

ISOTOPIC COMPOSITIONS OF CLAY
MINERALS AS INDICATORS OF THE TIMING AND
CONDITIONS OF SEDIMENTATION AND BURIAL DIAGENESIS

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The abundances of radioactive and radiogenic isotopes and of light stable isotopes can provide useful information about the origins of minerals of siliciclastic rocks and the nature of the diagenetic processes that have affected them. The K-Ar and Rb-Sr isotopic systems of sedimentary rocks and separated minerals have been used in many studies to determine the time of their deposition, although this approach remains controversial. While there are ambiguities in their application in stratigraphic studies, the K-Ar and the Rb-Sr systems have proven especially useful for determi-

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ning the time and in some cases, the duration of diagenetic processes. In addition, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are useful for tracing the origin of Sr incorporated in diagenetic minerals. The isotopes of O, H and C can provide information about sedimentary provenance, origins of diagenetic fluids, the degree of openness of water-rock systems to the movement of fluids, and the temperatures at which diagenetic reactions have occurred.

Knowledge of the environments and conditions under which the isotopic systems of minerals become set or reset is critical to their application to sedimentary rocks. If an isotopic composition of a detrital mineral is to be used to determine its provenance, it is necessary that the mineral retains its original isotopic signature during transportation and deposition as well as during the post-depositional history of the sediments in which the mineral occurs. If an isotopic composition is used to tell us about the timing or conditions of sedimentation, it is necessary to analyze either detrital phases that have entirely equilibrated isotopically with the depositional environment or authigenic phases that have formed in equilibrium with that environment. In either case, the phases must subsequently retain the isotopic signatures acquired in the deposition environment if the analytical data are to reflect conditions or timing of sedimentation. Finally, if the isotopic compositions of minerals in sediments are to provide information about the diagenetic history of a rock, it is necessary that the phases analyzed equilibrated or re-equilibrated with the diagenetic environment.

This review summarizes the results of many isotopic investigations of siliciclastic rocks, and especially their clay constituents, the study of which has dominated research on diagenesis of shales and sandstones during the last two decades. Special problems arise in the isotopic studies of siliciclastic rocks, which typically are mixtures of detrital and secondary or diagenetic particles, so that the same mineral is often represented in both the detrital and the secondary components of the rock. Furthermore, in many sedimentary rocks the diagenetic and detrital constituents are intimately intermixed or closely associated with one another. Quartz and feldspar overgrowths on detrital quartz and feldspar

cores, clay cements in clay-rich sandstones, and calcite cement in rocks containing detrital calcite are but a few examples of this. Further complications may arise when a diagenetic mineral formed during more than one episode; multiple generations of quartz, chlorite and carbonate minerals, for instance, are not uncommon. Consequently, if ambiguous or misleading interpretations of results are to be avoided in a geochemical or isotopic investigation of minerals in a sedimentary rock, it is necessary to precede the chemical or isotopic analyses by a detailed petrographic and mineralogic study. It is then necessary to separate the mineral constituents and to characterize thoroughly the separates to assess the relative proportions of diagenetic and detrital components.

In the present review, we will use the term epigenesis to describe any post-depositional formation of new minerals close to the sediment-water interface. Diagenesis is meant to include all of the post-depositional physical and chemical changes that occur in a mass of sediments during burial. These changes include dissolution or alteration of primary minerals, and formation of new minerals.

ISOTOPIC BEHAVIOR OF CLAY MINERALS DURING WEATHERING, TRANSPORTATION AND SEDIMENTATION

Isotopic analyses of detrital components in sedimentary rocks are generally done to obtain information about provenance. Epigenetic and diagenetic components in sedimentary rocks are thought to be analyzed for the purpose of determining either the time of deposition or of further specific diagenetic events, and the physical and chemical conditions that could prevail during the formation of the components analyzed.

Isotope Ratios of Terrigenous Clay Minerals: Evidence for Resistance to Alteration in the Marine Environment

Because clay minerals are extremely fine-grained, it is espe-

cially important to determine the extent to which, once formed, they remain as closed isotopic systems. In early Ar, Sr and O isotopic studies, it became apparent that these isotopic systems of clay minerals are usually extremely resistant to alteration during transportation on the continents as well as in the depositional environment, even when particle sizes are well below $1\mu\text{m}$. Isotopic compositions may become markedly altered, however, when clay minerals have undergone mineralogical modification.

The K-Ar system

K-Ar ages of illite are resistant to alteration during weathering and riverine transport. Hurley et al. (1961) examined the K-Ar ages of illite separated from a soil developed on illite-rich Devonian shale, and in spite of the fact that the soil clay had a lower K content than the illite in the underlying shale, both yielded nearly the same K-Ar ages. In the same study, Hurley et al. reported that the clay-sized fractions of recent sediments from the Mississippi River Delta had K-Ar ages consistent with their presumed detrital origin as mixtures of illite derived from weathering of Paleozoic shales exposed in the North American mid-continent and mixed-layer illite/smectite derived from bentonites, especially within the Missouri River drainage. In a later study, Hurley et al. (1963) measured K-Ar ages of 200 to 400 Ma for illitic clays from a number of Cenozoic pelagic sediment cores from the Atlantic Ocean. They concluded that the sediments consisted primarily of detrital clay derived from the weathering of Paleozoic shales on the continent. Exposure of the clay to sea water for long periods of time seems not to have produced gross alteration of its K-Ar systematics. However, because the K-Ar ages of the detrital constituents prior to deposition in the ocean basin were not known, the data could not be used to rule out modest effects of exposure to sea water.

The Rb-Sr system

During weathering of a variety of parent rocks, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the weathered material closely resembles that of the parent material (Dasch, 1969; Clauer, 1976). Brass (1975) noted significant differences in the Rb/Sr and in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios not only among different clay size fractions in a soil profile, but

also among different soil profiles developed on similar parent rocks. He proposed that these differences were due to differential loss of common and radiogenic Sr from the soil profiles during the weathering process. Clauer (1979) reported that the same type of clay minerals formed within weathering profiles developed on different parent-rock types, might have widely varying $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

The varied $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of continental detritus are reflected in modern ocean sediments. As he found no evidence for exchange of Sr isotopes between sea water and detrital clay minerals in ocean sediments, Dasch (1969) related the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of a suite of Recent, widely distributed, detrital Atlantic Ocean sediments to their presumed continental sources. In a complementary study of Recent sediments from the Argentine Basin, Biscaye and Dasch (1971) also used both Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as indicators of provenance. Thus, Sr isotopes can, in principle, be useful for distinguishing authigenic from detrital components in ocean sediments. However, this is difficult in predominantly terrigenous sediments containing small proportions of authigenic components.

The oxygen and hydrogen isotopes

Savin and Epstein (1970a) and Lawrence and Taylor (1971, 1972) showed that the aluminosilicate framework of pedogenic clay minerals forms in O and H isotopic equilibrium with the environmental water. Furthermore, pedogenic minerals seem to retain their original isotopic signatures through the processes of erosion, transportation and deposition. In contrast to the framework, O and H of the interlayer and adsorbed water of clay minerals are extremely labile.

Savin and Epstein (1970b) reported that no large-scale O isotope exchange occurred between the aluminosilicate framework of terrigenous clay minerals and seawater, and found inconclusive evidence for large-scale H isotope exchange. Yeh and Savin (1976) estimated that approximately 5 to 9% of the O of three ocean sediment samples composed primarily of detrital illite and smectite had apparently exchanged with seawater over periods from 14,000 yr to 2.7 Ma. However, they noted the possibility that what they termed exchange could, in fact, have been the growth of new diage-

netic clay upon detrital grains. The amount of apparent exchange they observed ranged from 13 to 18% in the 0.1 to 0.5 μ m fractions of their samples and 16 to 43% in the finer than 0.1 μ m fractions. Yeh and Epstein (1978) estimated that between 8 and 28% of the hydroxyl H in one of the same (smectite-rich) sediments apparently exchanged in 2.7 Ma. Eslinger and Yeh (1981) found no evidence for any O or H isotopic exchange in Pleistocene sediments rich in illite, chlorite and vermiculite and some mixed-layer clays from the Aleutian Trench.

In apparent conflict with the results discussed above, James and Baker (1976) reported that significant amounts of O isotopic exchange occurred between poorly crystalline illite and water in the laboratory at 22°C in periods of a few months to a few years. O'Neil and Karaka (1976) also recorded very small amounts of exchange between illite and water at 100°C after two years, and observed that smectite exchanged more readily, probably because of its smaller particle size and the easier access of the water to the aluminosilicate structure by way of the expandable layers. More recent work has suggested that at temperatures which are not greatly above those of the earth's surface, H isotopic exchange may occur between clay minerals and water. Bird and Chivas (1988) presented convincing evidence that Australian Permian kaolinite had undergone post-formational H (but not O) isotopic exchange at temperatures below 80°C. Souchez et al. (1990) have also presented intriguing evidence suggesting that illite may exchange both O and H isotopes with water in basal ice of the Greenland Ice Sheet, presumably as the result of subglacial abrasion. Additional testing of this idea is needed.

The $\delta^{18}\text{O}$ and δD values of clays formed on the continents in weathering or diagenetic environments are generally different from those of authigenic marine clays. Therefore, the $^{18}\text{O}/^{16}\text{O}$ and D/H ratios of clays in sediments can be used both to distinguish between detrital and authigenic marine components and to trace the provenance of the detrital components. Savin and Epstein (1970b) used this approach to infer that the illite, smectite and chlorite in a globally distributed suite of ocean sediments they analyzed were primarily of detrital origin, being derived from the

continents. Salomons et al. (1975) found a significant variation from river to river (15.8 to 21.7 per mil) in the $\delta^{18}\text{O}$ values of the $<2\mu\text{m}$ sediment fractions of major rivers flowing into the Atlantic from western Europe. They were able to use the different $\delta^{18}\text{O}$ values of these sediment sources to trace the origin and movement of fine-grained sediments along the western European coast. Lawrence (1979) measured $\delta^{18}\text{O}$ values of a large collection of Recent sediments sampled west of the Mid Atlantic Ridge in the South Atlantic. His results confirmed those of the Sr isotope study of Biscaye and Dasch (1971) about the different sources of sediment deposited in the Brazil Basin. Tsirambides (1986) used $\delta^{18}\text{O}$ values of separated size fractions of a suite of sediments from the western Indian Ocean to distinguish detrital from authigenic constituents.

Sediments are often complex mixtures derived from multiple sources. The isotopic approach to determining sedimentary provenance will be most definitive when multiple isotopic (O, H, Sr) and mineralogic signatures are used.

Isotope Ratios of Clays in Ocean Sediments: Evidence for Isotopic Equilibration and Neoformation in the Marine Environment

While detrital clays in ocean sediments have isotopic signatures which reflect, at least predominantly, their formation on the continents, there is also much evidence for both neoformation of clays and for partial resetting of the isotopic systems of detrital clay components in the marine environment. Quantitative estimation of the overall extent of these processes is especially important to the question of the feasibility of isotopic determination of the time of sedimentation.

Glaucinite

Glaucinite (often referred to as glauconite pellets) is a heterogeneous mixture of mixed-layer illite/smectite and other mineral constituents (Burst, 1958a). Glaucinite is an Fe- and K-rich highly illitic mixed-layer illite/smectite, which is commonly the predominant constituent of glauconitic pellets. Glaucinite often forms pene-

contemporaneously with the deposition of associated sediments. The glauconite phase contains both K and Rb, and consequently was analyzed in some of the earliest attempts to determine sedimentation times by isotopic methods (Cormier, 1956; Wasserburg et al., 1956). It quickly became apparent, however, that interpretation of glauconite ages could be problematic. The isotopic ages of glauconites, especially those from Paleozoic and older rocks, are commonly 10 to 20% lower than the stratigraphic ages of the sediments in which they occur (Amirkhanov et al., 1958; Lipson, 1958; Goldich et al., 1959; Hurley et al., 1960). Comparisons between stratigraphic and measured isotopic ages of glauconitic materials have been discussed in several circumstances (e.g. Keppens et al., 1978a, b) and a sketch is given in figure 1. Harris and Fullagar (1989) summarized a number of possible causes for the low isotopic ages. Thompson and Hower (1973) studied the dissolution kinetics of glauconite and suggested that Ar was most readily lost from "open" K sites in the expandable interlayers of mixed-layer clays.

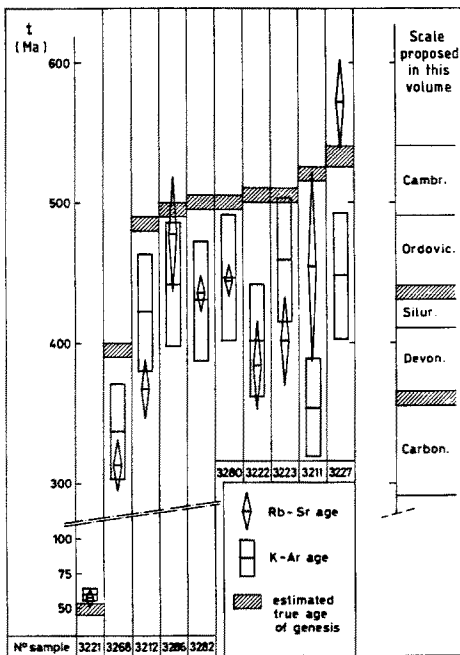


Figure 1: Comparison between stratigraphic and measured Rb-Sr and K-Ar isotopic ages for glauconites (Keppens and Pasteels, 1982)

Older glaucony pellets commonly contain fewer non-clay constituents than younger pellets, and the illite content of the mixed-layer illite/smectite is commonly higher in older pellets. These observations suggest that the pellets become diagenetically altered, with the gradual elimination of detrital components, after their initial formation (Odin and Matter, 1981). From a study of the mineralogy and K-Ar isotope systematics of glauconies in Recent sediments from the Atlantic Ocean, near the mouth of the Congo River, Odin and Matter (1981) noted that the detrital components of the pellets seem to be progressively removed, probably by dissolution, until the K_2O content reaches about 6 or 6.5%. They interpreted this process of glauconitization as de novo crystallization of authigenic smectite which then evolves progressively to form the glauconite (i.e., K-rich illitic) end member. A more detailed understanding of the glauconitization process comes from recent Sr, Nd and O isotope studies of the same west African off-shore glauconitic material and detrital clay from the associated mud previously studied (Keppens and O'Neil, 1984; Clauer et al., 1992a; Stille et al., 1992). The results of these studies indicate that the detrital clay from mud, which is initially present in the glauconitic pellets, gradually undergoes alteration until the K_2O content of the pellets reaches about 4.5%. On the basis of Sr and Nd isotopic data, Clauer et al. were able to determine that this early stage of glauconitization occurs by a process of dissolution and reprecipitation of the detrital clay material present in the pellets, in an environment in which the chemical and isotopic compositions were determined by the clay precursor, with no significant influence of seawater chemistry. In a subsequent step, the K_2O content continues to increase to as much as 7%, but in an environment which is influenced by sea water. This two-stage model of glauconitization is consistent with the observation that glauconitic pellets with K_2O contents less than 4.5% often yield isotopic ages higher than the stratigraphic ages. These high ages do not result from occurrence in the pellets of detritus that is not involved in the glauconitization process, but they do imply a genetic link to a detrital precursor clay that is progressively dissolved and modified into a Fe-smectite in a chemical system closed to sea water. This produces biases in the initial $^{87}Sr/^{86}Sr$ and $^{40}Ar/^{36}Ar$ ratios of the glauconitic minerals.

Smectites and mixed-layers illite/smectite

While $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of bulk clays in ocean sediments may be used to distinguish detrital from authigenic clays, this method may not be sufficiently sensitive to detect minute small proportions of authigenic components in predominantly terrigenous sediments. However, in comparing the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the predominantly detrital Atlantic Ocean sediments analyzed by Dasch (1969) with the clay mineralogy of the samples, Clauer (1976) observed that the samples with high smectite contents yielded $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that were much lower than those of radiogenic Sr derived from the continents (Fig. 2). Some were as low as 0.704 (i.e., lower than that of sea water) indicating that the analyzed smectites could have formed by alteration of volcanic parent materials, either on the continents or in the ocean. The latter possibility is consistent with the conclusion of Clauer et al. (1982a, 1984), discussed below, that leaching experiments can be useful for detecting small amounts of authigenic minerals in predominantly terrigenous marine sediments.

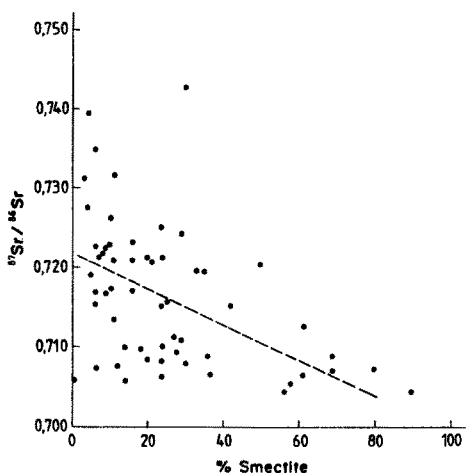


Figure 2: Variations of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with smectite contents of recent ocean sediments (Clauer, 1976)

Clauer et al. (1982a) studied the Rb-Sr system in a suite of deep-sea red clays cored in the southeastern Pacific Ocean where there is little or no detrital input. The clay mineral suite con-

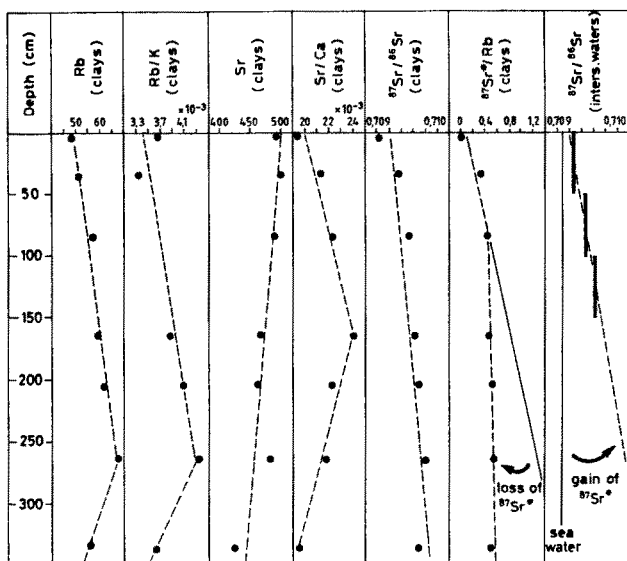


Figure 3: Variations of $^{87}\text{Sr}/^{86}\text{Sr}$, Rb/K and Sr/Ca ratios, and Rb and Sr contents of red clays from deep ocean in southeastern part of the Pacific Ocean (Clauer et al., 1982)

consists predominantly of nontronite (Fe-rich smectite) that very probably formed in the marine environment. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the nontronites are slightly, but significantly, lower than that of contemporaneous sea water. After removal of the marine Sr adsorbed on the nontronite particles by gentle leaching with 1N HCl, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the residual Sr in the clay lattices increases slightly with depth, from 0.7086 near the sediment-water interface to about 0.7115 at a depth of 265 cm below the interface (Fig. 3). As the nontronites collected at the water-sediment interface contain Sr with an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio below that of sea water, Clauer et al. concluded that these clays originated by hydrothermal alteration of basalt, either in association with intraplate volcanic activity or along mid-ocean ridges, and that they were subsequently transported by bottom currents to the abyssal plains where they were deposited. The increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the nontronite vs. depth was interpreted to reflect the decay of ^{87}Rb into ^{87}Sr with time. Hoffert et al. (1978) and Clauer et al. (1984) drew similar conclusions in complementary studies. Buatier (1989) recently showed that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of nontronites from the Galapagos Ridge are about 0.70814, while those of similar clays collected off

the ridge in nearby hydrothermal mounds are slightly higher (0.70990), suggesting that the clay minerals of these mounds are primarily authigenic but that they contain also small amounts of detrital phases that were altered and probably partly or completely rehomogenized by hydrothermal fluids similar to those collected within the rift valley by diving devices.

Alteration of detrital clay in the marine environment may be apparent from careful petrographic studies as well as from isotopic data. Clauer et al. (1990) used XRD, transmission electron microscopy (TEM), chemical analyses including rare earth element analysis (REE), microchemical determinations with a scanning transmission electron microscope (STEM) and isotopic (Sr, O, H) analyses to investigate detrital smectites from Albian-Aptian and Tertiary black-shales collected in the Atlantic Ocean. They concluded that the detritus initially consisted of detrital smectite with flaky morphology and that most of the flakes had become altered into lath-like smectite particles with similar chemical compositions. Smectites of both morphologies have very similar major element compositions, flat REE patterns without Ce anomalies, and only small differences in their initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{18}\text{O}$ and δD values. This chemical data led Clauer et al. to conclude that recrystallization had taken place in a restricted, almost closed environment, the chemistry of which was dominated by detrital clay. The time at which recrystallization occurred could not be determined directly from the Rb-Sr isotopic data, as all size fractions separated from each sample were mixtures of flaky detrital particles and lath-like authigenic particles. However, in correlating the apparent Rb-Sr ages of the different size fractions with the abundance of laths present, and by extrapolating to the pure lath-like authigenic end member, the time of formation (104-113 Ma for the Albian-Aptian and 58 Ma for the Tertiary samples) of the laths could be determined: for all samples studied, the ages calculated in this way agreed well with the stratigraphic ages of the sedimentary sequences, suggesting that the lath-like particles formed shortly after deposition.

ISOTOPIC DETERMINATION OF THE TIME OF SEDIMENTATION

Studies of the Sr isotope systematics of clays in ocean sediments indicate, as shown earlier, that equilibration of the isotopic systems can occur, to some degree, between predominantly detrital clay material and the marine environment. If the equilibrated Rb-Sr system or reset of the K-Ar system can be analyzed directly or indirectly, it ought to be possible to estimate more or less accurately the time of deposition of any sedimentary sequence containing such clay minerals.

Early Geochronologic Studies of Sediments

Bailey et al. (1962) examined the discrepancies between the stratigraphic ages of clay-rich sediments and the K-Ar ages of purified concentrates of $2M_1$ and $1M_d$ illite from underclays and shales of Pennsylvanian age. The K-Ar ages of the $2M_1$ polytypes were as much as 75 Ma greater than the depositional ages of the rocks, while the ages of the $1M_d$ polytypes were about half the stratigraphic ages of the rocks. The $2M$ polytypes of illite are known to form at high temperatures and, in shales that have not been markedly heated, they must be detrital. It is therefore not surprising that they yield K/Ar ages greater than stratigraphic ages. On the other hand, the $1M$ polytypes are of low temperature origin and could have formed during or after deposition. Bailey et al. suggested that after deposition the $1M_d$ polytype either lost ^{40}Ar by diffusion as a result of its very small particle size, or it underwent continued reorganization during which it fixed K and was converted to the $2M_1$ polytype. Neither of these suggestions is convincing in light of the results of subsequent studies. Indeed, Ar diffuses from clays only extremely slowly, as shown both by the study of natural samples in a contact metamorphic zone (Lee and Aronson, 1986) and by laboratory experiments (Odin et al., 1977). Clay minerals may often grow in the diagenetic environment long after deposition, at burial temperatures of 150°C or higher, and this by itself can result in K-Ar ages younger than stratigraphic

ages. In addition, if reorganization of 1M illite into 2M illite had occurred in their samples as suggested by Bailey et al., the isotopic ages of the 2M clays would have become younger than the 1Md clays.

Hurley et al. (1963) measured the K-Ar ages of different size fractions, ranging from $4\mu\text{m}$ to $<0.08\mu\text{m}$, in an Ordovician illitic marine shale. The ages were found to decrease with decreasing particle size. The age of the coarsest fraction was greater than the stratigraphic age and that of the finest fraction was less. It follows from the results of both Hurley et al. and Bailey et al. (1962) that the ages of either bulk shales or separated size fractions of shales reflect the weighted average ages of all of the detrital and authigenic components in the samples analyzed. Because authigenic particles are typically concentrated in the finest fractions of clay-rich rocks, the ages of these fractions normally most closely approximate the timing of authigenesis or diagenesis (Clauer, 1976; Huon, 1985; Reuter, 1987; Liewig et al., 1987a; Mossman et al., 1992).

Hurley et al. (1963) measured K-Ar ages of $<2\mu\text{m}$ clay fractions of several Paleozoic shales that had been paleontologically well-dated. The ages of nearly all the samples were about 10 to 20% lower than the stratigraphic ages of the rocks from which they were separated. This discrepancy is similar to that which Hurley et al. (1960) observed for Paleozoic glauconites. But Hurley et al. (1963) also found that: (1) the K-Ar ages of many clays from Mesozoic and Cenozoic rocks are in fairly good agreement with stratigraphic ages, and (2) the K-Ar ages of clay fractions from very young rocks were as much as 4 times greater than the stratigraphic ages. Hurley et al. interpreted their results to reflect mixtures in varying proportions, of detrital and authigenic clay constituents. They attributed the low K-Ar ages of clays from many Paleozoic rocks to the high proportions of diagenetic clay minerals they contained, whereas the high K-Ar ages of the younger rocks were attributed to the dominant influence of detrital constituents. In this interpretation, agreement between isotopic and stratigraphic ages could be the coincidental result of analysis of a mixture, in adequate proportions, of detrital and diagenetic components.

Low K-Ar Ages of Fine-Grained Clay Minerals

Two causes of low K-Ar ages of finer clay particles were proposed in early studies: (1) increasing diffusional loss of radiogenic ^{40}Ar with decreasing particle size, a suggestion which is no longer readily accepted, and/or (2) diagenetic addition of K to smectite and altered micas over an extended period of time. TEM observations (e.g. Hunziker et al., 1987) show that detrital clay particles often have irregular edges, whereas authigenic clays have sharp well defined edges. This morphological distinction has proven useful for differentiating between the two types of clay.

Initially, evidence in support of the hypothesis of diffusional loss of Ar from clay particles was very strong, as several experimental studies suggested the potential for loss of Ar by glauconite and related clay minerals in sedimentary environments (Amirkhanov et al., 1958; Evernden et al., 1961). However, as already noted, there was also substantial evidence in the early 1960's that fine-grained clays are retentive of radiogenic ^{40}Ar in sedimentary and diagenetic environments. For instance, Hurley et al. (1960) showed that the K-Ar and the Rb-Sr ages of glauconites can be similarly discordant with respect to stratigraphic age, even though the rates of diffusion of Ar and Sr differ greatly in clay minerals. Obradovich (1965) observed no differences in the K-Ar ages of different size fractions of a mineralogically homogeneous glauconite sample, and Clauer et al. (1984) did not find any difference in the Rb-Sr and K-Ar apparent ages of oceanic clay minerals from the southern Pacific Ocean, even at particle size as small as $0.2\mu\text{m}$.

Hunziker et al. (1986) proposed that Ar diffusion might occur in detrital clay of any size fractions because the edges of detrital particles tend to be diffuse and ill-formed. As neoformed crystals, which predominate in the finer clay fractions, typically have clean, sharp edges, Hunziker et al. suggested that diffusion is minimized in such neoformed fine particles. If this idea is correct, the proportions of large, diffuse-edged, leaky crystals and small, tight crystals probably vary from sample to sample,

reflecting the details of lithology, the degree to which recrystallization has occurred, and the sizes and locations of the clay particles within the rocks. Huon et al. (in prep.) question, on the basis of microstructural, mineralogical and morphological evidence, whether Ar diffuses in illite under diagenetic conditions, as proposed by Hunziker et al (1986).

Isotopic Age Determination of the Time of Sedimentation

By analysis of whole rocks

During the early 1960's, the Rb-Sr method was often applied to bulk sedimentary rocks (Compston and Pidgeon, 1962; Whitney and Hurley, 1964; Chaudhuri and Faure, 1967; Bonhomme and Prévôt, 1968). This approach, based on the assumption that the Sr isotopes of all of the rocks in any suite of samples had equilibrated with one another (and with the ambient fluids) during or shortly after deposition, was reexamined by Cordani et al. (1978; 1985). They showed that frequently the isotopic data for a suite of bulk samples did not plot along any line on an $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{87}\text{Rb}/^{86}\text{Sr}$ diagram that could be interpreted as an isochron.

Acid-leaching of shales was done in a number of studies to remove and analyze Rb and Sr which were either contained in carbonates or were less tightly bound within silicate mineral structures. The rationale for this was the idea that acid-leachable Rb and Sr would be more likely to constitute a system that had equilibrated with ambient fluids at the time of sedimentation (Bofinger et al., 1968; Chaudhuri and Brookins, 1969; Clauer, 1976; Chaudhuri and Brookins, 1979). In some instances, the isotopic compositions of the leachates and the residues plotted along straight lines on Sr-evolution diagrams. While in some cases those lines could be interpreted as isochrons indicating the time of sedimentation, most investigators concluded that Rb-Sr data from argillaceous sediments could not be used to estimate the time of sedimentation. Clauer (1982) examined the potential of whole-rock Rb-Sr dating in detail, and he concluded that the method is not reliable, because the basic assumption of complete isotopic homogenization of all silicate and acid-leachable components of whole rocks, is never achieved during

deposition.

By analysis of separated clay fractions

When isotopic compositions of separated size fractions of clays from a suite of related rocks are plotted on a Sr-evolution diagram, it is common for the data of the same size fractions to plot close to a straight line that can be interpreted as an isochron. However, as was found in early K-Ar studies, the Rb-Sr apparent ages of different size fractions separated from the same whole rock commonly decrease with decreasing particle size (Clauer, 1974; Dasch, 1969; Hofmann et al., 1974). This led to the conclusion that the Rb and Sr isotope systematics of clay minerals from shales primarily reflect the ages of the detrital components, that diagenetic alteration during burial chiefly affects the fine-grained clay components, and that stratigraphic dating of whole rocks using the Rb-Sr method is not feasible. Bonhomme et al. (1966) first emphasized the need for integrating the results of clay mineralogic analyses into geochronologic studies. Indeed, if it can be assumed that in situ formation or modification of clay is accompanied by Sr isotope equilibration with the environment, this certainly might be the most visible in the smaller size fractions. Agreements between stratigraphic and isotopic ages were found in a number of studies and were taken as evidence that Sr isotope equilibration had occurred (Bonhomme et al., 1970; Clauer, 1973; Harris and Bottino, 1974a, b; Harris, 1976; Harris and Baum, 1977; Keppens et al., 1978a, b).

Studies of clays in Recent sediments provide clear evidence that some of the detrital clays approach Sr isotopic equilibrium with the environments in which they have been deposited. Evidence also exists for Sr isotopic equilibration between some detrital clay minerals and interstitial fluids shortly after deposition. There are a number of examples in which glauconies formed by the alteration of detrital clays exhibit apparent age spectra which decrease, approaching stratigraphic age, in a manner similar to that seen by Odin et al. (1979) for Recent glauconies. These include the Eocene Weches Formation in Texas (Ghosh, 1972), Miocene glauconies from Morocco (Tisserant and Odin, 1979), and illite, smectite and attapulgite assemblages from Tertiary formations of

the Central Massif in France (Clauer, 1976). These examples indicate that the model of early diagenesis of clay minerals that is inferred from the study of Recent sediments, is applicable to the study of other authigenic clay components separated properly from their sedimentary rocks. The K-Ar and Rb-Sr isotopic systems and consequently the apparent depositional ages of clay fractions may also be affected by weathering and/or burial diagenesis.

It should also be mentioned here that determination of the time of deposition of Proterozoic sedimentary sequences by isotopic analysis of their clay minerals seems to need special care. Clauer et al. (1982b), for instance, found that the K-Ar ages of illites of Proterozoic age are always younger than the Rb-Sr ages obtained on the same aliquots. The reason for this is not clear, but a possibility exists that early diagenesis may persist for long intervals in some Proterozoic series that were never buried to great depths, as the result of very low sedimentation rates. The fact that the Rb-Sr and/or K-Ar methods often cannot be properly applied to Archean and Proterozoic sedimentary sequences for stratigraphic purposes, has led to attempts to date the time of deposition using the Sm-Nd method on authigenic clays (Stille and Clauer, 1986; Bros et al., 1992), and the Pb-Pb method on carbonates (e.g. Moorbath et al., 1987). The full potential of these relatively new isotopic methods of dating sediments has yet to be determined.

DETERMINATION OF THE TIMING AND MECHANISMS OF DIAGENESIS

Mechanism and Timing of Diagenetic Processes in Shales

When shales containing mixed-layer illite/smectite are buried deeply in a sedimentary basin, the proportion of illite layers in the clay increases with increasing depth of burial (Burst, 1958b; Powers, 1959, 1967; Weaver, 1959, 1960; Dunoyer de Segonzac, 1969; Perry and Hower, 1970; Hower et al., 1976; Boles and Franks, 1979; and others). This process has been examined in many sedimentary basins but has been studied most intensively in the sediments of

the Gulf Coast. Combined K-Ar, Rb-Sr and light stable isotope studies have helped elucidate the processes that occur in deeply buried shales and have clarified the significance of ages obtained in geochronologic studies of shales.

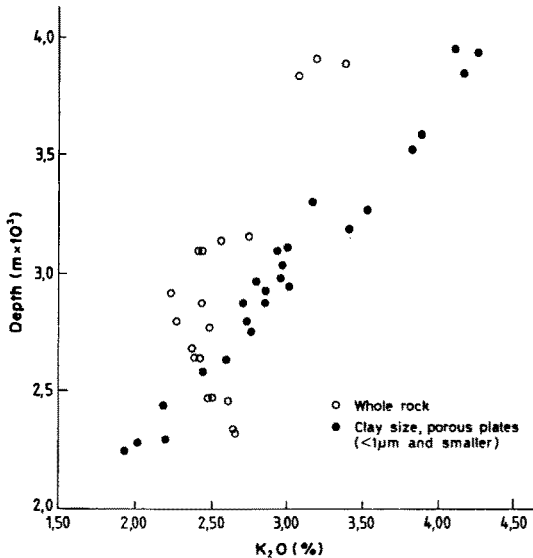


Figure 4: K content versus depth for clay fractions (<1μm) and bulk samples from Gulf Coast sediments (Perry and Hower, 1970)

Perry and Hower (1970) published a detailed examination of the mineralogical and chemical variations of deeply buried shales of Pleistocene to Eocene age from the Gulf Coast. In spite of progressive K-fixation with depth by the mixed-layer clays, accompanying the conversion of smectite to illite, the K contents of the whole rocks do not vary systematically with depth (Fig. 4). This suggested to the authors that each rock volume was closed to the movement of K, and that K was redistributed within each rock volume during burial diagenesis. Because the K-feldspar content of each sequence decreases with depth, Perry and Hower proposed that K-feldspar was the most likely source of the K fixed by the mixed-layer clay. In this interpretation, breakdown of detrital illite and feldspar supplied K and Al which were taken up in the conversion of smectite layers to illite layers in the mixed-layer illite/smectite. This was supported by the conclusions of a more detailed study by Hower et al. (1976) on samples from another well in the Texas Gulf Coast.

K-Ar isotopic evidence

Diagenetic reactions, as suggested by Perry and Hower (1970) and Hower et al. (1976), have a major effect on the K-Ar ages of whole rocks and clay fractions. This was confirmed in Perry's (1974) examination of the K-Ar systematics of separated clay size fractions from a sequence of Miocene shales buried to depths from 1,580 m to 5,525 m (estimated temperature 165°C) in the Louisiana Gulf Coast. In the $<0.5\mu\text{m}$ fractions, mixed-layer illite/smectite is the predominant mineral with smaller amounts of kaolinite, detrital illite, and sometimes discrete chlorite. The proportion of illite layers in the $<0.5\mu\text{m}$ mixed-layer illite/smectite increased from 20% at shallow depths to 80% in deeply buried sediments. This increase in the illite content is accompanied by a decrease in the K-Ar ages from 164 ± 3.3 Ma at 1,580 m to 100 ± 2.0 Ma at 5,525 m, but even the youngest of these ages is considerably greater than the depositional age of the sediments. The $0.5\text{--}2\mu\text{m}$ fractions contain less mixed-layer illite/smectite and more detrital illite, feldspar, and quartz than the finer fractions, and have K-Ar ages between 312 ± 6.2 Ma at a depth of 1,713 m and 129 ± 2.6 Ma at a depth of 5,980 m. The dispersion of ages among the size fractions of a sample decreases with increasing depth (Fig. 5), but at no depth are the K-Ar ages of the different size fractions concordant.

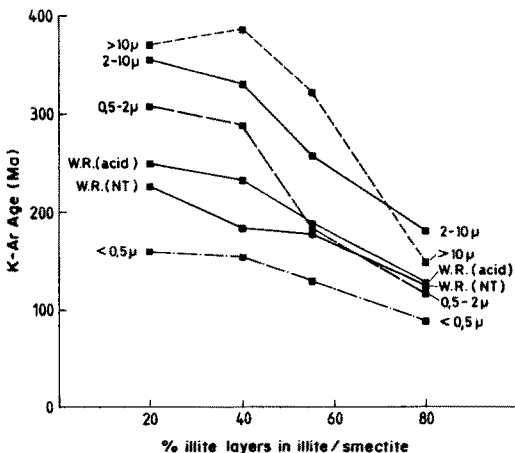


Figure 5: Variations of K-Ar ages with changing illite contents in smectite-illite minerals for different size fractions of sediments from the Texas Gulf Coast (Perry, 1974)

Weaver and Wampler (1970) and Aronson and Hower (1976) also measured K-Ar ages of clay fractions separated from deeply buried sediments in the Gulf Coast region. Weaver and Wampler, in their study of $<0.2\mu\text{m}$ clay fraction, noted a decrease in the age from 165 ± 60 Ma at a depth of about 1,320 m to about 125 ± 20 Ma at a depth of 5,140 m. These measurements required large corrections for atmospheric Ar, causing the measured ages at all depths to overlap within the experimental uncertainty, but the results can be assumed to agree well with those of Perry (1974). Aronson and Hower (1976) measured K-Ar ages of Oligocene illitic clay in the Texas Gulf Coast well studied by Hower et al. (1976). They examined the $<0.1\mu\text{m}$ clay fractions, i.e. finer than those examined by either Perry (1974) or Wampler and Weaver (1970), and reported lower ages ranging from 53.9 ± 2 Ma at a depth of about 1,185 m to 32.6 ± 2 Ma at a depth of about 5,250 m. The stratigraphic age of the sedimentary sequence ranges from approximately 28 to 35 Ma, so a complete resetting of the isotopic ages in the Gulf Coast region seems not to have occurred even in $<0.1\mu\text{m}$ clay particles buried to depths as great as 5,250 m.

In principle, isotopic ages of diagenetic components of shales should indicate the time of diagenesis, but in practice the time of diagenesis of shale may be determined only with a good deal of uncertainty. This uncertainty is primarily the result of the difficulty of separating detrital from diagenetic clay components (Clauer, 1982). In spite of this, however, Aronson and Hower (1976) were able to use K-Ar data to estimate the mean time of K-fixation by the mixed-layer phase. They did this by estimating the incremental amount of K added to the fine clay fraction during diagenetic illitization and the incremental amount of ^{40}Ar relative to the ^{40}Ar content of the more shallowly buried fine clay fractions. The age they computed from these incremental values was 18 Ma, which is consistent with the time estimated from burial history curves for heating of the sediments to temperatures in the range of 80 to 160°C .

Rb-Sr isotopic evidence

When it is deposited, each Sr-bearing detrital component of a sediment has an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio which reflects its origin. Each

diagenetic component acquires an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio which is determined by the Sr isotopic composition of the environment at the time it is formed or recrystallized. In Rb-containing phases the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, of course, evolve with time. In the early 1970's it became apparent that at least partial homogenization of Sr isotopes among minerals in a rock could accompany diagenesis. Perry and Turekian (1974) measured the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of different size fractions of clay from deeply buried Miocene shales in the Louisiana Gulf Coast (apparently the same well studied by Perry, 1974). They observed a trend toward Sr isotopic homogenization in the most deeply buried sediments, but $^{87}\text{Sr}/^{86}\text{Sr}$ ratios did not become completely homogenized even at a burial depth of 5,523 m (Fig. 6).

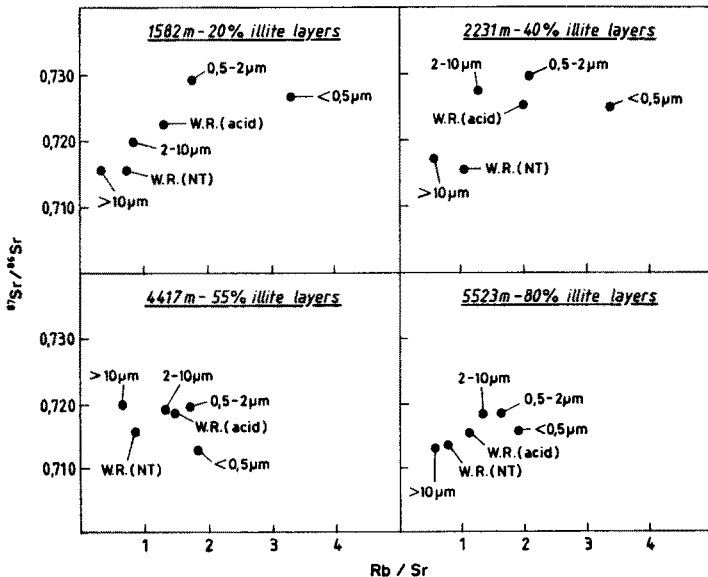


Figure 6: Variations of Rb-Sr isotopic compositions for different size fractions of sediments from different depths in the Gulf Coast area (Perry and Turekian, 1974)

In sharp disagreement with the inference by Perry and Turekian (1974) that homogenization of Sr isotopes among the different constituents within a shale sample is very slow, Morton (1985) argued that Sr isotopic homogenization among very fine ($< 0.05\mu\text{m}$) clay particles had occurred over a stratigraphic interval between 3,200 m and 4,900 m in a well in the Texas Gulf Coast during a period of 5 Ma or less. The data points for the samples Morton analyzed form a linear array on a Rb-Sr isochron diagram. Morton interpreted the

data as indicating that isotopic homogenization of the finest fractions of all of the samples occurred at 23.6 ± 0.8 Ma, compared to a depositional age of 25 to 29 Ma, and that the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at the time of homogenization was 0.7088 ± 0.0004 , similar to that of late Tertiary sea water (Fig. 7). Thus, in Morton's interpretation, homogenization of Sr isotopes of the finest clay fractions of Gulf Coast sediments would have occurred over a large stratigraphic interval shortly after deposition, probably in response to a change in the hydrologic regime which, in turn, affected the pore-water chemistry. That would have promoted the illitization of the mixed-layer illite/smectite to varying degrees throughout the stratigraphic interval. Morton also suggested that no further transformation of smectite layers to illite occurred subsequent to that early diagenetic episode. Although Morton's data are intriguing, his interpretation of the homogenization of Sr isotopes of fine-grained clay over an interval of thousands of meters during a brief episode has not met widespread acceptance. In an alternative view of the data, the apparent Rb/Sr isochron might suggest that a thick sequence of sediment, which was deposited and buried within a few million years, was rapidly heated as the result of burial and underwent diagenetic illitization during a relatively short interval. However, a detailed critique of Morton's conclusions has not yet been published.

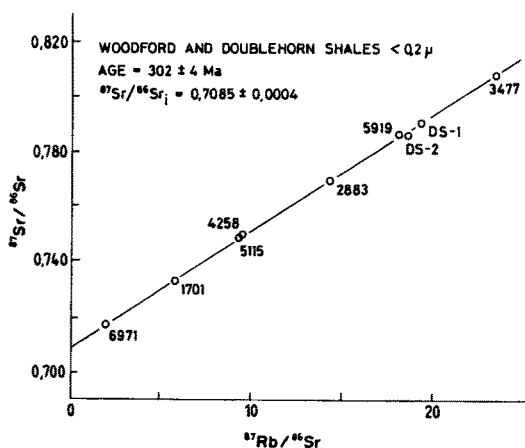


Figure 7: Rb-Sr isochron of very fine clay fractions ($< 0.2 \mu\text{m}$) from shales in the Texas Gulf Coast area (Morton, 1985)

Oxygen and Hydrogen isotope evidence

The O and H isotope geochemistry of minerals in shale sequences provide additional evidence about the nature of the burial diagenetic conversion of highly expandable illite/smectite to clay of lower expandability. Yeh and Savin (1977) examined the $\delta^{18}\text{O}$ values of separated size fractions of quartz and clay from three Gulf Coast wells, including the CWRU-6 well studied by Hower et al. (1976) and Aronson and Hower (1976). Yeh (1980) measured the δD values of separated clay size fractions from the same wells. In the shallowest sample of CWRU-6 studied (1,350 m, 44°C), each of the different clay size fractions had different $\delta^{18}\text{O}$ and δD values, indicating that there has been little or no isotopic exchange either among clay fractions within the sample or between pore fluids and clay fractions except, conceivably, the finest fraction. With progressive burial, the spread of $\delta^{18}\text{O}$ and δD values in a sample diminished (Fig. 8). The greatest decrease in the range of δ values occurred between 2,500 and 3,500 m, the depth range in which the greatest amount of illitization of illite/smectite occurred.

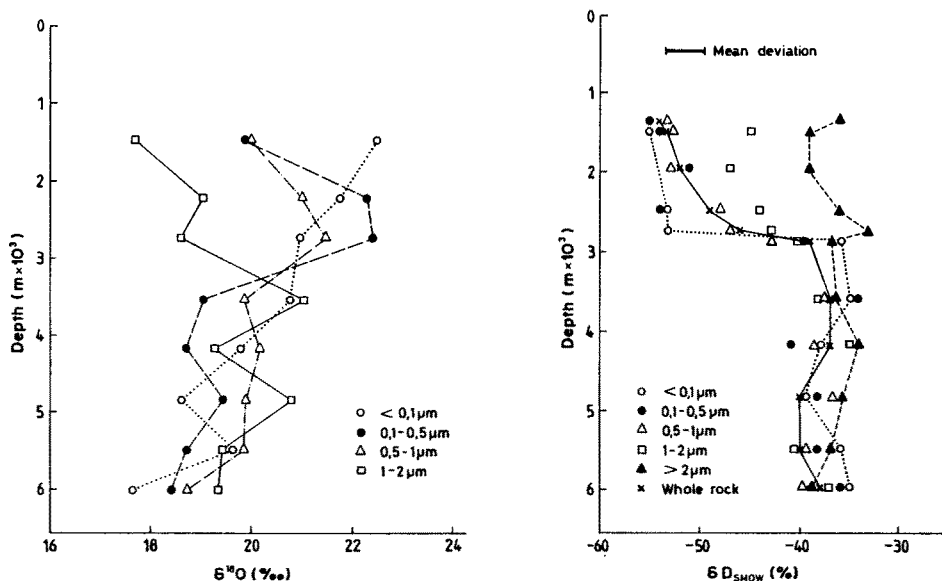


Figure 8: Oxygen- and hydrogen isotope variations with depth from various clay fractions in sediments from CWRU Gulf Coast Well N°6 (Yeh, 1980)

At every depth, there is a significant dispersion of $\delta^{18}\text{O}$

values of different size fractions of quartz. Below 2,500 m, the 2 to 1 μm quartz grains are isotopically zoned. The inner portions of the grains have $\delta^{18}\text{O}$ values typical of silt-size detrital quartz in the Mississippi River drainage system and the outer portions of the grains are substantially enriched in ^{18}O . Yeh and Savin (1977) interpreted the data as confirming the diagenetic mechanism for illitization proposed by Hower et al. (1976). That is, the breakdown of detrital K-feldspar and mica provides K and Al necessary for conversion of smectite layers to illite layers. The Si released during this breakdown and/or the Si released from the tetrahedral sites of the smectite when it is converted to illite becomes available to form quartz in the shale. Yeh and Savin proposed that at least a portion of that Si formed diagenetic quartz overgrowths on detrital silt- and clay-size quartz grains.

Diagenetic Processes in Sandstones

In many sandstone reservoirs, the finest particle sizes of the clay fraction are dominated by diagenetic clay. Separation of diagenetic clays from sandstone is less difficult than that from shale, and this has facilitated a number of studies of diagenetic processes utilizing radioactive and stable isotope measurements. The significance and utility of many of these studies derive to a large extent from the fact that they were based on integrated evidence of basinal history, careful petrography and mineralogy, geochronology and stable isotope studies.

From the $\delta^{18}\text{O}$ values of a pair of cogenetic minerals which formed in isotopic equilibrium with one another and with the ambient fluid, one can, in principle, determine both the temperature of mineral formation and the $\delta^{18}\text{O}$ value of the ambient fluid. However, cogenetic mineral pairs are extremely rare in sandstones. From the $\delta^{18}\text{O}$ value of a single mineral, the conditions of its formation can be constrained to lie upon a trajectory on a diagram of temperature of formation vs. $\delta^{18}\text{O}_{\text{fluid}}$. When either the temperature of formation or $\delta^{18}\text{O}_{\text{fluid}}$ can be constrained using non-isotopic data, it is possible to use the $\delta^{18}\text{O}$ value of the mineral to constrain the other. This is the approach that has been taken in interpreting

the O isotopic data obtained in several studies of sandstone diagenesis that are briefly summarized below.

Studies in the Rotliegendes of the North Sea

The Permian Rotliegendes Sandstone in the southern part of the North Sea basin has been the subject of recent geochemical studies focusing in part on the time of emplacement of the hydrocarbons in gas reservoirs (Lee et al., 1985, 1989). Lee et al. (1985) examined the variation with depth of the nature and extent of diagenetic changes in two wells from the Groningen gas field and the Broad Fourteens oil field. A basic assumption of their approach was that the smallest size fractions of diagenetic illite growing in sandstone pores as an alteration product of K-feldspar are most likely to have been derived from the edges and tips of the illite flakes. The smallest fractions should be those to be the last to have grown. Consequently, in the absence of any detectable contamination by detrital illite, the range of ages obtained from different clay size fractions ought to be indicative of the duration of the illite-forming process.

Lee et al. (1985) also postulated that the emplacement of gas in a sandstone would inhibit the progression of diagenetic alteration by displacing the formation water. In each field studied the intensity of both the alteration of detrital feldspar and the growth of diagenetic illite increases with depth over a relatively small interval (174 m in the Groningen well and 15 m in the Broad Fourteens well). The authors, therefore, suggested that the downward increase in the intensity of diagenetic alteration reflected the gradual emplacement of hydrocarbons in the reservoir and the downward migration of the gas-water contact. In this scenario, rocks which had been saturated with water for longer periods of time would have become more intensively altered.

The data for the Groningen gas field are consistent with this hypothesis. In the uppermost sample studied the K-feldspar was fresh and there was no diagenetic illite to date. Lower in the gas zone the diagenetic illite yielded K-Ar apparent ages of 143 Ma (0.2-0.5 μ m) and 151 Ma (<0.1 μ m); the depositional age of the Rotliegendes being about 270 Ma. The 0.2-0.5 μ m was contaminated

with highly altered detrital K-feldspar, and Lee et al. suggested that the relatively low age of that fraction reflected Ar loss from the feldspar. They interpreted the age of the $<0.1\mu\text{m}$ fraction as indicating the latest possible time of illite growth in the deeper gas zone sample, and by inference, the time of migration of gas into that level of the reservoir. Still lower in the section in the water zone, diagenetic illite gives K-Ar apparent ages of 133 Ma ($0.2\text{--}0.5\mu\text{m}$) and 120 Ma ($0.2\text{--}0.5\mu\text{m}$). The abundance of K-feldspar in both fractions of that sample being below the XRD detection limit (a few per cent), Lee et al. concluded that the formation of illite terminated much later in the water zone than in the gas zone.

Studies in the Brent of the North Sea

The uncertainty in the significance of K-Ar ages of different size fractions of illite from a reservoir sandstone is best illustrated by the disparate results on diagenetic illite from the Brent Formation in the North Sea. Hamilton et al. (1987) reported K-Ar ages between 46 and 59 Ma for the diagenetic illite of that oil-bearing sedimentary level. Hogg et al. (1987) also found scattered K-Ar ages between 45 and 60 Ma, whereas Jourdan et al. (1987) claimed, on the basis of K-Ar data, that the Brent Formation had a long and complex diagenetic history extending from Lower Cretaceous time (100 Ma) to the Eocene (40–50 Ma). In sharp contrast, Liewig et al. (1987a) observed that the average K-Ar age of the diagenetic illite from the Brent was measured to be about 41 Ma when the illite was separated following a gentle freeze-thaw disaggregation, but the K-Ar ages of similar size fractions of illite from similar nearby rocks collected varied between 130 and 50 Ma when the clays were separated following comminution by jaw crusher and ball mill. Glasmann et al. (1989) used gentle crushing and ultrasonic treatment to disaggregate Brent sandstones and found close K-Ar ages of about 38 Ma for the diagenetic illite fractions. Liewig et al. (1987a) concluded that sample preparation could introduce scatter in the dates due to the introduction of trace amounts of contaminant detrital components in the fractions analyzed. Clauer et al. (1992b) also examined the manner in which laboratory procedures might affect isotopic results of diagenetic clay minerals. As an alternative to diagenetic events of long

duration inferred by Jourdan et al. (1987) for the Brent, Cocker et al. (1988) found that the difference between the K-Ar age of illite formed in the water zone and illite formed in the oil zone of a Brent reservoir was only 1 to 2 Ma for the 40 Ma event. These illites were separated following disaggregation by a gentle technique. Lee et al. (1985) used a different gentle disaggregation technique and concluded from their study of the hairy illites in the Rotliegendes that the duration of diagenetic illite formation in the water zone was long, but the evolutionary history of the Rotliegendes in the southern North Sea may have been different than that of the Brent sandstones located further North.

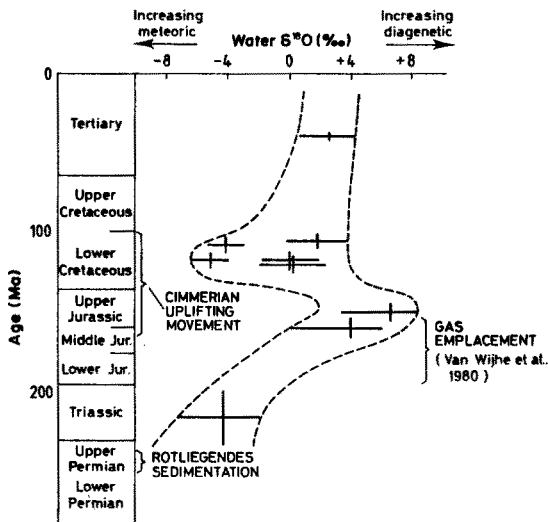


Figure 9: Oxygen isotopic compositions of fluids related to illite diagenesis in Rotliegendes sandstones, northeastern Netherlands (Lee et al., 1989)

In a survey of the K-Ar and O isotope systematics of a number of wells from several fields in the Rotliegendes sandstones, Lee et al. (1989) used the K-Ar age of diagenetic illite and the burial history curve for each sample to infer the depth at which any sample was buried when the illite formed. The temperature of illite formation was then calculated from the depth of burial and the estimated paleogeothermal gradient (taken to be similar to the modern one at each locality). The $\delta^{18}\text{O}_{\text{fluid}}$ was further estimated from calculated temperature and measured $\delta^{18}\text{O}$ value of the mineral. The

evolution of the $\delta^{18}\text{O}$ values of illite-forming fluids in north-eastern Netherlands is shown in figure 9. The relatively high values (0 to +4 per mil) obtained for the $\delta^{18}\text{O}$ of the fluids from which most of the illites formed, indicate that the fluids had been significantly affected by interaction with rocks. However, $\delta^{18}\text{O}_{\text{fluid}}$ values were relatively low (-4 to -5 per mil) during the time of the Kimmerian uplift early in the Cretaceous period, indicating a significant meteoric component at that time. Lee et al. were also able to show a geographic pattern in the inferred $\delta^{18}\text{O}_{\text{fluid}}$ values at that time, low values occurring closest to an early Cretaceous outcrop of the Rotliegendes and high values occurring furthest away. Thus, the O isotopic data were useful in the determination of the paleohydrological pattern in response to tectonic evolution.

Studies in the Alberta Basin

The diagenesis of the Cretaceous and Tertiary sandstones of the Alberta Basin has been extensively studied by F. Longstaffe and his colleagues. Of particular significance to this review are the studies devoted to the evolution of the fluids responsible for the formation of diagenetic cements (Longstaffe, 1984, 1986; Longstaffe and Ayalon, 1987, 1990; Ayalon and Longstaffe, 1988). The Alberta basin is an especially attractive region for studies of this sort because the $\delta^{18}\text{O}$ values of meteoric water in the region are much lower than values expected for water which has been modified isotopically to a significant degree by diagenetic reaction with rocks.

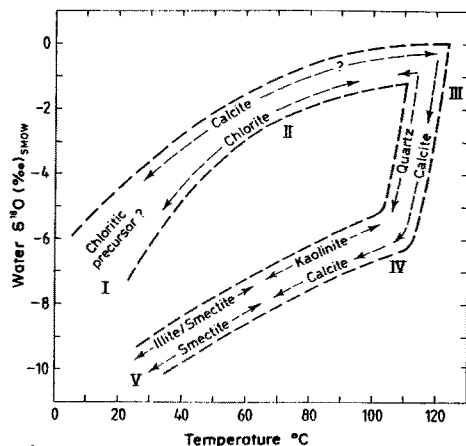


Figure 10: A model for the evolution of oxygen-isotope composition of pore fluids and diagenetic minerals in the basal Belly River sandstone, Alberta (Ayalon and Longstaffe, 1987)

The results of the above mentioned studies point out very clearly that different episodes of diagenesis may occur in a sandstone in the presence of fluids of very different nature. These different fluids enter the sandstone in response to the changing depositional and tectonic regimes in the sedimentary basin. Isotopic analyses of different diagenetic phases carefully documented by petrologic and mineralogic observations can be of prime importance in the reconstruction of the varied diagenetic episodes occurring during the evolution of a sedimentary basin. As an example, the upper Cretaceous basal Belly River Sandstone in Canada contains a complex suite of diagenetic minerals which includes, in order of formation, iron oxide, chlorite, quartz overgrowths, feldspar overgrowths, kaolinite, illite, illite/smectite and pyrite (Ayalon and Longstaffe, 1988). Using $\delta^{18}\text{O}$ values of several of the diagenetic phases, the conditions of formation of each could be constrained to lie upon a trajectory on a diagram of temperature vs. $\delta^{18}\text{O}_{\text{fluid}}$ (Fig. 10). Ayalon and Longstaffe (1988) concluded that the early diagenetic fluids were cool and were meteoric in origin. Later, phases formed after burial heating, in the presence of diagenetically modified ^{18}O -rich water. Still later, the formation cooled as the result of uplift and erosion, and the fluids from which minerals formed were again largely meteoric in origin.

Studies in the Powder River Basin

The Cretaceous Muddy Sandstone of the Powder River Basin (Law, 1983; Burrows, 1985; Savin et al., in prep.) is a fluvio-deltaic sequence with a depositional age of approximately 100 Ma containing abundant detrital illite/smectite mixed-layers. Burial history was relatively simple and present burial depths (approx. 1,000 to 2,500 m) that are probably close to maximum burial depths. Diagenetic phases include quartz overgrowths on detrital quartz sand-grains as well as intergranular kaolinite and illite/smectite. The mineralogic and mineral preparation procedures used were fairly primitive when compared to those of some more recent studies discussed above.

The 0.05-0.1 μm and <0.05 μm fractions were dated using the K-Ar method to distinguish the diagenetic from detrital illite/smectite mixed-layers. Figure 11 is a plot of K-Ar age vs. percent

illite layers in the illite/smectite for all except the most shallowly buried samples. Most of the coarser clay fractions, and a few of the finer fractions gave ages which were older than the depositional age, clearly indicating that they contain an abundant detrital component. The proportion of illite layers in the detrital illite/smectites varies widely from less than 5 to more than 70%. The K-Ar ages of most of the finer clay fractions and a few of the coarser ones were significantly younger than the age of deposition, suggesting that they were dominated by diagenetic material. The mineralogical and K-Ar data suggest that the conditions of formation of the diagenetic illite/smectite were fairly uniform over the area studied, at least with respect to the parameters that determine the percentage of illite layers in that mineral.

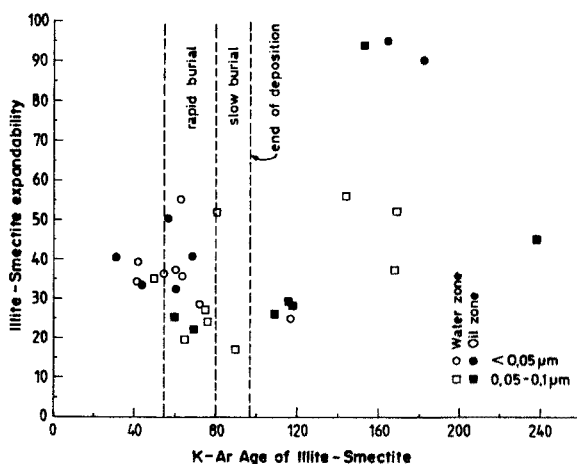


Figure 11: K-Ar age vs. percent illite in mixed-layer illite-smectite clays in Cretaceous Muddy sandstone in the Powder River basin (Savin et al., in preparation)

The ^{18}O values of the size fractions were also measured. Most of these fractions were mixtures of two or three of the three end-member components: detrital illite/smectite, diagenetic illite/smectite and kaolinite. Burrows (1985) and Savin et al. (in prep.) used plots of mineralogical composition vs. $\delta^{18}\text{O}$ value in suites of related size fractions (usually from a single small oil field) to extrapolate to the $\delta^{18}\text{O}$ values of the diagenetic kaolinite and illite/smectite components of each of these suites. The K-Ar ages were used to distinguish and eliminate from consideration those

illite/smectites that were predominantly of detrital origin.

The ^{18}O values of the diagenetic components differed markedly from one sample suite to another and were used to constrain the conditions of formation of each of the components on diagrams of temperature vs. $\delta^{18}\text{O}_{\text{fluid}}$. The temperature of formation of the diagenetic mixed-layers illite/smectite in each field was further constrained using burial history diagrams, assumed geothermal gradients and K-Ar ages. The results indicate that the fluids from which the illite/smectite mixed-layers formed in the more deeply buried samples were warmer and more enriched in ^{18}O than those in the more shallowly buried samples. This is consistent with a mixing model in which cool, ^{18}O -depleted meteoric fluids enter the formation in groundwater recharge zones and mix in varying proportions with warm, ^{18}O -enriched diagenetically modified waters generated at depth. However, the authors suggested an alternative model in which the illite/smectite forming fluids were expelled over a range of burial depths from the thick shales enclosing the relatively thin sandstone. In this model, the chemistry of the fluids would have been fairly similar at all depths, accounting for the relative uniform mineralogy of the diagenetic illite/smectite.

Studies of Arkoses along the Coastal Margin of Angola

Girard et al. (1988, 1989) examined a complex suite of diagenetic phases in Cretaceous arkoses buried along the Angola margin. The times of formation of K-feldspar overgrowths and illitic clay (illite and illite/smectite) were determined using the K-Ar method. Several size fractions of each sample were analyzed to assist in the assessment of whether, and to what extent, the ages are affected by detrital contamination. As discussed earlier, similar K-Ar ages for different size fractions of a sample were interpreted as representing the time of mineral formation. K-Ar ages decreasing with decreasing particle size (Fig. 12) were assumed to be affected by detrital contamination and to represent maximum ages of mineral formation.

The studies of Girard et al. combined the basinal history, petrographic, mineralogic, isotopic and fluid inclusion microthermometry data. The combined data permitted the authors to show that

while the depth of burial of the arkoses had increased during most of the post-depositional history of the sequence, temperatures experienced by the samples had decreased during much of that time. They attributed this to the tectonic setting of the sediments, and concluded that the geothermal gradient in the region was anomalously high when the sediments were deposited, as a result of proximity to the mid Atlantic spreading axis. With time, the sampling site moved away from the ridge axis and the geothermal gradient decreased.

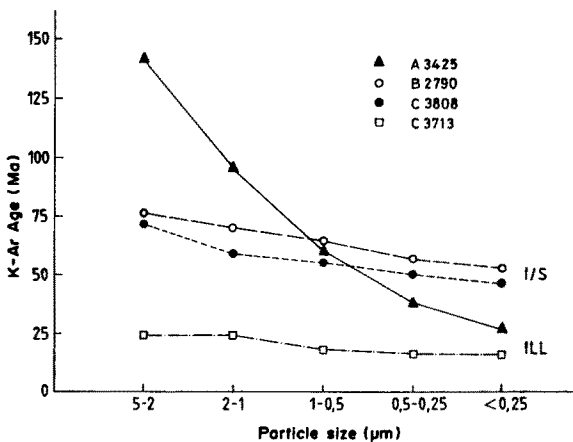


Figure 12: Changes in K-Ar ages with respect to particle sizes for illitic materials from Cretaceous arkoses in the coastal margin of Angola (Girard et al., 1988, 1989)

Studies in the Paris Basin

Mossmann et al.'s (1992) study of diagenetic clay minerals from the Rhaetian (Uppermost Triassic) sandstone of the Paris Basin is another illustration of the advantage of integrating the results of K-Ar analyses of clay minerals with the geologic history of the sedimentary basin and the results of petrographic, mineralogic, and morphologic (TEM and SEM) observations. The clay minerals studied came from a single stratigraphic unit sampled across the basin. Depth of burial ranged from surficial outcrop at the edge of the basin to about 2,700 m deep near the center.

The sandstone samples were gently disaggregated and analysis of the $<0.2\mu\text{m}$ clay fractions by XRD indicated the presence of three

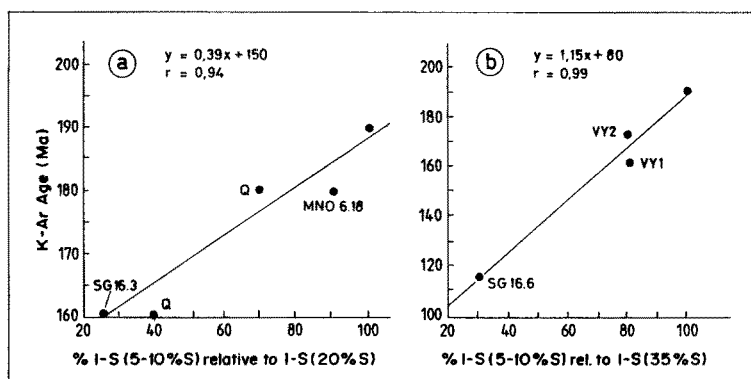


Figure 13: K-Ar ages of different generations of illite-smectite mixed-layer phases in Triassic sediments from Paris Basin (Mossman et al., in press)

generations of illite/smectite mixed-layer clay: one with 5-10% expandable layers, one with about 20% expandable layers, and one with about 35% expandable layers. The most illitic phase is the dominant clay in most samples. The ages of those clay fractions that consist predominantly (more than 90%) of the illite-rich phase and that are free of any detrital components are between 189 and 192 Ma. Mossman et al. interpreted these ages as being close to the age of crystallization of the illite-rich illite/smectite phase. The times of crystallization of the two other phases were calculated from the mineralogical data and the ages of samples that were two-component mixtures of the highly illitic 190 Ma phase and one of the other illite/smectite components (Fig. 13). The phase with 20% expandable layers formed at about 150 Ma and the phase with about 35% expandable layers formed at about 80 Ma. The calculated temperature of formation of the early formed illite-rich phase is about 150°C or higher and those of the two other illite/smectite components are lower. The temperature of 150°C is higher than would result from burial of these sediments in a region of normal geothermal gradient. Mossman et al. suggested that this temperature may have resulted from upward migration of hydrothermal fluids along fault zones related, as in the previous example of Angola offshore, to a tectonic activity. This interpretation is consistent with inferences by others that contemporaneous tectono-hydrothermal activity had occurred at several other places in

western Europe at the time (Bonhomme, 1982, Bonhomme et al., 1983; Bonhomme and Millot, 1987; Liewig et al., 1987b).

Diagenetic Processes in Associated Shales and Sandstones

Rinckenbach (1988) and Rinckenbach et al. (in prep.) studied $<0.4\mu\text{m}$ clay fractions of shales and associated sandstones from a 4,000 m thick Miocene to Pliocene sedimentary succession in the Mahakam delta in eastern Kalimantan (Borneo). The study afforded an examination of the crystallochemical evolution of clay particles in environments of different water-rock ratios at nearly identical temperatures. XRD analyses indicated a classical pattern of evolution of the mixed-layer illite/smectite of both the shales and sandstones with depth, changing from randomly oriented mixed-layer clay in the top 1,000 m, through mixed-layer clays with short-range ordering at intermediate depths, to phases exhibiting long range ordering at depths greater than 3,000 m. The XRD data also emphasized that throughout the sequence, the expandability of the mixed-layer clays in the shales was strictly identical to that of the mixed-layer clays in the adjacent sandstones. Qualitatively, a graph of percentage of illite layers in the mixed-layer clay vs. depth resembled that reported by Hower et al. (1976) for the Gulf Coast shale sequence and Jennings and Thompson (1986) for the delta of the Colorado River.

The clay size-fractions from shales and associated sandstones of the Mahakam delta deposits were separated following a gentle disaggregation technique. In the uppermost part of the sequence, the K-Ar ages of clay size-fractions from the shales are reasonably close to those from adjacent sandstones. In more deeply buried sediments the K-Ar ages of the clay minerals separated from the two lithologies differ considerably from one another (Fig. 14). Ages of the $<0.4\mu\text{m}$ clay fractions from the shales decrease from 80 Ma near the surface to 52 Ma at 3,160 m, whereas those from associated sandstones decrease from 80 Ma near the surface to 25 Ma at 2,595 m. TEM observations showed considerable morphological differences between the clays from the two types of rocks. The $\delta^{18}\text{O}$ values of the $0.4\mu\text{m}$ clay fractions from shales decrease from +14.7

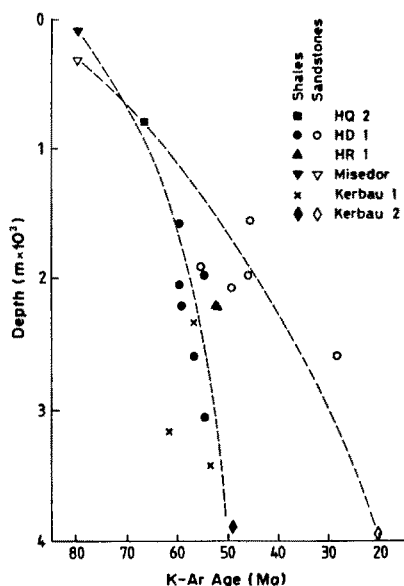


Figure 14: Variations of K-Ar ages of clay fractions ($<0.4\mu\text{m}$) between shales and associated sandstones from the sedimentary sequence of the Mahakam delta deposits, Indonesia (Rinckenbach, 1988)

per mil to +12.6 per mil, while those from the associated sandstones decrease from +15.6 per mil to +10.5 per mil. Rinckenbach et al. postulated that the isotopic and morphological differences between the clays in the two lithologically distinct rock types require two distinct mechanisms of clay alteration. They proposed that the mixed-layer clays in the shales evolved by a process of transformation within existing clay structures, whereas similar clays in the sandstones grew by a process of dissolution and reprecipitation. Different water/rock ratios, and the resulting differences in chemical environments in the two lithologies seem to have been responsible for the differences in mechanism. Temperature is clearly not the factor responsible for the difference. If the proposal is correct that the alteration of shaly clay minerals during progressive burial does not occur through a mechanism of dissolution-recrystallization of pre-existing clay structures, it might be the reason why complete homogenization of O isotopes among different clay size fractions was not observed, even at great depths, in the Gulf Coast shales studied by Yeh and Savin (1977).

Diagenetic Processes in Bentonites

Mineralogic and K-Ar studies of diagenesis of Gulf Coast shales have shown that the rate and extent of conversion of smectite layers to illite layers in mixed-layer illite/smectite depends upon temperature and time, as well as on the availability of K and probably of Al. But the model of illitization for the Gulf Coast shales may not be applicable for illitization elsewhere. This is evident for the middle Devonian K-rich bentonites in eastern North America. Most of these bentonites were never buried sufficiently deeply to reach the temperatures at which smectite layers were converted to illite layers in the Gulf Coast. Also, the source of K incorporated in the mixed-layer clays of the bentonites was neither feldspar nor mica in the volcanoclastic sediments, as both the feldspar and the mica concentrations remained more or less unchanged as illitization progressed (Huff and Turkmenoglu, 1981).

Elliott and Aronson (1987) analyzed the K-Ar ages of mixed-layer illite/smectite from Middle Ordovician bentonites from Alabama, Tennessee, Virginia, and Kentucky in the southern Appalachian basin. The K-Ar ages of the $<0.125\mu\text{m}$ clay fractions, which were free of detrital non-clay minerals, fell in a narrow range between 272 and 303 Ma. This suggested that a widespread illitization episode of short duration had occurred during late Pennsylvanian/early Permian time. Elliott and Aronson proposed that this might have occurred as the result of expulsion of K-rich, hot, saline fluids from deeper parts of the basin to the edges during the Alleghenian orogeny.

ISOTOPIC INDICATORS OF PALEOTEMPERATURES AND PALEOHYDROLOGY IN SEDIMENTARY BASINS

Estimation of Paleotemperatures

Attempts to use O isotopic fractionations between cogenetic

diagenetic minerals in clastic sediments have met with only limited success. This approach is generally not applicable to sandstones because only very rarely does petrographic examination indicate that more than one diagenetic phase forms at a time. Therefore, in general, there is no expectation that the diagenetic minerals in a sandstone formed in isotopic equilibrium with one another.

Yeh and Savin (1977) attempted to use the O isotope fractionation between coexisting fine-grained clay and fine-grained quartz in three sequences of Gulf Coast shales as an isotope geothermometer indicative of the maximum temperature reached during burial. They used a clay fraction $<0.1\mu\text{m}$ and a quartz size range of 0.1 to $0.5\mu\text{m}$. They reported that isotopic temperatures approached measured borehole temperatures progressively with increasing depth, but the two were never concordant in the Gulf Coast samples, even at temperatures as high as 170°C . It is possible that accurate isotope geothermometry of shales heated to temperatures of 170°C or less might be possible under some circumstances, especially if very fine grained clay and quartz were analyzed, but this has not been well explored. Eslinger and Savin (1973) calculated temperatures from $\delta^{18}\text{O}$ values of quartz and illite in a series of outcrop samples from the Precambrian Belt Supergroup, Montana. These temperatures, between 225 and 310°C , are consistent with the maximum burial depths of 5.5 to 6 km estimated from stratigraphic and structural considerations.

Characterization of Water-rock Interactions

Eslinger and Savin (1973) calculated the $\delta^{18}\text{O}$ value of the fluid with which the clay and quartz of each of several Belt Supergroup samples had equilibrated (at the temperature indicated by the isotopic fractionation between the two phases), and concluded that the fluids were all greatly enriched in ^{18}O (+7 to +11 per mil). Those high $\delta^{18}\text{O}$ values indicated that the fluids had evolved through interaction with sediments under conditions of very low water/rock ratio. In other words, each rock volume had been largely closed to the movement of water when isotopic exchange between the

quartz and clay occurred. Yeh and Savin (1977) calculated the $\delta^{18}\text{O}$ values of the fluids with which the finest size fractions of clay might have equilibrated in their Gulf Coast wells. These calculations were based on the $\delta^{18}\text{O}$ values of the clays and measured borehole temperatures. Consistent with the calculation of $\delta^{18}\text{O}$ values of diagenetic fluids in the Belt Supergroup (Eslinger and Savin, 1973), the calculated $\delta^{18}\text{O}$ values of the fluids which exchanged with the Gulf Coast shales ranged as high as +11 per mil, suggesting very low water/rock ratios. Marked differences between calculated fluid $\delta^{18}\text{O}$ values at different depths in the holes suggested a lack of communication between the fluids at different depths. Since that time, Kharaka et al. (1977) and Milliken et al. (1981) have measured $\delta^{18}\text{O}$ values of pore waters from the Frio Formation in the Gulf Coast and found values between approximately +3 and +7 per mil, in general agreement with the values calculated by Yeh and Savin (1977).

Suchecky and Land (1983), in a study of the burial diagenesis of the Jurassic and Cretaceous volcanoclastic mudstones and shales of the Great Valley Sequence, California, modeled the change in ^{18}O values of clay and pore water in a hypothetical system of clay-rich sediments undergoing burial and conversion of smectite to illite. The results of the calculation depended upon the parameters used. A reasonable choice of parameters yielded calculated $\delta^{18}\text{O}$ values of illite/smectite that were consistent with the measured values. Corresponding calculated $\delta^{18}\text{O}_{\text{fluid}}$ values were as high as 7 to 10 per mil at depths where temperatures reached 175°C. These values are similar to the values measured in the Gulf Coast shales.

CONCLUSIONS

Clay minerals mostly retain their pre-depositional isotope signature in a sedimentary basin, unless they have undergone major alteration or recrystallization. The isotopic data of clays which may have completely recrystallized can be used as a tracer for syn-sedimentary and burial history of the sediments, which include dis-

tinct events of diagenesis, and for reconstructing paleotemperatures and paleohydrological conditions. However, it is often very difficult to determine whether a clay fraction is entirely detrital, authigenic or a mixture of the two.

The mechanisms of epigenetic and diagenetic clay formation have not been discussed here in detail, because these processes have not yet been clearly understood. Presently the debate is between primary precipitation, dissolution-recrystallization, and lately, Oswald ripening advocated by Eberl et al. (1990). It should also be considered at this point that "punctuated diagenesis", as it was suggested by Morton (1985), seems to be only possible under abnormal thermal conditions which cannot be met in sedimentary basins having average thermal gradient.

Among the criteria which should be considered for distinguishing between epigenetic/diagenetic and detrital clays in any study in which time of sedimentation is to be determined by isotopic dating methods, we suggest the following:

- field observations and/or visual examination of the core samples in their stratigraphic and structural context,
- careful petrographic observations to determine the temporal relationships among detrital and authigenic or diagenetic mineral phases,
- careful separation of a range of fine clay fractions following gentle disaggregation of the rocks to avoid size reduction of the coarse detrital components,
- thorough characterization of the clay fractions including determination of their mineralogic and crystallographic properties,
- observations of the clay particle morphology by SEM and TEM,
- chemical analysis and Sr isotopic determinations of paragenetic phases, such as carbonates or sulfates, associated with the clay fractions, or of the formation waters when available.

One of the most important steps in isotopic studies of clay materials is their separation and characterization. Separation procedures are not generally very difficult but are usually very time consuming. To avoid this, attempts are now underway in a number of laboratories to develop microprobe techniques for

isotopic analysis of unseparated minerals within rock samples (Shanks and Criss, 1989; Girard and Onstott, 1991; Clauer et al., this volume). These techniques, which involve either secondary ion mass spectrometry (SIMS) or spot-heating with a laser beam, may in the future eliminate some of the experimental problems, and the enormous expenditure of time required for the separation of clay minerals.

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