a function of:

1. its temperature of formation
2. the isotopic composition of the fluid present during mineral authigenesis
3. the mass balance of oxygen, hydrogen, etc., between the liquid and solid phases (e.g., the water/mineral ratio for the element of interest)
4. the stable isotope equilibrium fractionation factor between the mineral and the fluid phase
5. the extent to which isotopic equilibrium was maintained during mineral formation
6. the extent and nature of isotopic exchange between the mineral and fluids following crystallization.

At temperatures normal for sedimentary environments, most minerals do not experience significant isotopic exchange with surrounding fluids. Isotopic exchange between minerals and fluids occurs only during dissolution and reprecipitation reactions. Only as temperatures rise does isotopic exchange begin at significant rates.

The rate of isotopic exchange between minerals and fluids depends upon the temperature of the system, the chemistry and structure of the mineral and the grain-size of the mineral. Of the common minerals, quartz is most resistant to isotopic exchange subsequent to crystallization. No evidence exists for exchange between quartz and water at surface temperatures, even for the finest size-fractions of the mineral. For example, during burial metamorphism no oxygen-isotope exchange between quartz and pore-fluids was observed for any size-fraction up to temperatures of  $170^{\circ}\text{C}$  (Savin, 1980, 1982; Yeh and Savin, 1977; see also Clayton et al., 1978). More details concerning this phenomenon are given later in this paper.

Clay minerals can exchange isotopes with water under certain conditions. Inter-layer water in swelling clays isotopically

reequilibrates with water vapour at room temperatures within a few days (Savin, 1967). In contrast, exchange of oxygen- and hydrogen-isotopes between water and structural sites in clay minerals is normally unimportant at temperatures typical of sedimentary environments (O'Neil and Kharaka, 1976; James and Baker, 1976; see reviews by Savin, 1980 and Savin and Yeh, 1981). As temperatures rise, the rate of exchange increases, with notable exchange of hydrogen being achieved at temperatures near  $100^{\circ}\text{C}$  and significant oxygen exchange occurring by  $300^{\circ}\text{C}$  (O'Neil and Kharaka, 1976). Swelling clay minerals are usually affected most rapidly.

These experimental findings have been substantiated by studies of natural systems. Yeh and Savin (1976) and Eslinger and Yeh (1981) showed that oxygen-isotope exchange between Recent clay minerals and ocean water is significant for only the very finest size-fractions ( $<0.2 \mu\text{m}$ ). As first suggested by Savin and Epstein (1970a,b), most detrital oceanic clays have not reequilibrated with seawater over periods at least as long as hundreds of thousands of years. Similar observations have been reported for hydrogen-isotopes (Yeh and Epstein, 1978; Eslinger and Yeh, 1981).

Isotopic exchange rates for clay minerals increase during burial metamorphism. As will be illustrated later, Yeh and Savin (1977) showed that isotopic exchange between pore-fluids and clay minerals accelerates with increasing depth of burial (increasing temperature), finer size-fractions being significantly affected at shallower depths and lower temperatures than are coarser clay materials.

Carbonates such as calcite exchange oxygen-isotopes with water much more readily, and at lower temperatures, than do silicate minerals (Clayton, 1959). Such behaviour is reflected by the tendency of limestones towards lower  $\delta^{18}\text{O}$  values with increasing geological age, most likely because of continuous, post-depositional isotopic exchange with  $^{18}\text{O}$ -poor meteoric waters (Keith and Weber, 1964).

### Stable Isotope Variations in Water

Water is one of the most important reservoirs that control the oxygen- and hydrogen-isotope compositions of minerals formed or modified during diagenesis. When water/rock ratios are high, the isotopic composition of the aqueous fluid imparts a characteristic isotopic signature upon precipitating or exchanging solid phases.

Unmodified ocean water has  $\delta^{18}\text{O} = 0$  and  $\delta\text{D} = 0$ ; these values vary only slightly in a few localities due to dilution with fresh (meteoric) water or because of extreme evaporation. Ocean water has not varied greatly in isotopic composition throughout

geological time, at least since the Precambrian (Knauth and Epstein, 1976).

Most fresh waters show a wide but systematic variation in isotopic composition ( $\delta^{18}\text{O} = -50$  to  $0$ ;  $\delta\text{D} = -400$  to  $0$ ). The isotopic behaviour of most fresh water can be described by the meteoric water line, first expressed by Craig (1961b), as:

$$\delta\text{D} = 8\delta^{18}\text{O} + 10 (\text{‰}) \quad (4)$$

This regularity results from evaporation and condensation cycles; in an equilibrium process,  $^{18}\text{O}$  and D are enriched in water condensed from a vapour (see Hoefs, 1980 or Taylor, 1974 for a fuller discussion and original references). The liquid-vapour isotope-fractionation increases with decreasing temperature. Water initially evaporated from the ocean becomes progressively depleted in  $^{18}\text{O}$  and D as it participates in successive evaporation-condensation cycles while travelling across the continents. This Rayleigh-type distillation creates distinct latitude and altitude dependencies of  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , freshwaters becoming depleted in the heavier isotope at higher altitudes and latitudes (Fig. 1a).

In most cases, isotopically unmodified ocean water or meteoric water are not directly involved in the diagenesis of clastic rocks. Pore-waters trapped with Cenozoic oceanic sediments show small variations in  $\delta\text{D}$  and  $\delta^{18}\text{O}$  from those of modern ocean water (see review by Savin and Yeh, 1981). Their  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values tend to decrease with increasing depth. Friedman and Hardcastle (1973) concluded that the change in  $\delta\text{D}$  of pore-waters reflects primary variations in the D-content of bottom waters trapped during sedimentation. The observed decrease in the  $\delta\text{D}$  values of the bottom waters ( $+5$  to  $-7$ ) can be related to changes in the isotopic composition of ocean water due to glacial episodes (Savin and Yeh, 1981). Friedman and Hardcastle (1974) also concluded that the  $\delta\text{D}$  variations of pore-waters from Red Sea cores derive from bottom water compositions that varied because of evaporation.

Lawrence and his colleagues (Lawrence, 1973, 1974; Lawrence *et al.*, 1975; Gieskes and Lawrence, 1976, 1981 and Lawrence *et al.*, 1975) determined that the decrease in  $\delta^{18}\text{O}$  of pore-waters ( $0$  to  $-4$ ) from many oceanic sediments results from interaction and exchange with underlying basalt or volcanic ash included within the sediment. In contrast, Savin and Yeh (1981) suggested that the decrease in  $\delta^{18}\text{O}$  of pore-waters from Red Sea sediments reflect primary differences in the oxygen-isotopic composition of the entrapped bottom waters.

The isotopic variations of formation fluids present in sandstone reservoirs are of

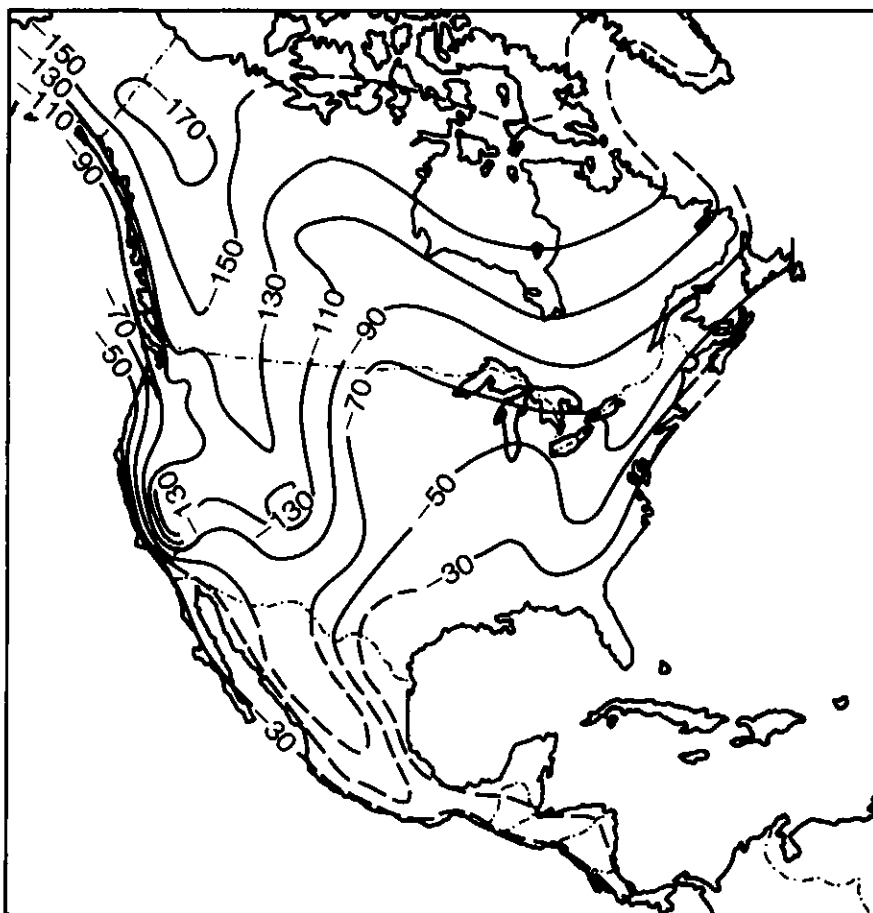


Figure 1a Average  $\delta\text{D}$  values for meteoric surface waters in North America. This diagram is taken from Taylor (1974) and based largely

upon data from Dansgaard (1964), Friedman *et al.* (1964) and Hitchon and Krouse (1972).

particular interest. Although Clayton *et al.* (1966), Hitchon and Friedman (1969) and Kharaka *et al.* (1973) have demonstrated that many oil-field brines contain a sizeable fraction of meteoric water, these formation waters do not have  $\delta^{18}\text{O}$  or  $\delta\text{D}$  values that plot along the meteoric water line (Fig. 1b). Instead, formation waters from a given basin trend away from the meteoric water line towards higher values of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  (Fig. 1b). Samples with the highest salinity and temperature are usually most enriched in  $^{18}\text{O}$ . The least saline, coolest fluids within a particular basin generally have the lowest  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values. Formation waters from sedimentary basins at high latitudes plot on trends that intersect the meteoric water line at lower  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values than formation waters from sedimentary basins at low latitudes (Fig. 1b). This behaviour demonstrates the presence of meteoric water in the formation fluid.

The deviation of the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of the formation fluids from the meteoric water line can result from a number of different processes. The various possibilities

have been discussed by Clayton *et al.* (1966), Hitchon and Friedman (1969), Coplen and Hanshaw (1973), Fleischer *et al.* (1977), Schwartz and Muehlenbachs (1979), Knauth *et al.* (1980), Land and Prezbindowski (1981) and Graf (1982), and include:

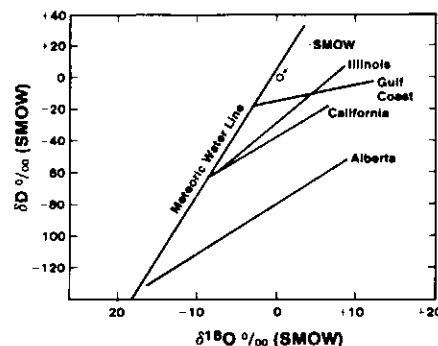


Figure 1b A  $\delta\text{D}$  versus  $\delta^{18}\text{O}$  diagram for formation waters (oil-field brines; after Taylor, 1974 and Hoefs, 1980). Original data from Clayton *et al.* (1966), Hitchon and Friedman (1969) and Kharaka *et al.* (1973).

1. isotopic exchange between water and <sup>18</sup>O-rich phases such as carbonate minerals and D-rich phases such as hydrocarbons, H<sub>2</sub>S, and hydrated minerals
2. mixing of meteoric and connate waters due to dispersion-type processes
3. dewatering of clay minerals during burial
4. isotopic fractionation due to diffusion of water through micropore systems in shales and mudstones (e.g., membrane-filtration)

All processes could be involved at various times during the evolution of a given formation fluid.

**Oxygen-Isotope Geochemistry of Clastic Sedimentary Rocks: An Introduction**

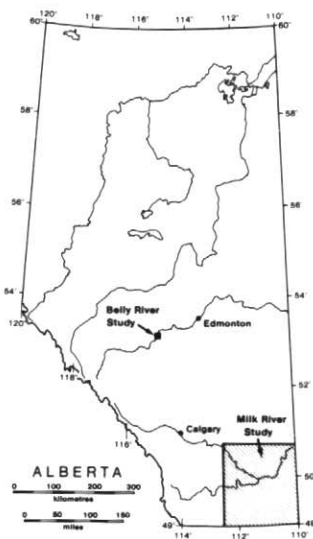
Sediments and sedimentary rocks generally have high whole-rock δ<sup>18</sup>O values. Clastic sediments range in δ<sup>18</sup>O from about +8 to +25; chemical sediments and sedimentary rocks can have still higher δ<sup>18</sup>O values (up to +40) (Garlick, 1974; Savin and Epstein, 1970a,b,c; Hoefs, 1980; Magaritz and Taylor, 1976; Longstaffe and Schwarcz, 1977; Longstaffe *et al.*, 1980, 1981, 1982; Nesbitt and Longstaffe, 1982).

Clastic sedimentary rocks are composed of (i) detrital components which normally retain oxygen-isotope compositions typical of the source rock, (ii) contributions from the weathering of source rocks (e.g., detrital clay minerals) that are usually rich in <sup>18</sup>O and (iii) minerals formed during authigenesis (e.g., carbonate, clay and silica cements and pore-filling materials) that are also <sup>18</sup>O-rich (Savin and Epstein, 1970a,b,c). Consequently, most clastic sedimentary rocks have δ<sup>18</sup>O values between those typi-

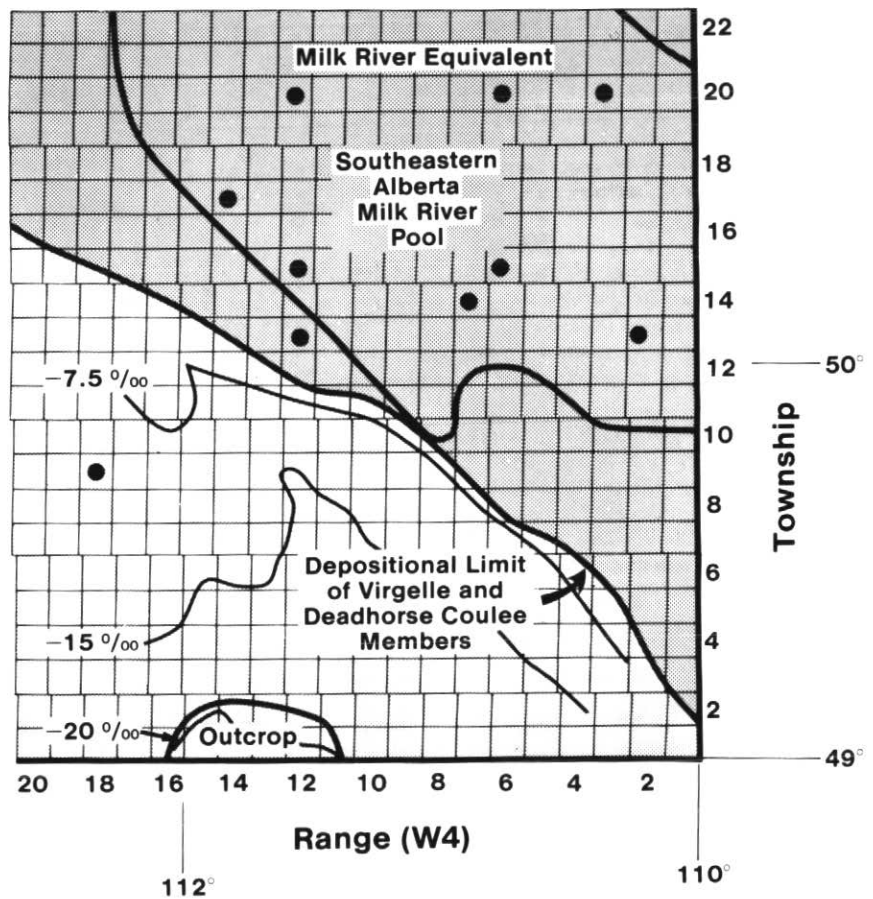
cal of igneous rocks (+5 to +10; Taylor, 1968) and clay minerals (+15 to +30; Savin and Epstein, 1970a,b; Lawrence and Taylor, 1971, 1972). For example, certain Archean clastic metasedimentary rocks have quite low δ<sup>18</sup>O values (+8 to +10) simply because they are composed largely of unweathered igneous rock fragments (Longstaffe and Schwarcz, 1977). In contrast, sediments which are composed almost entirely of minerals precipitated at low temperatures (e.g., many cherts and limestones) have very high δ<sup>18</sup>O values.

Minerals formed during weathering or authigenesis are rich in <sup>18</sup>O because they

crystallize at low temperatures in isotopic equilibrium with water. The oxygen-isotope fractionations for carbonate-water, silica-water and clay-water are large at low temperatures (Friedman and O'Neil, 1977; Savin and Epstein, 1970a,b; Lawrence and Taylor, 1971, 1972). Kaolinite, for example, formed in isotopic equilibrium with water of δ<sup>18</sup>O = 0 at 25°C will have an <sup>18</sup>O/<sup>16</sup>O ratio of about +25. Should the fluid be low-<sup>18</sup>O meteoric water, the oxygen-isotopic composition of the precipitating mineral will be lower. As the crystallization temperature of the mineral rises, the mineral-water oxygen-isotope fractionation



**Figure 2** Location map for the Milk River and Belly River study areas, Alberta, Canada.



**Figure 3** Map of the Milk River study area (after Myhr and Meijer Drees, 1976). The locations of subsurface samples are indicated by ●. Sampled outcrop locations also are shown. Contours for the δ<sup>18</sup>O of groundwaters are simplified after Schwartz and Muehlenbachs (1979). The extent of sandstones from the Milk River Forma-

tion is shown by the light stipple. The dark stipple indicates the more argillaceous rocks of the Milk River Equivalent. The heavy line within the field for the Milk River Equivalent approximately delineates the boundary of the Southeastern Alberta Milk River Gas Pool.

becomes smaller. Kaolinite precipitating in a hydrothermal environment (270°C) in equilibrium with seawater ( $\delta^{18}\text{O} = 0$ ) will have  $\delta^{18}\text{O}$  values of +5 to +6 (e.g., Longstaffe *et al.*, 1982).

#### Meteoric Water and Low-Temperature Authigenic Mineral Formation in Sandstones

Clay minerals that crystallize during low temperature weathering and soil formation very closely approach isotopic equilibrium with the meteoric waters from which they formed (Lawrence, 1970; Lawrence and Taylor, 1971, 1972; Savin and Epstein, 1970a). Stable isotope evidence is accumulating to suggest that meteoric water can play an important role in the formation of authigenic minerals during diagenesis of sandstones.

#### A. The Milk River Formation, Southeastern Alberta

The control that meteoric water can exert upon diagenesis can be illustrated by isotopic results for sandstones from the Milk River Formation, southeastern Alberta (Fig. 2; Longstaffe, 1981, in preparation). In Alberta, formation waters can be significantly depleted in  $^{18}\text{O}$  relative to seawater because of mixing between low- $^{18}\text{O}$  groundwaters and pre-existing formation fluids (Fig. 1b; Clayton *et al.*, 1966; Hitchon and Friedman, 1969). Authigenic minerals formed in equilibrium with such fluids at low temperatures should have predictably lower  $\delta^{18}\text{O}$  values than phases of detrital origin or minerals formed earlier in the diagenetic history of the sandstone from connate (i.e., more  $^{18}\text{O}$ -rich) waters.

The Milk River Formation is composed of interbedded sandstone and shale that changes upwards into massive sandstone (Myhr and Meijer Drees, 1976; Meijer Drees and Myhr, 1981). The massive sandstone (Virgelle Member) crops out along the Milk River. The Virgelle Member is overlain by interbedded shale and sandstone collectively described as the Deadhorse Coulee Member. These two units undergo a facies change as they plunge northward into silty shales, mudstones and very fine grained sandstone of the Milk River Equivalent. Gas-bearing portions of the Milk River Equivalent form the Southeastern Alberta Milk River Gas Pool (Fig. 3). At the facies boundary, the units of interest are at a depth of about 300 metres.

Schwartz and Muehlenbachs (1979) and Schwartz *et al.* (1981) studied groundwater movement in the sandstones of the Virgelle Member. The  $\delta^{18}\text{O}$  values of groundwaters increase from about -20 in the southernmost parts of the study area (Fig. 3) to about -6 near the depositional limit of the massive sandstone. The permeable portions of the Milk River Formation

are being recharged by meteoric water to the south where these rocks crop out or are near to the surface. This meteoric water is displacing pre-existing more  $^{18}\text{O}$ -rich formation water. The flushing is incomplete, with a zone of mixing remaining between the modern meteoric fluid and earlier formation waters. The extent of flushing depends upon the transmissivity of particular zones within the groundwater flow system. The highly permeable sandstones of the Virgelle Member receive a much larger influx of meteoric water than the less transmissive, more shaly rocks of the Milk River Equivalent.

To determine the extent to which these hydrogeological conditions have affected diagenesis in the Milk River Formation and Milk River Equivalent, the isotopic compositions of authigenic and detrital minerals from both units were measured. The dominant clay mineral in the Virgelle Member sandstone is kaolinite; smectite is also present (Longstaffe, 1981). These phases occur as pore-linings and pore-fillings; their morphologies are typical of authigenic clays (Wilson and Pittman, 1977; Figs. 4a,b,c). At least two carbonate minerals are present in the sandstone; dolomite occurs as framework grains (detrital) whereas calcite (authigenic) coats grains and fills pores (Fig. 4d). The dominant clay minerals in the argillaceous Milk River Equivalent are detrital illite and kaolinite; minor amounts of chlorite and smectite also are present. Dolomite is the main carbonate mineral analyzed from the Milk River Equivalent; authigenic calcite occurs only in sandy lenses where it has crystallized within the pore system.

The  $\delta^{18}\text{O}$  values of the clay minerals (<2  $\mu\text{m}$ ) range from +11 to +19 and generally increase from south to north within the study area (Fig. 5). The clays with the lowest  $\delta^{18}\text{O}$  values (+11 to +14) occur in sandstone outcrops of the Virgelle Member and are authigenic. Authigenic clays from the sandstone lenses within the Milk River Equivalent have higher  $\delta^{18}\text{O}$  values (+13 to +16). The  $\delta^{18}\text{O}$  values for detrital clays from the silty shales, mudstones and argillaceous siltstones of the Milk River Equivalent are higher still (+16 to +19). The  $\delta^{18}\text{O}$  values for <0.2  $\mu\text{m}$  versus <2  $\mu\text{m}$  size-fractions of authigenic clays from the same sample are virtually identical. This similarity confirms that the isotopic composition of the clay minerals is not simply a result of ongoing isotopic exchange with meteoric waters. If increasingly smaller size-fractions of the same clay mineral phase were progressively lower in  $^{18}\text{O}$ , isotopic exchange with the low- $^{18}\text{O}$  fluids would be indicated. The similarity between the isotopic compositions of the different size-fractions suggests that both size-fractions attained their isotopic composi-

tions in a similar fashion (e.g., both are of authigenic origin).

Dolomite from both the Milk River Formation and the Milk River Equivalent has  $\delta^{18}\text{O}$  values of +24 to +28 (SMOW) regardless of rock type (Fig. 6). Authigenic calcite from the Virgelle Member sandstone has much lower  $\delta^{18}\text{O}$  values (+15 to +19, SMOW; Fig. 6). Like those of the clays, the oxygen-isotope ratios of the calcite increase from south to north (Fig. 6). Dolomite from both the Milk River Formation and the Milk River Equivalent has  $\delta^{13}\text{C}$  values of about -1 (Fig. 7). In contrast, the carbon-isotope ratios of authigenic calcite from sandstones of both the Virgelle Member and the Milk River Equivalent are much lower (-10 to -3; Fig. 7).

The  $\delta^{18}\text{O}$  values of the clays from the shales and mudstones are typical of detrital clays from sedimentary rocks (+16 to +20; Savin and Epstein, 1970a,b; Longstaffe *et al.*, 1982) and are virtually identical to results obtained for detrital clays from other shallow Cretaceous rocks in Alberta (Fig. 8). The dolomite grains have oxygen- and carbon-isotope compositions typical of most platform carbonates (Land, 1980). The isotopic compositions of the detrital clays and carbonates have remained unchanged since deposition. Their isotopic compositions have not been modified by exchange with meteoric water.

The lower  $\delta^{18}\text{O}$  values of the authigenic clays (Fig. 8) and calcite in the sandstone aquifer are best explained by crystallization at low temperatures in the presence of low- $^{18}\text{O}$  groundwaters. Mineral and fluid oxygen-isotope values and temperature can be related by the following equations:

$$10^{21}n\alpha_{\text{kaolinite-H}_2\text{O}} = (2.5)10^6T^{-2} - 2.87, \quad (5)$$

(Land and Dutton, 1978)

$$10^{21}n\alpha_{\text{smectite-H}_2\text{O}} = (2.67)10^6T^{-2} - 4.82, \quad (6)$$

(Yeh and Savin, 1977)

$$10^{21}n\alpha_{\text{calcite-H}_2\text{O}} = (2.87)10^6T^{-2} - 2.89, \quad (7)$$

(Friedman and O'Neil, 1978)

where  $\alpha$  is the oxygen-isotope equilibrium fractionation factor between A & B and  $T$  = temperature ( $^{\circ}\text{K}$ ). For example, an isotopic temperature of  $2 \pm 5^{\circ}\text{C}$  can be calculated for the crystallization of the authigenic clays in outcrop samples of the Virgelle Member sandstone (measured  $\delta^{18}\text{O}$  of water = -19). In a similar manner, an isotopic temperature of  $0 \pm 5^{\circ}\text{C}$  can be calculated for the formation of the calcite that coexists with the clay. Both estimates agree reasonably well with the mean temperature at this location (5 to  $10^{\circ}\text{C}$ ). These calculations suggest that the authigenic phases of the Milk River sandstone have (and still are being?) precipitated from

meteoric waters like those presently in the aquifer system.

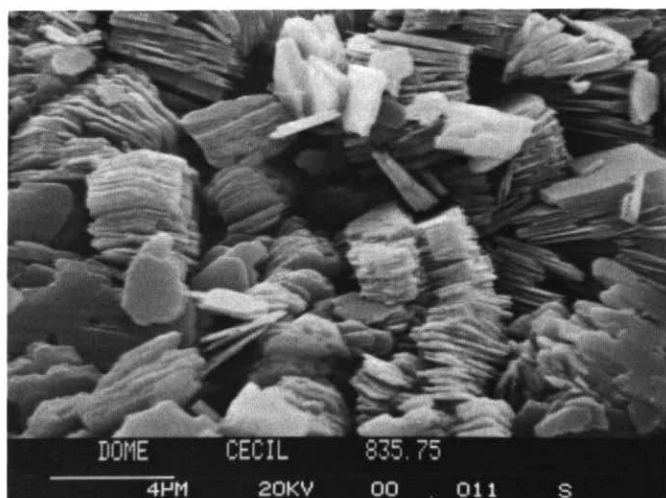
The relatively modest increase in the oxygen-isotope values of the authigenic clays and calcite from south to north with increasing depth (0 to 300 m) reflects the progressively higher  $\delta^{18}\text{O}$  values of the formation waters (Figs. 3,5,6), and higher temperatures of mineral authigenesis. The first effect dominates the system. Because the  $^{18}\text{O}/^{16}\text{O}$  ratio of the formation fluid increases, the  $\delta^{18}\text{O}$  values of the crystallizing minerals rise. The second effect, that of temperature, moderates the  $^{18}\text{O}$ -enrichment of the precipitating phase. With increasing temperature, the oxygen-isotope mineral-water fractionation decreases, causing the precipitating minerals to become less enriched in  $^{18}\text{O}$  than at lower temperatures.

The low  $\delta^{13}\text{C}$  values of the authigenic calcite throughout the sandstones of the Milk River Formation and Milk River Equiv-

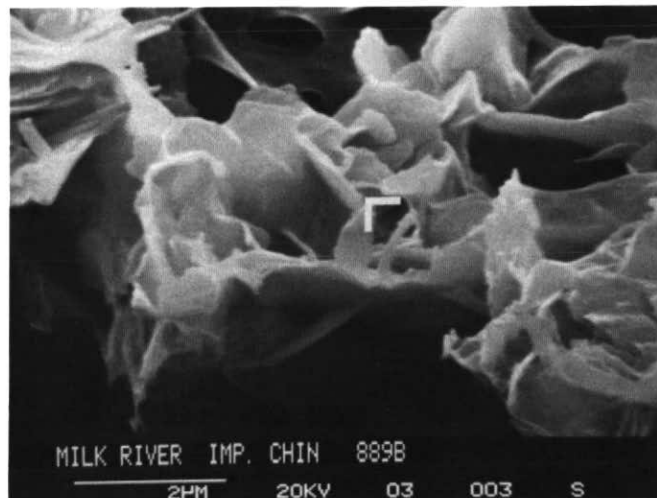
alent most likely reflect involvement of organically-derived  $^{13}\text{C}$ -depleted  $\text{CO}_2$ , probably from overlying soils and tills. The distinct difference in the carbon-isotope compositions of calcite and dolomite from the same sample rules out the possibility that their respective oxygen-isotope compositions merely represent an equilibrium fractionation of  $^{18}\text{O}$  (see Land, 1980, for a review of this controversial issue).

Other investigators have reported stable isotope data that indicate low temperature precipitation of authigenic clays and carbonates in sands and sandstones by meteoric water (Cumella, 1981; Barber and Eslinger, 1980; Hassanipak, 1980; Pitman *et al.*, 1982). The process certainly seems to be prevalent for many sandstone units in Alberta (Fig. 8). A similar origin for kaolinite and calcite from cleat-fillings in Pennsylvanian coals has been proposed by Shieh and Suter (1979). I suggest that such

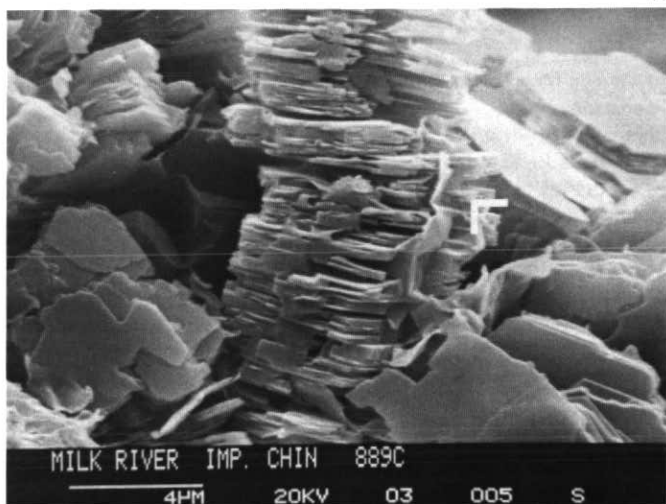
behaviour is common in clastic sedimentary basins where large-scale regional flow, dominated by meteoric water, has flushed or is flushing the pre-existing formation fluids from the sandstone. The extent to which the isotopic composition of the meteoric water is modified by mixing with pre-existing formation fluids will depend upon flow rates in the sandstone, dewatering of modified connate fluids from adjacent argillaceous units, and the extent of cross-formational leakage of fluids between successive sandstone-shale packages. Oxygen- and hydrogen-isotope measurements of authigenic minerals may provide an elegant method by which the operation of this process can be identified in ancient sandstones. The Milk River example shows that trends in the stable isotope compositions of authigenic minerals in sandstones can provide clues to directions of paleo-groundwater movement.



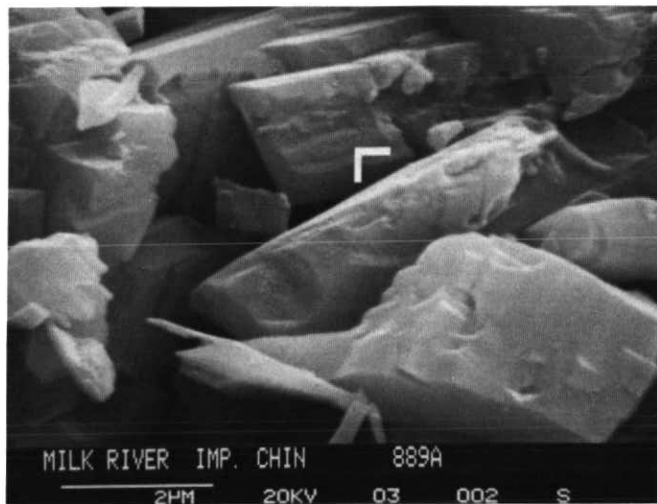
A.



C.



B.



D.

**Figure 4** SEM photographs of authigenic minerals from the Milk River sandstone:

A. booklets of kaolinite  
B. vermicular growth of kaolinite

C. smectite  
D. calcite.

### Burial Diagenesis of Sandstones: Stable Isotope Evidence for Paragenesis and Thermal History

The application of stable isotope measurements in elucidating the history of burial diagenesis for sandstones can be illustrated by three studies: Land and Dutton's report on the Pennsylvanian "Gray" sandstone, north-central Texas (1978, 1979), Milliken *et al.*'s (1981) and Land and Milliken's (1981) investigations of the Oligocene Frio sandstone, Brazoria County, Texas, and Longstaffe's observations for the Cretaceous Pembina-I pool, Belly River sandstone, Alberta (1982). In the Texan examples, diagenesis has been facilitated by formation fluids originally derived from seawater or brackish water ( $\delta^{18}\text{O} = -5$  to 0) and subsequently enriched in  $^{18}\text{O}$  by reaction with enclosing sediments. In the Albertan example, meteoric waters were important in the evolution of the formation fluids.

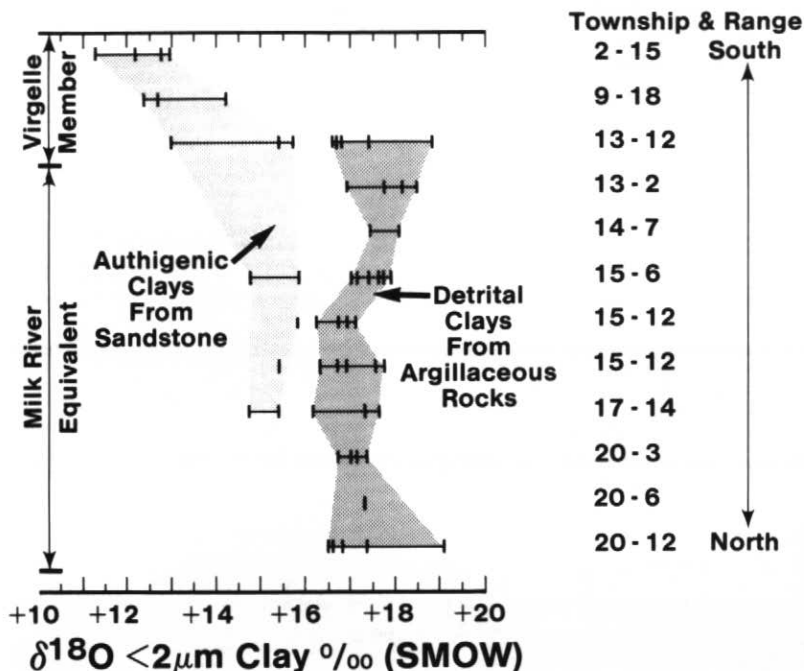
#### B. The "Gray" Sandstone

The following sequence of diagenetic events, from earliest to latest, was recorded for the "Gray" sandstone by Land and Dutton (1978) on the basis of petrographic data:

1. formation of chlorite rims on quartz grains
2. formation of quartz overgrowths on quartz grains
3. cementation by calcite
4. dissolution of feldspar, rock fragments and calcite
5. precipitation of ankerite, Fe-calcite and kaolinite in primary and secondary pore systems

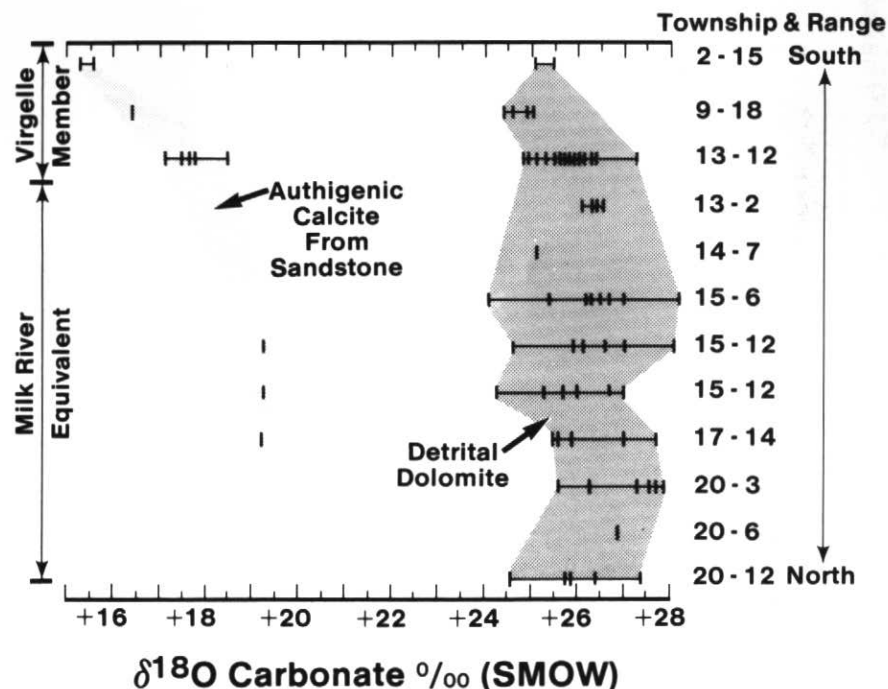
Land and Dutton calculated *isotopic temperatures* for the authigenic chlorite, quartz, kaolinite and carbonate minerals using equations available for equilibrium isotope fractionation between these phases and water. They found that the oxygen-isotope compositions of coexisting late-stage kaolinite (+18.8) and Fe-calcite (+21.5, SMOW) were compatible with crystallization at about 50°C in the presence of formation fluids with  $\delta^{18}\text{O}$  values of about -2 to -3 (Fig. 9). These theoretical values are virtually identical to present conditions in the sandstone: temperature = 43° to 50°C,  $\delta^{18}\text{O}$  of formation fluids = -2.6 to -2.2 (Fig. 9). Land and Dutton (1978) concluded that the late-stage authigenic kaolinite and Fe-calcite formed in equilibrium with modern formation fluids at existing formation temperatures.

The  $\delta^{18}\text{O}$  values of the early calcite cement are identical to those of the later Fe-calcite. The early calcite probably re-equilibrated during the latter stages of diagenesis and lost any isotopic signature characteristic of its origin.



**Figure 5**  $\delta^{18}\text{O}$  values of clays (<2µm) from the Milk River study area. Sample locations are indicated by township and range, as shown by Figure 3. Results for authigenic clays from

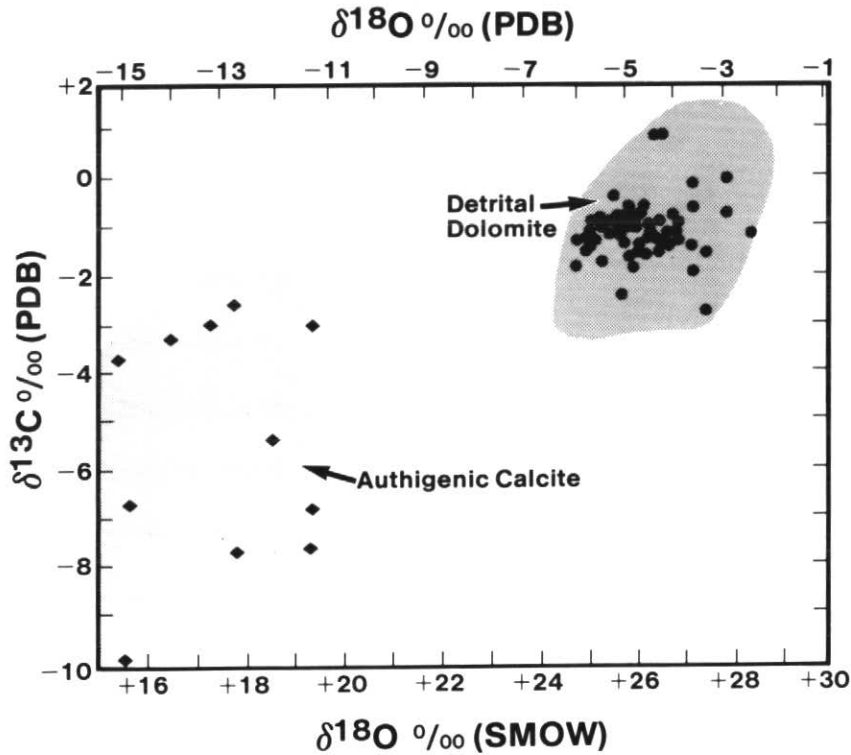
the sandstone are shown in the light stippled pattern; results for detrital clays are indicated by the dark stippled pattern.



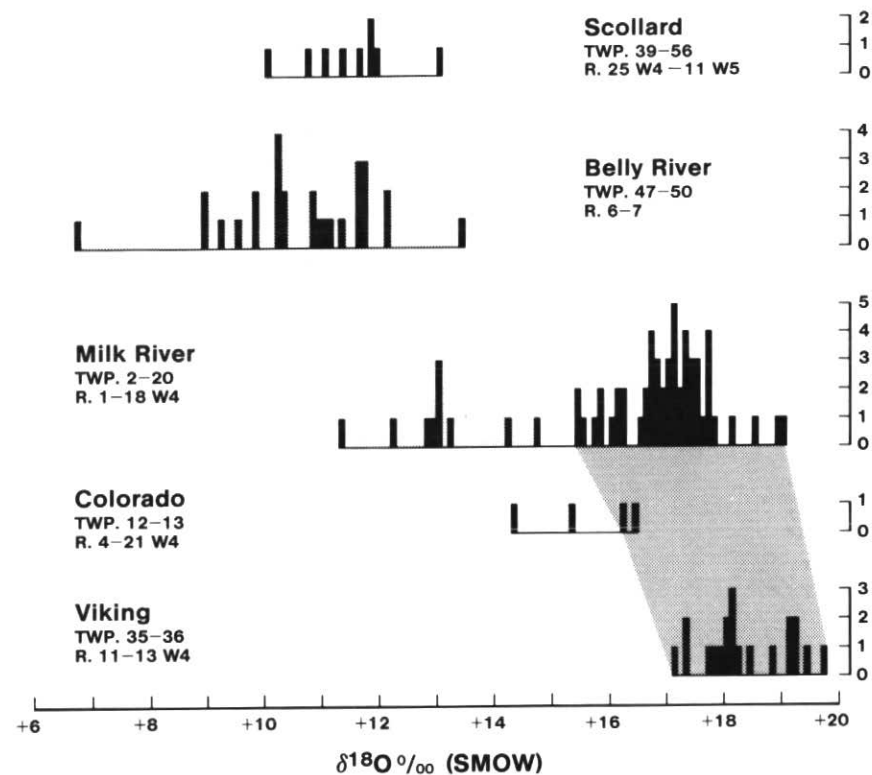
**Figure 6**  $\delta^{18}\text{O}$  values of carbonates from the Milk River study area. Sample locations are given by township and range, as shown by Figure 3. Results for authigenic calcite from the

sandstone are shown in the light stippled pattern; results for the dolomite are indicated by the dark stippled pattern.





**Figure 7**  $\delta^{13}\text{C}$  versus  $\delta^{18}\text{O}$  for calcite (light stipple) and dolomite (dark stipple) from clastic rocks in the Milk River study area.



**Figure 8** Summary of  $\delta^{18}\text{O}$  values for  $<2\ \mu\text{m}$  clay fractions from shallow Cretaceous rocks, Alberta. The clays with low  $\delta^{18}\text{O}$  values ( $< +16$ ) are from clay-poor sandstones (light stipple); clays with high  $\delta^{18}\text{O}$  values ( $> +16$ ) are from clay-rich rocks (shales, mudstones, argillaceous sandstones—dark stipple). The number of sam-

ples analyzed from each unit is indicated in histogram fashion and shown by the vertical axis of the diagram. The approximate geographical location of samples is indicated by township and range. Most clays with  $\delta^{18}\text{O}$  values  $< +16$  probably formed from formation fluids containing a sizeable fraction of low- $^{18}\text{O}$  meteoric water.

The oxygen-isotopic composition of the quartz overgrowths (+24.6) indicates authigenesis at higher temperatures and/or from less  $^{18}\text{O}$ -rich fluids than the late-stage cements (Fig. 9). Land and Dutton (1978) considered the latter hypothesis to be unlikely. Deeply buried formation waters in this locality are more likely to have become enriched in  $^{18}\text{O}$  by isotopic exchange with limestones at depth than depleted by mixing with low- $^{18}\text{O}$  meteoric waters. They concluded that the early quartz overgrowths formed under conditions approaching maximum burial of the "Gray" sandstone (probably  $65^\circ$  to  $70^\circ\text{C}$ ; Fig. 9), most likely from fluids expelled by adjacent shales.

The oxygen-isotope compositions of the early-formed chlorites are difficult to interpret because the chlorite-water oxygen-isotope fractionation is poorly known at low temperatures. However, Wenner and Taylor (1971) suggest that the fractionation is considerably smaller than for other clay minerals (see Equation 8). The  $\delta^{18}\text{O}$  values obtained for the chlorite (+14.2 to +14.4) probably indicate crystallization at sedimentary temperatures, assuming the formation fluids to have an oxygen-isotope composition near that of seawater. Such conditions could exist during early stages of burial (Land and Dutton, 1978).

In their paper, Land and Dutton (1978) demonstrated that the isotope compositions of the authigenic minerals indicate a reasonable pattern of thermal events during burial diagenesis. They have shown for this particular sandstone that the late diagenetic phases are a response to present-day conditions, that the earlier episode of quartz overgrowth formation occurred near conditions of maximum burial and that the chlorite probably formed during early stages of diagenesis at low temperatures.

**C. The Belly River Sandstone, Alberta**  
Longstaffe (1982) has reported stable isotope results for diagenetic minerals from the Pembina-I pool of the Cretaceous Belly River sandstone, Alberta (Figs. 2, 8). The authigenic minerals in the sandstone consist mostly of early pore-lining chlorite and late pore-filling kaolinite and calcite. The authigenic chlorite has  $\delta^{18}\text{O}$  values of +6 to +7; the kaolinite-rich, pore-filling clays have  $\delta^{18}\text{O}$  values of about +12 (Figs. 8, 10). The calcite that coexists with the kaolinite within the pore system has  $\delta^{18}\text{O}$  values of +12 to +14 (SMOW) and  $\delta^{13}\text{C}$  of -9 to -3 (Fig. 11). Hitchon and Friedman (1969) reported a  $\delta^{18}\text{O}$  value of -9.2 for the formation fluid.

Isotopic temperatures of  $60^\circ\text{C}$  (calcite) and  $50^\circ\text{C}$  (kaolinite) can be calculated for crystallization of the late authigenic minerals, presuming equilibration with waters similar in isotopic composition to that of the formation fluids (see Equations

5, 6). These estimates are higher than an available downhole temperature measurement (36°C; Hitchon and Friedman, 1969). In many cases, downhole temperature measurements are minimum estimates only. However, the discrepancy between the temperature data is too large to result from this effect alone. Lower isotopic temperatures would be obtained if the fluid from which the kaolinite and calcite formed was more depleted in <sup>18</sup>O than modern formation waters. However, the most likely history of fluid evolution probably involves progressive mixing of <sup>18</sup>O-poor meteoric fluids with preexisting <sup>18</sup>O-rich connate waters. The existing formation water should be the most <sup>18</sup>O-poor fluid encountered by the sandstone. That the fluid involved in formation of the late diagenetic minerals may have been more <sup>18</sup>O-rich than modern formation fluids cannot be ruled out. If so, even higher crystallization temperatures for the kaolinite and calcite are indicated. All of these data suggest that the late diagenetic phases crystallized when the Belly River sandstone was more deeply buried than at present (present depth is about 1080 metres).

The low δ<sup>13</sup>C values of the authigenic calcite indicate that <sup>13</sup>C-depleted organic-derived CO<sub>2</sub> was involved in its crystallization. Whether this <sup>13</sup>C depletion is related to hydrocarbon migration within the sandstone or to the introduction of organic CO<sub>2</sub> and HCO<sub>3</sub><sup>-1</sup>-associated with meteoric water is the subject of ongoing investigation.

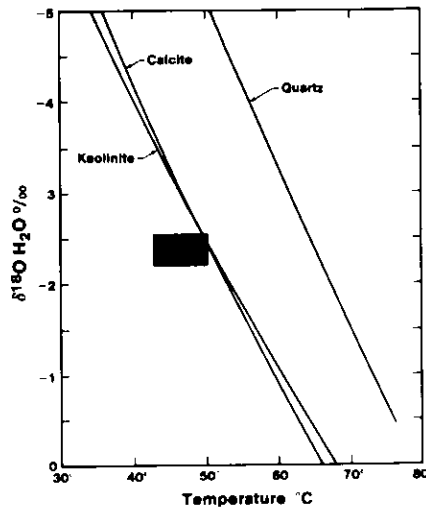


Figure 9 Oxygen-isotope values for water versus temperature for kaolinite, calcite and quartz (from Land and Dutton, 1978). The shaded area indicates present conditions within the "Gray" sandstone. Equations used for calcite and quartz are from Friedman and O'Neil (1977). The equation for kaolinite is derived from Eslinger (1971) by Land and Dutton (1978).

The early-formed chlorite is out of isotopic equilibrium with the late calcite and kaolinite and the modern formation fluids. By extrapolating the chlorite-water equation of Wenner and Taylor (1971) to low temperatures,

$$\Delta^{18}\text{O}_{\text{chlorite-H}_2\text{O}} \approx (1.56)10^6T^{-2} - 4.7 \quad (8)$$

certain limits for the formation of the chlorite can be deduced. A minimum estimate of 5°C can be calculated for chlorite crystallizing in equilibrium with present formation waters. Such temperatures are probably too low for sedimentary environments during the deposition and early diagenesis of the sandstone in Cretaceous times. In contrast, an isotopic temperature of about 100°C can be calculated for crystallization of the chlorite in equilibrium with seawater. This estimate is too high for early diagenesis. These computations suggest that the chlorite formed in equilibrium with brackish water; waters with δ<sup>18</sup>O values of -5 to -7 would yield isotopic temperatures of 20° to 40°C for chlorite precipitation during early stages of burial. Better data on the low temperature oxygen-isotope fractionation between chlorite and water are necessary before details concerning the low temperature crystallization of chlorite can be proposed.

**D. The Frio Formation, Texas**

In their oxygen- and carbon-isotope studies of the Frio sandstone, Milliken et al. (1981) and Land and Milliken (1981) have documented the importance of extensive reaction between pore-fluids and sediment during burial diagenesis. Unlike the previous examples, in which maximum burial depths probably never exceeded 1600 to 2400 metres, samples from as deep as 5400 metres were examined in this investi-

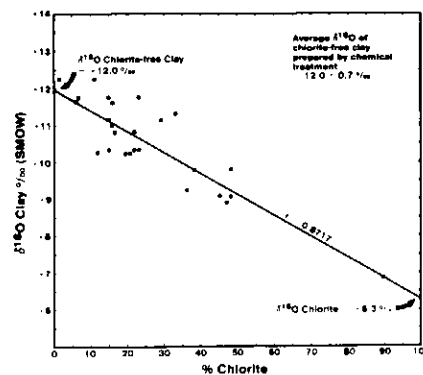


Figure 10 δ<sup>18</sup>O values for clay mixtures from the Belly River sandstone. The mixtures are composed of kaolinite and chlorite. Regression of the results to pure end-member compositions suggests a δO value of +12 for the kaolinite and +6 for the chlorite. Analysis of chlorite-free clay, prepared by chemical methods, also yields a value of +12 for the kaolinite.

gation. The formation fluids involved in the reactions are <sup>18</sup>O-rich (+3.5 to +7.5, Kharaka et al., 1977).

Authigenic carbonates are present throughout the entire range of the Frio sandstone examined. The <sup>18</sup>O/<sup>16</sup>O ratios of the carbonates trend towards lower values with depth, decreasing in <sup>18</sup>O by about 8 permil from 1500 to 5000 metres. The carbon-isotope composition of the carbonates also shows interesting variations with depth. Between 3000 and 4000 metres, the zone of hydrocarbon generation in these rocks, the δ<sup>13</sup>C values of the carbonate minerals are less than -6; higher values (> -5) are observed elsewhere in the formation. The low δ<sup>13</sup>C values probably reflect the introduction of isotopically depleted organic carbon into the carbonate system (Milliken et al., 1981).

Quartz overgrowths (δ<sup>18</sup>O = +30) are unimportant above 3600 metres. Nevertheless, petrographic data indicate overgrowth formation prior to the creation of secondary porosity. Kaolinite (δ<sup>18</sup>O = +20) is found mostly as secondary pore-fillings and replacing feldspar; it formed after quartz cementation and after the major episode of leaching. Albitization of feldspars occurs below about 4200 metres. The authigenic albite has a δ<sup>18</sup>O value of +17 (Milliken et al., 1981).

Using the isotopic data and the available isotope geothermometers (e.g., Friedman and O'Neil, 1977), Milliken et al. (1981) calculated that the quartz overgrowths formed between 65° and 80°C, kaolinite at about 100°C and albite at about 150°C. The paragenetic sequence of authigenic phases implied by the temperature calculations is in agreement with petrographic data available for these rocks (Loucks et

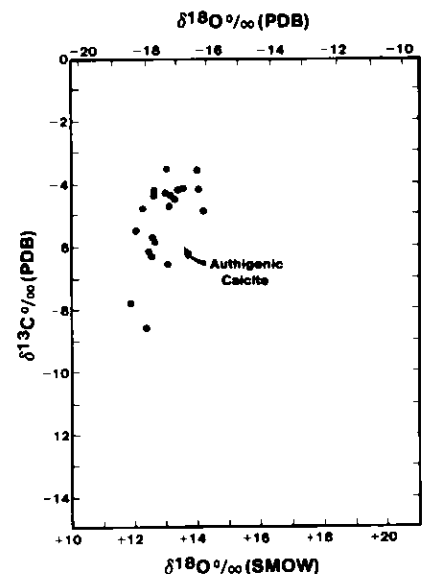


Figure 11 δ<sup>13</sup>C versus δ<sup>18</sup>O for authigenic calcite from the Belly River sandstone.

*al.*, 1979). These isotopic temperatures suggest that the authigenic phases, except for albite, crystallized before burial to present depths.

From these data, Milliken *et al.* (1981) developed a model for the Frio sandstone using the concepts of passive and active diagenesis. Crystallization of quartz and carbonates in intergranular pores, down to about 2600 metres (beginning of the smectite-illite transition) marks the passive stage of diagenesis. The active stage occurs below this depth and includes extensive reaction between detrital phases and pore-fluids plus the crystallization of kaolinite and carbonates. Thus, Milliken *et al.* (1981) and Land and Milliken (1981) have been able to use the stable isotope method not only to describe the thermal history of diagenesis in a sandstone but also to show that albization at depth exerts an important control upon the production of secondary porosity and the evolution of pore-fluid chemistry.

#### Oxygen-Isotope Geothermometry and the Burial Diagenesis of Shales

Another important problem to which oxygen-isotope geochemistry can be applied concerns the burial diagenesis of shales. The post-depositional history of mudstones and shales during shallow burial, and the isotopic evolution of associated porewaters, have been examined using oxygen- and carbon-isotope analyses of carbonate concretions and calcilutite units contained within the clastic sediments. The reader is referred to papers by Coleman and Raiswell (1981), Curtis *et al.* (1972), Hudson and Friedman (1976), Hudson (1978), Irwin *et al.* (1977), Irwin (1980) and Marshall (1982) for detailed discussions of this particular topic. I wish to focus upon the application of oxygen-isotope geothermometry in the study of deeply buried shales. Some aspects of this topic have been reviewed by others (Eslinger *et al.*, 1979; Savin, 1980); only a brief discussion is presented here.

Rather stringent conditions must be fulfilled before oxygen-isotope geothermometry can be used to determine the maximum temperature to which a shale has been heated during burial (Eslinger, 1971; Eslinger *et al.*, 1979):

1. At least two coexisting minerals must have achieved isotopic equilibrium with each other at the maximum temperature attained by the shale.
2. The nature of the oxygen-isotope fractionation between the two minerals must be known and must be sufficiently sensitive to the changes in temperature within the range of interest.
3. The minerals to be analyzed must not have exchanged oxygen-isotopes subse-

quent to attaining equilibrium at the temperature maximum.

#### E. The Precambrian Belt Supergroup

In a pioneering effort by Eslinger and Savin (1973b), oxygen-isotope temperatures were calculated for shales from the Precambrian Belt Supergroup using a quartz-illite geothermometer:

$$10^3 \ln \alpha_{\text{quartz-illite}} = (0.95)10^6 T^{-2} + 0.88 \quad (9)$$

after Eslinger and Savin (1973a).

Isotopic temperatures for the Precambrian shales ranged from 225°C to 310°C and increased with stratigraphic depth. Encouragingly, the geothermal gradient calculated from these data, 36°C/km, was

consistent with stratigraphic estimates for maximum burial of the unit.

#### F. The Texas Gulf Coast

Yeh and Savin (1977) studied the behaviour of oxygen-isotopes during burial metamorphism of Tertiary-Upper Cretaceous argillaceous sediments in the Gulf of Mexico region. Mineralogical studies of these rocks revealed a systematic decrease in the percentage of smectite layers within mixed-layer illite/smectite with increasing depth of burial (Hower *et al.*, 1976). The oxygen-isotope compositions of different size-fractions of illite/smectite and quartz, >2 μm, 1-2 μm, 0.5-1 μm, 0.1-0.5 μm and <0.1 μm were determined for samples from 1300 to 5500 metres in depth.

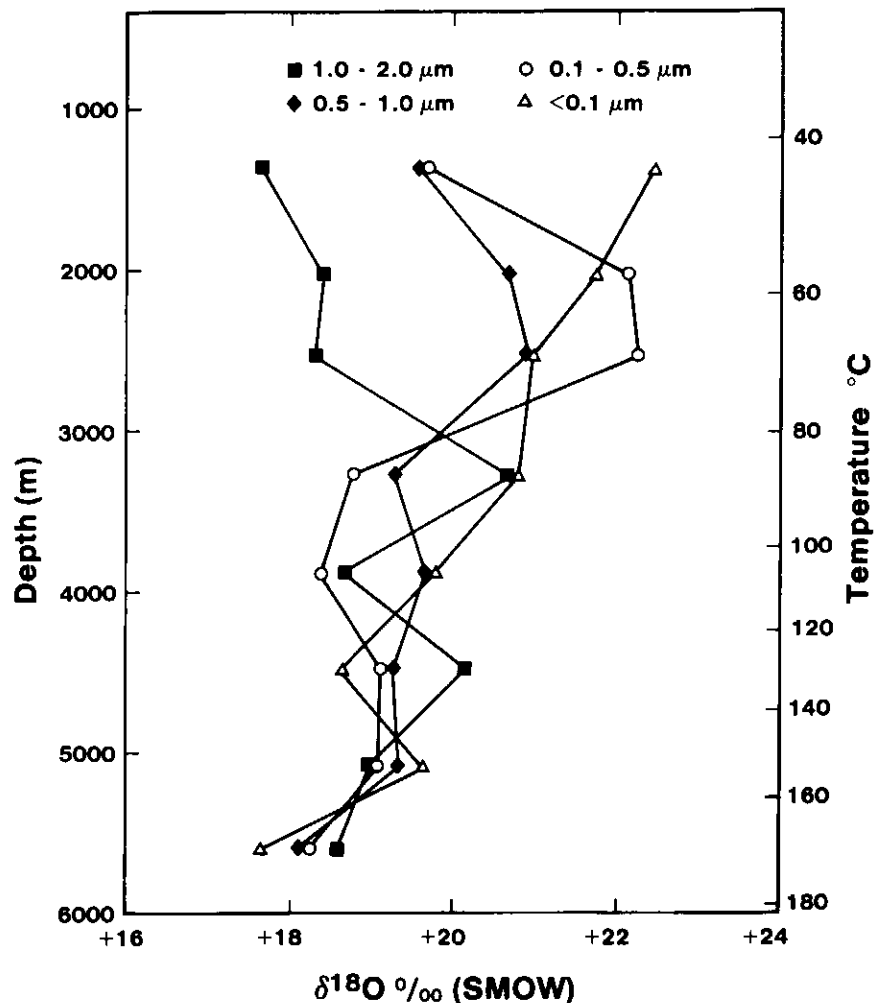


Figure 12  $\delta^{18}\text{O}$  values for different size-fractions of clay minerals versus depth for CWRU Gulf Coast Well No. 6 (from Yeh and Savin, 1977).

The study showed that the detrital clay minerals were not in isotopic equilibrium with each other when deposited. Different clay size-fractions from shallow samples varied in  $\delta^{18}\text{O}$  by up to 5 permil (Fig. 12). With increasing depth of burial, variation in  $\delta^{18}\text{O}$  between size-fractions of clays was reduced to less than 1 permil. Significant isotopic exchange between the clays and the pore fluids had occurred in concert with the dehydration and conversion of smectite layers to illite layers within the illite/smectite.

Different size-fractions of quartz also varied by up to 10 permil in their oxygen-isotope compositions (Fig. 13). In contrast to the clay minerals, no evidence for isotopic exchange between detrital quartz and pore fluids was observed, even for the hottest and deepest samples obtained (170°C). However, authigenic silica released by the conversion of smectite to illite during burial diagenesis appears to have coated detrital grains. This material, which dominates the smallest size-fractions, is probably in isotopic equilibrium with the pore fluids.

Using the isotopic data available for the finest size-fractions of coexisting clay and quartz, Yeh and Savin calculated isotopic temperatures and compared them with actual down-hole temperatures. A modified quartz-illite/smectite oxygen-isotope geothermometer was employed for these calculations:

$$10^3 \ln \alpha_{\text{quartz-illite/smectite}} = [0.95 - 0.24 (\text{expandability})] 10^3 T^{-2} + 1.42, \quad (10)$$

where expandability = fraction of expandable layers in the illite/smectite after Yeh (1974). For samples from one well studied in detail, good agreement between calculated and measured temperatures was obtained above about 90°C. Temperatures calculated for samples from other wells examined in less detail did not agree with measured results, but the discrepancy between measured and calculated values decreased with increasing temperature. Yeh and Savin (1977) suggested that this less than satisfactory outcome resulted from isotopic analysis of partly detrital rather than purely diagenetic silica.

Attempts by Yeh and Savin to calculate temperatures using a quartz-calcite oxygen-isotope geothermometer were completely unsuccessful. This failure probably derives from the continued isotopic exchange between calcite and pore waters during geological events subsequent to maximum burial. Such behaviour has been noted earlier in this discussion.

**G. The Great Valley Sequence**

The papers by Eslinger and Savin (1973b) and Yeh and Savin (1977) demonstrated the potential of the oxygen-isotope geothermometry in the study of burial diagenesis of shales. A soon-to-be presented oxygen-, hydrogen- and carbon-isotope study of both mudstones and sandstones from the

Great Valley Sequence, northern California, provides an elegant example of how both thermal and fluid evolution during burial diagenesis can be modelled from stable isotope data.

Suhecki and Land (1981) found that changes in the  $\delta^{18}\text{O}$  values of authigenic minerals resulted from the smectite to illite conversion. The oxygen-isotope values for illite/smectite decreased with depth from +22 to +16 as the percentage of illite layers in the illite/smectite increased. This variation in the  $^{18}\text{O}/^{16}\text{O}$  ratio of illite/smectite was modelled mathematically using the available oxygen-isotope fractionation data. Changes in the oxygen-isotope compositions of hypothetical pore-fluids that could coexist in equilibrium with the illite/smectite during burial were also calculated. Variables such as initial temperature, temperature gradients and relative amounts of smectite converted to illite are included in the model. Factors that allow for open or closed system reequilibration between clay minerals and putative pore-fluids are also incorporated into the computation. The model permits calculation of oxygen-isotope compositions for other mineral phases that might coexist in equilibrium with a hypothetical pore-fluid and illite/smectite at any given temperature. Using this model, Suhecki and Land estimated the geothermal gradient and maximum depths and temperatures of burial achieved in the Great Valley Basin rocks.

Agreement between model (i.e., calculated) and measured  $\delta^{18}\text{O}$  values for authigenic calcite, quartz and chlorite present in the mudstones and sandstones suggested that these phases formed in near isotopic equilibrium with formation fluids that became progressively enriched in  $^{18}\text{O}$  with depth. Suhecki and Land also noted that D/H ratios of the illite/smectite sharply increased by about 20 permil at and below about 3 km depth (approx. 100°C). Similar behaviour has been reported by Yeh (1980) for the Gulf Coast clays. This change towards D-rich clays at depth is accompanied by an increase in the percentage of illite layers in the illite/smectite (Fig. 14). This correlation is probably related to the late-stage dehydration of shales during burial at about 80° to 100°C (Suhecki and Land, personal communication; Yeh, 1980). For the Great Valley Sequence, Suhecki and Land concluded that late-stage dehydration of the smectite had buffered the oxygen- and hydrogen-isotopic composition of formation waters from that like seawater to values of +8 and -25 for  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , respectively.

These results graphically illustrate the control that illite/smectite reactions can exert upon the isotopic evolution of formation waters during burial diagenesis. As mathematical models and appropriate data sets

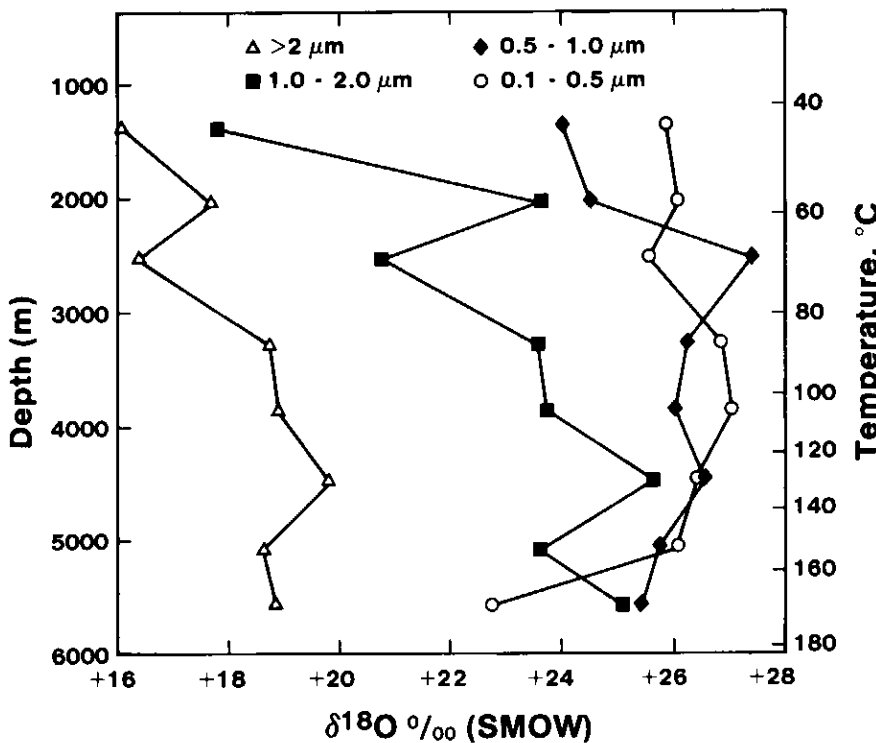


Figure 13  $\delta^{18}\text{O}$  values for different size-fractions of quartz versus depth for CWRU Gulf Coast Well No. 6 (from Yeh and Savin, 1977).

migration can be identified. The stable isotope signatures of authigenic minerals can also record paleohydrologic events, such as the flushing of preexisting formation fluids by meteoric water. The changes in style of diagenesis that may accompany such a shift in formation fluid chemistry may be of ultimate importance in the creation or destruction of diagenetic hydrocarbon traps. Oxygen-isotope geothermometry of shales, when perfected, should be useful when evaluating the thermal history of potential petroleum source rocks.

Perhaps the most exciting potential contribution to clastic diagenesis from stable isotope studies will be a better understanding of the geochemical reactions and hydrodynamic pathways between sandstones and shales during burial. As Land and his colleagues have begun to demon-

strate, stable isotope measurements of shales and sandstones within a sedimentary basin can help reveal the relative importance of feldspar dissolution, albitization, illite/smectite transformations and the dewatering of shales to the supply and transport of components for authigenic mineral formation in sandstones. Important conclusions concerning the directions and distances of mass transfer by fluids within and/or across formation boundaries may be realized.

#### Closing Remarks

Stable isotope studies of diagenesis in clastic rocks are of growing interest to both academically and industrially oriented researchers. The potential knowledge to be gained about the thermal history and fluid evolution in sedimentary basins warrants this attention. The method can provide unique information about the paragenesis of sandstones, including temperature estimates for the precipitation of authigenic minerals. In some cases, the relationship between specific episodes of carbonate authigenesis and hydrocarbon

such as those of Suchecki and Land become available, increasingly more sophisticated hypotheses for the origin and evolution of formation fluids in sedimentary basins will become feasible.

Successful application of the method will depend upon how well the stable isotope data are integrated with other types of information. Detailed petrographic studies and scanning electron microscopy are obvious prerequisites to isotopic measurements. Complete mineralogical characterization of the solids to be analyzed also is mandatory. The most powerful stable isotope models for thermal evolution will be those that also integrate temperature estimates obtained by other means (e.g., fluid inclusions, organic maturation indices, mineral crystallinity). Much work remains before many of the oxygen- and hydrogen-isotope mineral-water fractionations within the sedimentary and diagenetic temperature range will be defined adequately. A particularly acute need exists for such information on chlorite (both Fe and Mg-rich varieties). The effects upon isotopic composition of elemental variation and substitution within specific clay or carbonate mineral species also requires more investigation. Details concerning the extent of isotopic equilibrium achieved between fluids and precipitating minerals in pore systems are desperately needed.

Whenever possible, the stable isotope data for authigenic minerals should be considered within the available thermodynamic and geochemical framework for the phases of interest. Modellers of stable isotope results will benefit greatly from a close association with hydrogeologists. Such collaboration will help ensure the hydrodynamic feasibility of physical paths and mechanisms proposed for fluid production, migration, modification and mixing on the strength of geochemical data alone.

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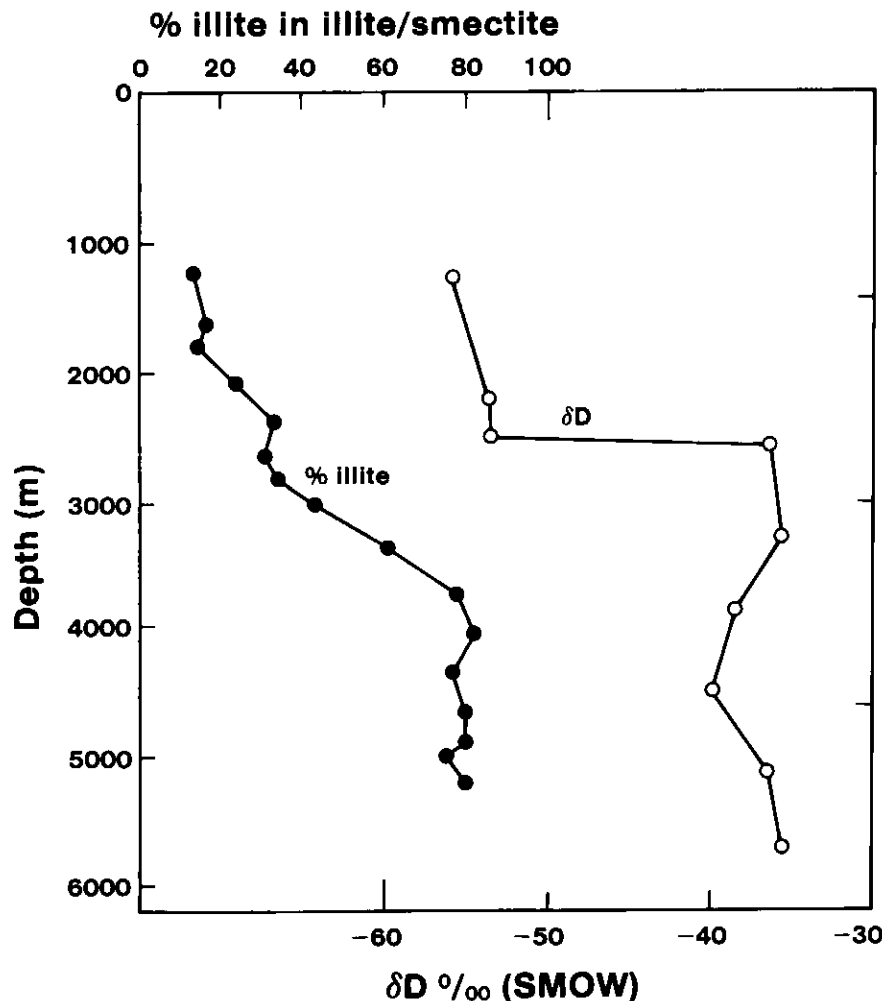


Figure 14 Percent illite in illite/smectite and  $\delta D$  of  $<0.1 \mu\text{m}$  clay size-fractions versus depth

for samples from Gulf Coast Well No. 6 (from Yeh, 1980).

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