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GEOTHERMAL ALTERATION OF CLAY MINERALS AND SHALES: DIAGENESIS

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TECHNICAL REPORT

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GEOTHERMAL ALTERATION OF CLAY MINERALS AND SHALES: DIAGENESIS

TECHNICAL REPORT

July 1979

Charles E. Weaver
Georgia Institute of Technology
Atlanta, GA 30332

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EXECUTIVE SUMMARY

The objective of this report is to perform a critical review of the data on the mineral and chemical alterations that occur during diagenesis and low-grade metamorphism of shale and other clay-rich rocks--conditions similar to those expected from emplacement of heat-producing radioactive waste in a geologic repository. The conclusions drawn in this document are that the following types of alterations could occur:

Smectite alteration - Because of their high water content (20 to 40 percent) and relatively rapid reaction rate at low temperatures, smectites are the clay minerals most likely to be affected by heat. Water loss and mineralogic changes caused by an increase in temperature will increase the porosity and permeability of the shale. This should increase the rate of water movement and decrease the structural stability of the shale. The pore water in smectite will presumably move towards the heat source. Interlayer water will then be released from smectites at temperatures encountered in a repository for high-level radioactive waste. This water will be transferred to the pores and may initially cause an increase in porosity and plasticity. As the original and new pore water moves into the repository the thermal conductivity of the shale will decrease and the temperature increase; fractures may develop and settling may occur. The structural stability of the shales in the immediate vicinity of the repository is likely to be weakened. Only minor chemical and mineralogical changes should occur in the dehydrated shale; however, where water is present chemical and mineralogical changes (conversion to illite and chlorite) could begin at temperatures as low as 40°C and continue to temperatures in excess of 300°C. Some of these changes may take place over a period of a few years or less. These mineral transformations will increase the grain size of the clay minerals. This should cause an increase in porosity and permeability, facilitating the movement of water through the shale.

Ion mobilization - Permeability barriers and high pressure zones may be created in shale when ions precipitate from solution. This may create problems but in the long term could be beneficial. The heat generated by radioactivity will increase the solubility of the minerals and accelerate chemical changes. This should cause an increase in the ion concentration of the shale pore waters. The mobilized ions (Si, Mg, Fe, K, Ca, Na) will migrate along the temperature gradient and at various intervals precipitate and cause a decrease in the porosity and permeability of the shale and interbedded sandstones and siltstones. This could lead to the development of high pressures in the vicinity of the repository and increase the possibility of rock failure. As the temperature of the repository decreases the possibility of problems arising from the formation of high pressures should decrease. Ultimately a permeability barrier should be beneficial because it will inhibit the flow of water into and out of the repository.

Illitic shales - It is unlikely that heat generated by radioactive waste will cause any major chemical or mineralogical changes in shales with a high content of illite. In illitic shales the possibility of rock failure and water migration will be minimal. Most illite-rich shales have been exposed to burial temperatures of 200° to 300° C for millions of years and contain <5 percent pore water and <5 percent water-bearing clay layers.

Kaolinite reactions - The porosity and permeability of thin sandstone and siltstone beds in shales can be modified, probably decreased, by the formation of kaolinite. Moderate (50° to 100° C) increases in temperature, particularly if organic material is present, will cause kaolinite to form from pre-existing minerals. Kaolinite is a minor component of most shales and though it can be altered in the temperature range of 80° to 220°C, the alteration should have little effect on the physical properties of the shale.

<u>Chlorite reactions</u> - Porosity and permeability, in both shales and interbedded sandstones and siltstones can be decreased by the formation of chlorite. Chlorite can form by the alteration of other clay minerals at temperatures as low as 70°C. At approximately 200°C ions can be mobilized to the extent that chlorite may grow in fractures and other voids that might develop after the temperature is increased.

<u>Organic reactions</u> - Methane and CO_2 could create pressure problems in the repository. For this reason, rocks with a high organic content should be avoided. Most shales contain 1 to 3 percent organic material. When the temperature is increased, starting at <50 C, organic material will decrease in porosity and moisture content and methane and CO_2 will be released. Oil may be generated in the temperature range of 65 to 150 C; condensate, wet gas, and methane may be produced at higher temperatures. If the shale has been previously exposed to high burial temperatures these reactions will not occur.

<u>Paleotemperatures</u> - It is essential that the maximum temperature to which a shale has been exposed be determined before it is considered for a repository site. Knowing this, it should be possible to predict the reactions that will occur when the shales are exposed to additional heat. Changes in both organic material and clay minerals can be used to determine the maximum paleotemperature to which a rock has been exposed; however, the reaction rates for organic material are more time dependent than those for the clay minerals. Thus, the clay minerals should be a more accurate geothermometer.

<u>Low temperature shales</u> - When shales are subjected to temperatures of 200° to 300°C for hundreds of years, chemical, physical, and mineralogical changes

will occur. The extent of these changes will depend largely on the maximum burial temperature to which the shales have previously been exposed. Montmorillonitic shales and shales with mixed-layer illite-montmorillonite containing a high content of montmorillonite layers have not been exposed to high burial temperatures and will undergo the most extensive changes. The most serious change will probably be the release of interlayer water and the development of shrinkage cracks and fractures. This will increase porosity and permeability and decrease the rock strength. Bench tests and field tests will need to be conducted to determine the seriousness of this problem; however, because of the effects of time on the reactions, the tests may have limited predictive value. Though montmorillonite may be dehydrated in a few minutes, it may require several years, or considerably longer, to convert it to illite.

High temperature shales - Illite-chlorite shales, largely of Paleozoic age, which have been subjected to burial temperatures in excess of 200°C will undergo only minor changes when exposed to heat that produces temperatures of 200° to 300°C. The heat will have relatively little effect on the adsorption properties of illite. Water problems will be minimal and structural strength should not be decreased. Additional bench and field tests will have to be made to confirm these conclusions. Because shallow buried shales commonly contain fractures and surface waters it may be necessary to conduct field tests at a depth of approximately 300 m (1000 feet) to obtain realistic data.

Phase equilibrium - Theoretical and experimental phase equilibrium studies provide an insight to the phase changes which occur in shales as temperature and pressures change. However, because of kinetic restraints, information from such studies can be considered only a crude approximation of what happens in the natural system where time is a major factor in overcoming sluggish reactions.

Experimental phase equilibrium studies of shales rather than individual clay minerals could possibly provide information that would be useful in predicting the long term effects of heat on in-place shales.

CONCLUSIONS AND DISCUSSION

Shales and other rocks containing a high content of clay minerals (Weaver, 1977) have a number of properties that make them an attractive host rock for a radioactive waste repository. These properties include low porosity and permeability, good sorptive characteristics, low solubility, and the potential for plastic flow. These properties would all be modified by the heat generated by radioactive waste if a radioactive waste repository were established in a shale deposit. The nature of the short-term response of the rocks to heat can be established by laboratory and field studies; however, the response of clay minerals and associated minerals to heat depends on time and can best be established by examining the diagenetic reactions that have occurred in the natural system.

The available data indicate that the heat (200°-300°C) from radioactive waste could probably cause some layer contraction in montmorillonite in a few months. Layer contraction due to diagenesis (permanent dehydration) will be a major factor over a short time interval only if appreciable pore water is present; however, if the pore water is removed, the layers will contract due to thermal dehydration. In the latter case, the contracted layers will have the capacity to rehydrate. This type of dehydration could occur after the clays are exposed to temperatures of 100° to 200°C for several hours. In either case, the cation exchange capacity will be considerably reduced. Contraction will increase with time and extend outward a hundred meters or so from the repository. The release of interlayer water and the development of new pore volume and pore water will be greatest in the vicinity of the repository and decrease outward. It has not been established exactly where this water will go. Temperature will increase towards the repository, and porosity and permeability will decrease in the opposite direction. A pressure buildup could occur. If thin but continuous sandstone or siltstone beds are present, they could serve as channels through which some of the hot water or steam can move; however, porous beds of wide lateral extent are rare in thick sections of shale. The development of new pore space (10 to 30 percent) and pore water (from interlayer water) should increase the plasticity of the shale and cause or increase plastic flow. The subsequent loss of pore water will cause a decrease in thermal conductivity and could lead to consolidation and the development of fractures.

Under natural conditions, the Al content of montmorillonite layers has started to increase, probably by the loss of Si, at temperatures of 40° to 60°C. This is accompanied by the release of interlayer water to the pores, layer contraction, and the fixation of K (from K-feldspar) between the contracted layers. The layers are called illite. Initially, only a few randomly distributed contracted layers are formed. Chemical modifications and layer contraction continue at a regular rate until 70 to 80 percent of the layers are contracted. At the same time, some Mg and Fe may be released from the octahedral layer to form chlorite. The degraded K-feldspar may enter into the reaction. The released Si is believed to form quartz. The exchange capacity is decreased.

The temperature at which 70 to 80 percent contraction is reached ranges from 90° to 160°C. There is little further layer contraction until temperatures are increased to in excess of 200°C; however, chemical changes may continue. A relatively high layer charge is needed to contract the final 20 to 30 percent expanded layers. The temporal distribution of mixed-layer illite-montmorillonite and hydrothermal experiments indicates that reaction rates are relatively rapid and that time is not a major factor. This is in contrast to organic diagenesis, where time is as important as temperature. Calculated activation energies indicate that at 120°C, 80 percent of smectite layers would be converted to illite in approximately 5,000 years. In laboratory experiments, the same amount of contraction was obtained in 167 days at 250°C.

High pressures could develop in montmorillonitic shales due to the formation of permeability barriers similar to those existing in the Cenozoic of the Gulf Coast.

Water released from between the montmorillonite layers has a higher cation concentration than normal pore water. Some of the released interlayer cations (Na, Ca, Mg) and the Si, Mg, and Fe released during the modification of the montmorillonite layers, along with CO_2 from organic material and Si and Al from the degraded feldspar, presumably migrate with the pore water. As the temperature decreases, both as a function of distance and time, secondary minerals such as calcite, siderite, ankerite, dolomite, quartz, chlorite, and kaolinite (if conditions are acid) are deposited in the shale, and in sandstone and siltstone beds, causing a decrease in porosity and permeability. Calcite, kaolinite, and quartz (or opal) can form at temperatures as low as 50°C. Ankerite and chlorite develop at temperatures slightly in excess of 100°C, though some varieties of chlorite can form at temperatures of 60°C.

Under basic conditions, illite can form in thin sandstone and siltstone beds causing a decrease in permeability and possibly porosity. It can form from the alteration of feldspar or possibly from ions derived from the adjacent shales.

From the standpoint of waste storage, it is important to establish the maximum paleotemperature to which a shale has been exposed. Even though some expanded water-bearing layers are present, if the shale has been subjected to temperatures on the order to 200° to 300°C for millions of years it is unlikely that the heat generated by radioactive waste will cause any major chemical or mineralogical changes; however, thermal dehydration could still occur. The problems caused by dehydration will depend on the volume of expanded layers that are present.

Pure 10 A illite is not likely to be affected much by temperatures encountered in a repository; however, Paleozoic illitic shales commonly contain from 5 to 30 percent mixed-layer illite-montmorillonite (4:1 to 9:1). The final 20 percent of expanded layers in the mixed-layer illite-montmorillonite in shales can persist to temperatures in excess of 220°C. At the same temperature, associated sandstones can contain clays with 40 percent expanded layers. The composition of montmorillonite layers is variable. Some presumably have a sufficiently high Al content so that they convert to illite at 40° to 60°C. Other layers have compositions strikingly different from illite. Much higher temperatures are required to convert these layers to illite. The geometry of the charge distribution also requires that the final layers attain a higher charge and undergo more chemical modification to cause contraction than the layers that are contracted at lower temperatures. Chemical constraints, lack of K and Al, may inhibit layer contraction.

When the Na/K ratio is sufficiently high, paragonite can form at temperatures as low as 200°C (anchizone) and can be used as an indicator of miminum temperature.

At temperatures of 200° to 300°C about the only changes that would take place in an illitic shale that had not previously been heated that high would be some slight modification of the structure and fabric of the shale. In the natural system, an increase in temperature is usually accompanied by an increase in pressure, and illite diagenesis produces a decrease in porosity and an increase in shale density. In the vicinity of a repository, overburden pressure should remain constant and the effect of heat on illite might be to cause a slight increase in porosity. Exchange capacity should be slightly reduced by the changes that occur at high temperatures.

The more obvious changes that take place in illitic clays with increasing burial temperature occur in the 2M/1Md ratio, the sharpness ratio, and the crystallinity index. The relative proportion of 2M illite increases with increasing temperature, but it has not been established whether 2M illites form before all expanded layers are converted to illite. The data are conflicting.

As the proportion of expanded layers (most "illites" contain 2 to 5 percent expanded layers or more) decrease with increasing temperature, the width of the "illite" peak decreases. These changes are measured in terms of peak width (crystallinity index) and peak shape (sharpness ratio). Both of these measurements demonstrate that the width of the (001) x-ray peak decreases through the burial temperature range of 100° to approximately 400°C (greenschist facies). At lower temperatures, the peak width and spacing reflects the proportion of expanded or chloritic layers interstratified with 10 A illite layers. At higher temperatures, the peak width can be influenced by crystallinity, flake size, and the destruction of non-10 A layers. It is not known which or if all of these factors are important.

Numerous authors have used crystallinity values and sharpness ratio values to characterize the stages of diagenesis and low-grade metamorphism. The three widely used divisions are the diagenesis zone (montmorillonite to "illite"), anchizone, and epizone (greenschist facies). The boundary values used by various authors are not consistent, and little attempt has been made to relate the boundaries to temperature.

The 10 A/5 A ratio can be used to measure a chemical rearrangement that takes place within a shale. The ratio is apparently a measure of the amount of K that moves from K-feldspar to illite and the amount of Fe and Mg that moves from illite to form chlorite. This rearrangement should cause a change in the physical properties of the shale.

The 10 A/5 A ratio of illite tends to decrease with increase in grade of diagenesis and of metamorphism and presumably of temperature. The ratio decrease is caused by an increase in K and/or a decrease in Fe (accompanied by Mg). Both chemical changes indicate an increase in the "muscovitic character" of the illite. At temperatures less than 200°C, where a mixed-layer phase exists, the 10 A/5 A ratio is strongly influenced by the mixed-layer ratio and is of questionable chemical significance.

When the 10 A/5 A ratio is plotted versus the crystallinity index, there is a great deal of scatter; however, in the Conasauga shale there is a good linear relation between the ratio and the depth of burial. This may be because the samples were from one formation and the original composition of the illitic clays was relatively uniform. When the samples are from one formation the ratio can possibly be used as a geothermometer.

The factors controlling the destruction of kaolinite are so complex that it is unlikely that kaolinite can be used as a geothermometer. In most shales kaolinite is a minor component and its destruction or alteration in a repository shale is likely to cause only minor physical changes. The major problem with kaolinite will occur in the sandstones and siltstones. Elevated temperatures could accelerate the formation of CO_2 from organic material, creating the acid conditions which favor the formation of kaolinite. The newly formed kaolinite should decrease the porosity and permeability; the destruction of feldspar, rock fragments, and possibly some quartz would cause an increase in porosity and permeability. The net effect could be complex. Porosity and permeability will likely decrease in some portions of the beds and increase in nearby areas.

Kaolinite in shales may be destroyed at temperatures as low as 80°C but can persist to temperatures in excess of 220°C under some conditions. In part the temperature of alteration is a function of time, but the organic content (pH) and the composition of the associated clay minerals are probably more important factors. In clay beds associated with coal seams it is believed that kaolinite converts to illite and chlorite when the semianthracite stage (200°C) is reached. In shales it is suggested that the Mg and Fe released from the mixed-layer illite-montmorillonite react with kaolinite to form chlorite. Kaolinite may also alter to an Al-rich dioctahedral chlorite or supply the Al, with the release of Si, for the formation of higher-charged illites. Where kaolinite is abundant in shales, it can be converted to pyrophyllite at temperatures as low as 200°C.

Most sandstones and siltstones interbedded with shales contain more kaolinite than the associated shales. Most of the kaolinite is secondary and formed from feldspar and clay minerals under acid conditions, commonly created by the breakdown of organic material. Kaolinite can start to form at surface temperatures, but formation is probably accelerated with increasing temperature. The kaolinite can convert to dickite at temperatures as low as 70°C, but this is not common. Kaolinite can also persist to temperatures of 325° to 375°C. Experimental hydrothermal studies indicate that in the presence of K, kaolinite readily forms illite.

It can be expected that the heat generated by radioactive waste will cause some chlorite to be formed in nearly any type of shale that has not been preheated to near 300°C. This may cause some minor textural changes. At temperatures slightly below 300°C, chlorite porphyroblasts and veins may form. This chlorite could conceivably fill fractures and other voids that might develop in the shale. In sandstone and siltstone beds, secondary chlorite would tend to decrease permeability but possibly not porosity. It is also possible that low-temperature chlorite will be destroyed when exposed to higher temperatures.

Chlorites can form at surface temperatures when either Mg or Fe are readily available. In soils, Al and Fe hydroxides precipitate between expanded layers to form a chlorite-like material and limited data suggest that minor amounts of chlorite are forming in the present ocean. Authigenic Mg-rich chlorites and mixed-layer chlorite-smectites are relatively abundant in evaporite rocks and tidal carbonate rocks. Fe-rich chlorites and chamosites are commonly present in ironstones.

In shales, chlorite is believed to form as a by-product when montmorillonite layers are converted to illite. This reaction can start at temperatures as low as 70°C. Chlorite is also believed to form from kaolinite when Mg and Fe are present. The formation temperature ranges from 150° to 200°C. Chlorite may also form during the late stages of diagenesis, 200° to 300°C, from material released during the final stages of illite recrystallization. This material usually forms porphyroblasts or veins. In hydrothermal areas, chlorite has first been encountered at temperatures ranging from 130° to 220°C. At higher temperatures it converts to chlorite or trioctahedral mica. Corrensite, regular mixed-layer chlorite-montmorillonite, can form in shales at a temperature of approximately 100°C and persist to temperatures near 300°C.

Chlorite forms at relatively low temperatures in sandstones and limestones. The chlorite fills or lines voids and replaces such minerals as feldspar, biotite, volcanic material, calcite, and montmorillonite. Compositions are highly variable. At a temperature of approximately 150°C the chlorite undergoes a structural transformation. The source material for the chlorite is commonly volcanic material, feldspar, clay minerals, and mafic heavy minerals. Corrensite may form at the same time.

The composition of chlorite formed during diagenesis is dependent on the composition of the host rock and temperature. This makes it difficult to use chlorite as a paleotemperature indicator. However, once formed, the composition of chlorite changes with increasing temperature. The author is presently trying to measure these chemical changes and relate them to paleotemperatures.

The heat from high level radioactive waste could conceivably generate methane gas or oil from the organic material in shales, though the minimum time necessary for these reactions to occur is not known. Methane occurs in very young sediments. The oil is not likely to be a problem, but the methane could produce high pressures and possibly move into the repository. Another problem can arise in shales that have not been previously exposed to high temperatures. CO_2 will be generated and carbonate minerals may be precipitated in the shale pores and in sandstone and siltstone beds. The CO_2 could also decrease the pH to the extent that the feldspars and other minerals would alter to kaolinite, causing further changes in the porosity-permeability system. It would be desirable to select a host shale with a minimum amount of organic material and preferably one that has been exposed for a considerable time to temperatures in excess of 250°C. Most major chemical modifications of organic material appears to be complete by 250°C, though some dry gas may be generated at higher temperatures.

Shales commonly contain 1 to 3 percent organic material. Because this material is continuously changing character as a function of increasing temperature, it is necessary to determine what reactions might be expected. Further, considerable data have been accumulated relating stages of organic metamorphism to temperature.

During coalification there is a decrease in porosity and moisture content and CH_4 and CO_2 are released. Numerous other changes occur but are not particularly pertinent. Coal rank, peat through meta-anthracite, is primarily determined by temperature, but time is also a major factor. Temperatures of 60°C to 150°C will normally produce bituminous coal and 200°C anthracite. Anthracite can be formed at temperatures ranging from 100° to 300°C, depending on the length of time the material has been subjected to the particular temperature.

Coalification of organic material in shales commonly results in the formation of hydrocarbons, particularly if the organic material was derived from lower organisms (algae, animal plankton, and bacteria). Various attempts have been made to relate hydrocarbon generation to coal rank and temperature. Because time is a factor, the temperature values are not consistent.

Methane gas is produced during the early stages of coalification. Oil generation commonly starts at temperatures of 65° to 100°C and ends at temperatures of 130° to 150°C. At higher temperatures, condensate and wet gas are produced, followed by the formation of dry gas (methane) at temperatures generally in excess of 160°C. The liquid hydrocarbon zone generally coincides with the high volatile bituminous and the upper portion of the medium volatile bituminous coal zones. Vitrinite reflectance values for the hydrocarbon zone range from 0.5 to 1.3.

Organic material and clay minerals both progress through diagenetic and metamorphic changes with increasing temperature. Attempts have been made to correlate the changes that take place in the two materials, but correlation is difficult becuase the changes in the organic material are more time dependent than those that occur in clay minerals and the changes in the clay minerals are dependent on rock and water chemistry. The data suggest the clay minerals are more reliable than organic material as paleotemperature indicators.

A comparison of coal rank and metamorphic mineral facies suggests that the boundary between the diagenesis zone and the anchizone coincides with the change from semianthracite to anthracite coal (V.R. 2.5, V.M. 8 percent). On the basis of coal studies, this change in coal rank occurs at an average temperature of 200° C. The boundary between the anchizone and the epizone (greenschist facies) falls somewhere near the boundary between low-rank and high-rank meta-anthracite. This change occurs somewhere between 300° and 400° C. As anthracite can form at temperatures ranging from 100° to 300° C, its relation to specific mineral facies is not good. For example, kaolinite is commonly destroyed at temperatures higher than 200° C and is considered to be destroyed in the anchizone, yet it is commonly present, along with pyrophyllite, in Carboniferous anthracite coals. The persistence of kaolinite in high-rank coals is probably due to the absence of other silicate minerals and a restricted chemistry.

In clay-rich rocks, the diagenetic-metamorphic zonation is based largely on the character of illite. The diagenetic zone-anchizone boundary is based on a crystallinity index of 7.5 (or 4.0) and a sharpness ratio of 2.3, and it has been suggested that it is equivalent to the semianthracite-anthracite boundary. Kaolinite and random mixed-layer illite-montmorillonite are presumed to be absent in the anchizone stage, and pyrophyllite, allevardite, paragonite, and phengite are presumed to be formed. The anchizone-epizone boundary is based on a crystallinity index of 4.0 (or 2.5) and a sharpness ratio of 12. The epizone or greenschist facies in shales is characterized by the presence of muscovite, chlorite, and at a more advanced stage biotite; all expanded layers are gone and Mg and Fe have been removed from the illite, converting it to muscovite. However, phengite with an abundance of Mg and Fe in the octahedral sheet commonly occurs in the greenschist facies.

Most of the expanded layers in mixed-layer illite-montmorillonite are lost at a temperature of 120° to 150°C, in the zone of diagenesis. However, the final 20 percent expanded layers can persist to temperatures well in excess of 200°C (upper anchizone boundary based on coal-rank). The crystallinity index and sharpness ratio of these samples would place them well within the diagenetic zone even though they have been exposed to temperatures higher than 200°C. Illitic clays that have crystallinity values (<7.5) that would place them in the anchizone commonly contain only a minor amount (~10 percent) of mixed-layer material; this material contains 5 to 20 percent expanded layers. Thus, in the argillaceous rock the upper boundary of the anchizone is indicative of a temperature in excess of 200°C, possibly something on the order of 250°C. The lower boundary of the anchizone, upper greenschist facies boundary, is estimated to occur at approximately 400°C.

In Figure 1, I have shown the clay mineral changes which occur in shales during burial and have related these changes to temperature. The temperature scale is a best estimate based on the data discussed. Also shown are the estimated temperature boundaries for the anchizone. Most of the mineral

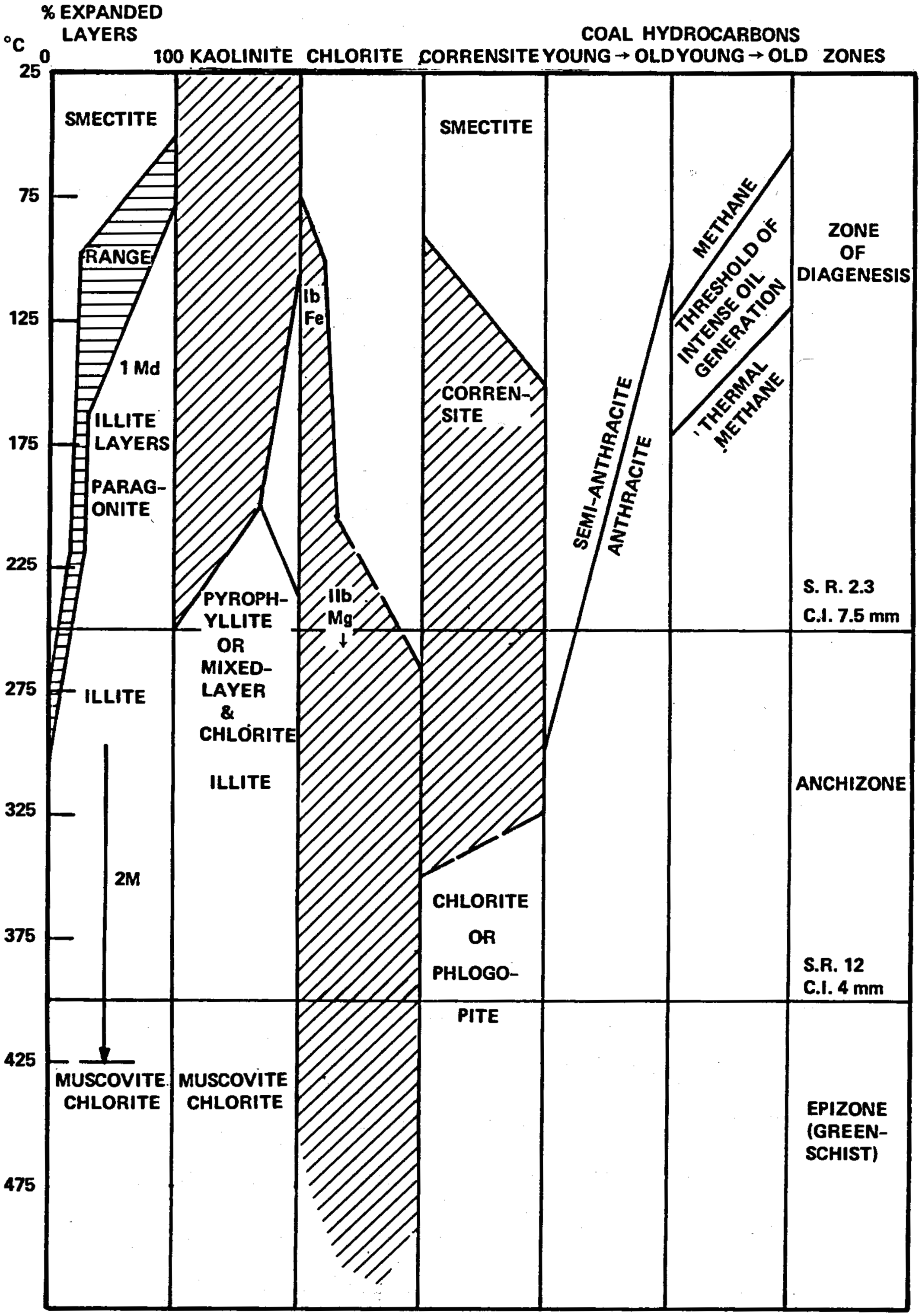


Figure 1. Relation of diagenetic-metamorphic changes in clay minerals and organic matter to temperature. Discussion is on the following page.

Figure 1. This figure summarizes the relation of diagenetic-metamorphic changes in clay minerals and organic matter in shales to temperature. Most mineralogic changes occur over a relatively wide temperature range; however, structural and chemical changes should prove to be useful paleotemperature indicators.

The first column shows the temperature interval over which smectite (montmorillonite) is converted to illite. The area with the horizontal lines indicates the range in the proportion of illite layers that can form at a given temperature. All of the layers of montmorillonite are converted to illite at temperatures of 275 to 300 C. Paragonite may form at temperatures as low as 200 C. At temperatures in excess of approximately 425 C illite is converted to muscovite (or phengite) and chlorite.

The second column shows the reaction of kaolinite to temperature. Kaolinite may be destroyed at temperatures as low as 100 C but can persist to temperatures in excess of 220 C. At 200 C it can be converted to pyrophyllite and if Mg, Fe and K are present, to mixed-layer illite-montmorillonite and chlorite.

Fe-rich chlorite may be formed from a variety of materials at a temperature as low as 70 C or lower. The amount of chlorite formed increases with increasing temperature. The chlorites become more Mg-rich with increasing temperature. Corrensite, mixed-layer chlorite-vermiculite (or montmorillonite), forms at temperatures in the range of 90 to 150 C and persists to at least 325 to 350 C. At higher temperatures it converts to chlorite or Mg-rich trioctahedral mica.

Over a long period of time (old) coal can be converted from semi-anthracite to anthracite at 100 C. In younger sediments a temperature of 300 C is required for the equivalent conversion. Hydrocarbons have a similar time-temperature relation.

The right-hand column shows the zones of diagenesis and low-grade metamorphism. The boundary between the zone of diagenesis and the anchizone is based on a crystallinity index (C.I.) of 7.5 and a sharpness ratio (S.R.) of 2.3. The boundary between the anchizone and epizone (greenschist) is based on a C.I. of 4 and a S.R. of 12.

changes are not as temperature specific as indicated, because variable chemical and mineral compositions will influence the transformation temperature. The sloping boundaries between phases indicate the temperature range over which these reactions occur and also indicate, in a general way, the relative probability of the change occurring at a given temperature.

In an effort to relate the silicate changes to some organic changes, the published temperature ranges are shown for the formation of anthracite and the threshold of intense oil generation.

The color of conodonts changes from pale yellow to black as the temperature to which they have been exposed increases from 50° to 400°C. The color alteration index (CAI) correlates reasonably well with the vitrinite reflectance values of associated organic material. The CAI is not particularly sensitive and can be used only to estimate temperatures to within a hundred degrees. Conodonts occur primarily in limestones, but if limestone beds are present in a shale the CAI can be used to give a general idea of the paleotemperature to which the shale has been exposed.

Finally, it should be mentioned that the zeolite minerals have a diagenetic-metamorphic temperature range similar to the clay minerals, i.e., 50° to 400°C. The zeolites are abundant in volcanic rocks and relatively rare in shales. The zeolites should be thoroughly evaluated before any serious plans are made to use volcanic rocks for a repository.

In conclusion, there is no doubt that when shales are subjected to temperatures of 200° to 300°C for hundreds of years, chemical, physical, and mineralogical changes will occur. The extent of these changes will depend largely on the maximum burial temperature to which the shales have previously been exposed. Montmorillonitic shales and shales with mixed-layer illite-montmorillonite containing a high content of montmorillonite layers will undergo the most extensive changes. The most serious change will probably be the release of interlayer water. Bench tests and field tests will need to be conducted to determine the seriousness of this problem; however, because of the effects of time on the reactions, the tests will have limited predictive value.

Illite-chlorite shales, largely of Paleozoic age, which have been subjected to burial temperatures in excess of 200° will undergo only minor changes when exposed to radioactive heat that produces temperatures of 200° to 300°C. The heat will have relatively little effect on the adsorption properties of illite. Water problems will be minimal. Additional bench and field tests will have to be made. It may be necessary to conduct field tests at a depth of approximately 300 m to obtain realistic data.

Theoretical and experimental phase equilibrium studies provide an insight to the phase changes which occur as pressure and temperature change. However, because of kinetic restraints, this information can be considered only as a crude approximation of what happens in the natural system where time is a major factor in overcoming sluggish reactions. Thermodynamic calculations of equilibrium reactions requires a knowledge of the standard free energies of formation and the composition of the phases involved. Many of these data have not been accurately determined.

A more empirical approach to constructing phase diagrams is based on obtaining experimental information and interpreting it on the basis of observations of natural mineral associations. The phase changes observed in laboratory experiments are generally similar to those observed in nature; however, many of the rates of reaction are slow and it is difficult to determine which phases are stable and which are metastable. Thus, it is difficult to conclude from many of the studies which phases will develop during natural diagenesis where equilibrium conditions are more likely to prevail. Laboratory experiments are of short duration and the temperatures at which phase changes occur cannot usually be projected to the natural system with any degree of certainty.

SMECTITE

Conversion to Mixed-Layer Phase

Smectites, largely montmorillonites, are more temperature sensitive than the other clay minerals. Numerous studies (Burst, 1959; Powers, 1959; Weaver, 1959; Teodorovich and Konyukhov, 1970; Perry and Hower, 1970; Dunoyer De Segonzac, 1970; Weaver and Beck, 1971; Moort, 1971; Foscolos and Kodama, 1974; Heling and Teichmuller, 1974; Hower et al., 1976) have demonstrated that with depth and temperature montmorillonite is transformed to mixed-layer illite-montmorillonite. Many authors relate the disappearance of smectite to specific depths or temperatures but it is not clear what is meant by the "disappearance of smectite". Generally it is assumed that the absence of the 17 A x-ray peak, after the sample is treated with ethylene glycol, represents the absence of smectite. However, calculations (MacEwan et al., 1961; Reynolds, 1967) indicate that expandable clay can contain up to 60 percent 10 A layers (40 percent 17 A layers) and still produce a 17 A peak. Thus, diagenetic effects start at shallower depths and lower temperatures than the depths at which the 17 A x-ray peak disappears. The studies of Burst (1969), Weaver and Beck (1971), and Hower et al. (1976) show that, in the Gulf Coast, diagenetic effects can be detected at temperatures approximately 20°-30°C lower than the temperature at which the amount of layer collapse is sufficient to cause the 17 A peak to disappear (Figure 2). In the Gulf Coast the temperature at which layer contraction is first detected ranges from approximately 50°C for the Pliocene to 85°C for Oligocene sediments. It is not clear why contraction appears to start at a lower temperature in younger sediments. The identification of the depth of initial layer contraction is subjective and further is dependent on the size fraction analyzed. Chemical changes presumably occur before layer collapse is observed by x-ray analysis.

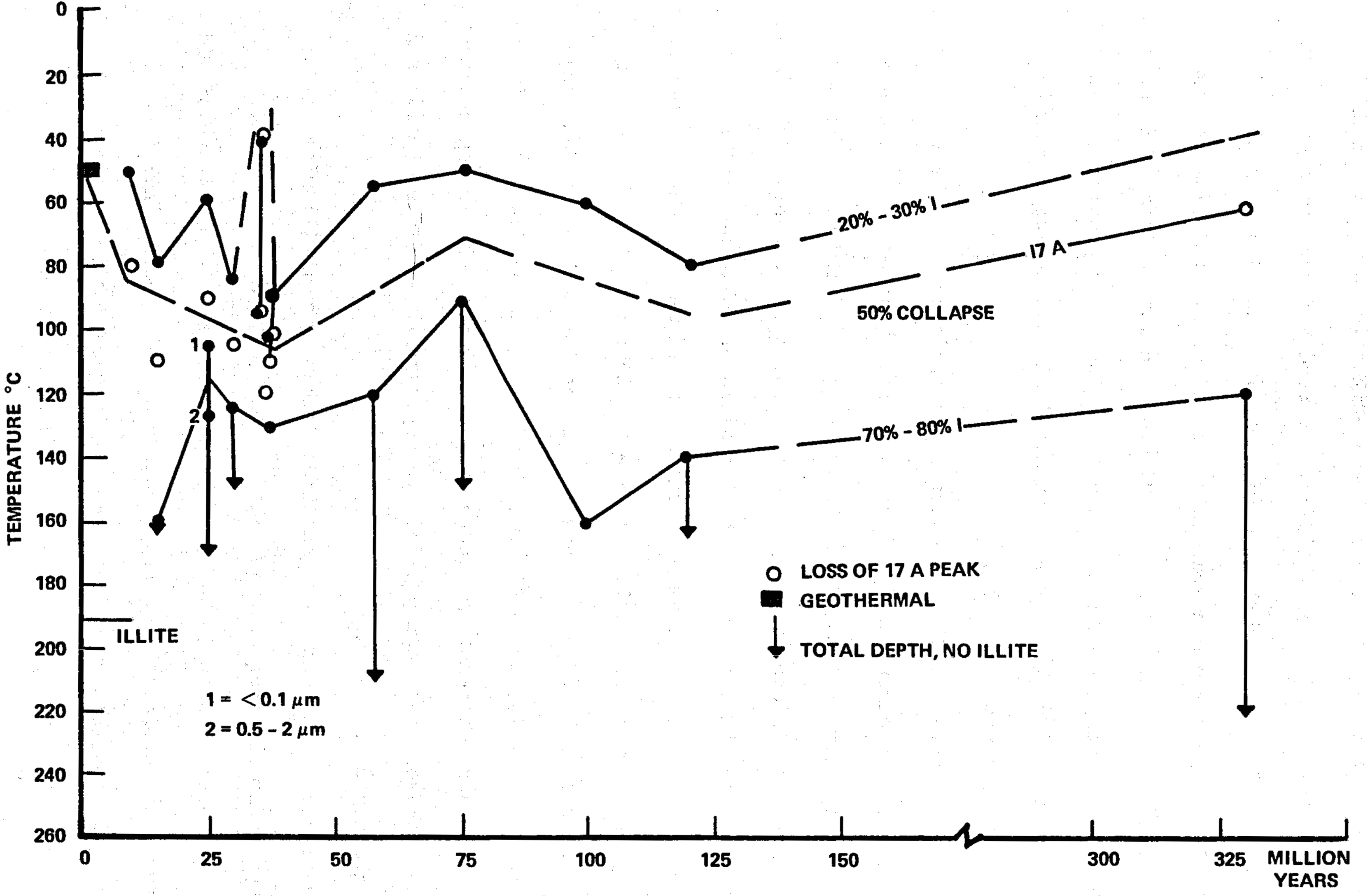


Figure 2. Temperature of conversion of smectite layers to illite as a function of time. Upper line indicates temperature of "initial" conversion (20%-30% illite layers). Bottom line indicates temperature at which 70%-80% illite layers ("stable" phase) are first encountered. Arrows indicate temperature interval over which this latter phase persists with little change. In no instance was montmorillonite completely converted to illite. Dashed line indicates temperature to which 17 A x-ray peak persists. References in text.

Perry and Hower's (1972) data indicate that in the Gulf Coast Oligocene the 17 A peak is lost at a temperature of approximately 105° C and in the Miocene at approximately 110° C. Pusey (1973b) reported a temperature of 120° C. Weaver and Beck (1971) reported that the peak is lost at a temperature of 80°C in Gulf Coast Upper Miocene sediments; Aoyagi et al. (1975) found that it was lost at the same temperature in a Miocene section in Japan. In Cretaceous sediments of North Africa the 17 A peak is lost at approximately 70°C (Dunoyer de Segonzac, 1969). In the Upper Mississippian shales of Oklahoma it disappears at approximately 60°C.

Burst's (1969) data for 29 Gulf Coast wells indicate that the temperature at which collapse of montmorillonite layers is "first" observed (broadening of 17 A peak) ranges from 90° to 130°C with an average of 102°C. It is more likely that these values are the temperature at which 60 percent of the layers collapse rather than the temperature of initial layer collapse. In the offlap sequence of the Gulf Coast, many of the older sediments occur at shallower depths than younger sediments. Thus, in the Eocene the 17 A peak can be gone at depths of less than 1,500 m, whereas it can persist to 3,600 m in younger sediments. Unfortunately, the geothermal gradient generally increases in the direction (north and northwest) of increasing age of the subcropping sediments. With the present data it is not possible to separate the effects of time and geothermal gradient.

In the Oligocene sediments of the Rhine Graben, montmorillonite (17 A peak) disappears at temperatures ranging from 40° to 96° C (Doebl et al., 1974); Heling, 1974), though in one well it persists to a temperature of 115° C. In the latter case subsidence was rapid and relatively recent and it was suggested that high temperatures did not prevail long enough to complete the transformation. The 40° C collapse temperature is believed by Heling (1974) to be due to a high permeability caused by the presence of intercalated porous limestones. If the 40°C value is correct, then layer collapse must have started at temperatures of 20°C to 30°C. This does not seem likely.

Teodorovich and Konyukhov (1970) observed mixed-layer clays forming at relatively shallow depths in the Jurassic and Lower Carboniferous sediments of Russia. They believed this was due to the ready availability of K from biotite.

In the Salton Sea thermal area, the 17 A peak disappears at a temperature of approximately 50°C (Muffler and White, 1969). Studies of the New Zealand geothermal area by Eslinger and Savin (1973 a and b) show that the alteration of montmorillonite to illite is not a simple direct function of temperature. In borehole Br16, smectite persists to a temperature of approximately 150°C, where it gives way to a mixed-layer illite-smectite containing about 10 percent smectite layers. This material persists with depth until a temperature of 180°C is reached. No expanded layers are present at temperatures higher than 180°C. The development of two-layer monoclinic (2M) illite is not linear with temperature. At 895 m (241°C), 2M illite was detected (80%), but at 1356 m (270°C) only 35 percent of the illite was the 2M variety. None was detected at temperatures less than 200°C.

In borehole Br7 at a depth of 162 m (112°C) the mixed-layer clay contains 15 to 20 percent expanded layers; at 433 m (209°C) it contains 90 to 95 percent expanded layers. The latter is believed to have formed metastably, because in most boreholes the upper stability limit of smectite is 130°C to 150°C. Illite develops at 750 m (240°C).

In the New Zealand geothermal area, the hydrothermal conversion of smectite to illite is more complex than normally encountered in sediments which have undergone burial diagenesis. In all likelihood this is because in areas like the Gulf Coast the original sediments contain detrital montmorillonite and beidellite, whereas in the geothermal areas the rocks are volcanic and are first altered to smectite before being converted to illite.

The initial montmorillonite layers which are converted to illite are randomly interspersed among the montmorillonite layers. Random interstratification of illite and montmorillonite layers continue until the illite layers constitute approximately 65 percent. As dehydration and illitization continue, the interlayering becomes ordered (Reynolds and Hower, 1970; Perry and Hower, 1970; and Weaver and Beck, 1971). The rate at which the illite layers form depends on the geothermal gradient (Perry and Hower, 1972, and Doebl et al., 1974) but may not be time dependent. Once an illite-montmorillonite reaches a ratio of 7:3 to 8:2, little additional change occurs until there is a considerable increase in temperature.

In Gulf Coast sediments the collapse of mixed-layer illite-montmorillonite with a ratio of 1:4 to that with a ratio of 4:1 can occur over a temperature range of approximately 40°C. Where the geothermal gradient is low or in younger sediments, the same amount of collapse occurs over a range of 70° to 90°C. In the Paleocene-Cretaceous, the collapse occurs over an interval of approximately 40°C (50° to 90°C)(Dunoyer de Segonzac, 1969). In the Cretaceous of British Columbia (Foscolos and Kodama, 1974), this collapse is reported to occur over a temperature range of approximately 60°C (80° to 140°C). In the Upper Mississippian Spring shales of Oklahoma, the equivalent collapse occurs over a temperature range of approximately 60°C (60° to 120°C). These data (Figure 2) suggest that temperature is considerably more important than time in determining the rate of layer contraction.

In the Gulf Coast Cenozoic sediments, the top of the 7:3-8:2 phase has been observed at a temperature of 90°C in Upper Oligocene (Hower et al., 1976), 120°C in Lower Eocene (Boles and Franks, 1979), 125°C in Oligocene and 160°C in Miocene (Perry and Hower, 1972). In these wells no additional change was observed as temperatures increased to 170°C (maximum temperature reported). In another Upper Miocene section, this phase was not reached at a temperature of 119°C (Weaver and Beck, 1971). In the Cretaceous of British Columbia (Foscolos and Kodama, 1974), the phase first occurs at 140°C. In the Upper Mississippian Springer Shale of Oklahoma, the 8:2 phase first occurs at approximately 120°C and persists to a temperature of at least 220°C (Shell, Rumberger No. 5, 7,254 m). It also persists to 220°C (9,083 m) in the Devonian of the Lone Star Badin No. 1 well in Oklahoma.

For the Cretaceous bentonites of the Denver Basin (Rettke, 1976), there is a curvilinear relation between in situ temperatures and proportion of illite-montmorillonite layers. At 60°C the clay contains 20 percent illite layers and at 100°C 50 percent illite layers. Extrapolation of the curve indicates a ratio of 7:3 would be attained at a temperature of approximately 160°C. As might be expected, reaction rates are relatively rapid during the initial stage of collapse (illite layers increase from 15 percent to 40 percent over a temperature range of 60° to 75°C) and then became progressively slower (over the temperature range of 75° to 100°C the illite layers increase from 40 percent to 50 percent.

Part of the reason for the reported difference in the temperatures required to produce a given illite-montmorillonite ratio is the different size fractions examined. Hower et al. (1976) show that mixed-layer clay in the <0.1 μm fraction attains a ratio equivalent to that of the 0.5 to 2 μm fraction at a temperature of 20° to 40°C lower than that of the coarser fraction. It is not clear why the finer fraction should have a higher percentage of illite layers than the coarser fraction. The initial montmorillonite flake size is small, and flake size is assumed to increase as the proportion of illitic layers increases. The data from Hower et al. suggest otherwise. Dispersion may be a factor.

Figure 2 summarizes much of the data discussed in the preceeding pages. Considering the inherent errors and the subjectiveness of the interpretation the relation between the amount of layer collapse, temperature, and time appears reasonable. Of major interest is the fact that the temperatures at which the various collapse stages are reached do not appear to vary regularly with time. This can indicate that the reaction rate is so slow that time is not a major factor or that the various mixed-layer ratios are temperature-stable equilibrium phases. However, the reliability of the data is such that temperature changes of 20° to 40°C, with time, should be difficult to detect. The availability of K is another factor and may determine the temperature at which the mixed-layer clay is converted completely to illite.

In geothermal areas, under hydrothermal conditions, montmorillonite is completely converted to illite at approximately 200°C; in shales, an appreciable percentage of expanded layers is present at burial temperatures of 220°C. It may be that complete conversion to illite in shales may require a temperature close to 300°C. It should be noted that porous sands in geothermal areas may be completely cemented by secondary quartz at temperatures of <105°C (Elders and Bird, 1973).

Other Complications

It is assumed that there is a continuous increase in the proportion of contracted layers with depth. A plot of the mixed-layer ratio versus depth (Figure 3), for core samples, indicates that there are several reversals. The data of Hower et al. (1976), and other studies of Gulf Coast wells I have

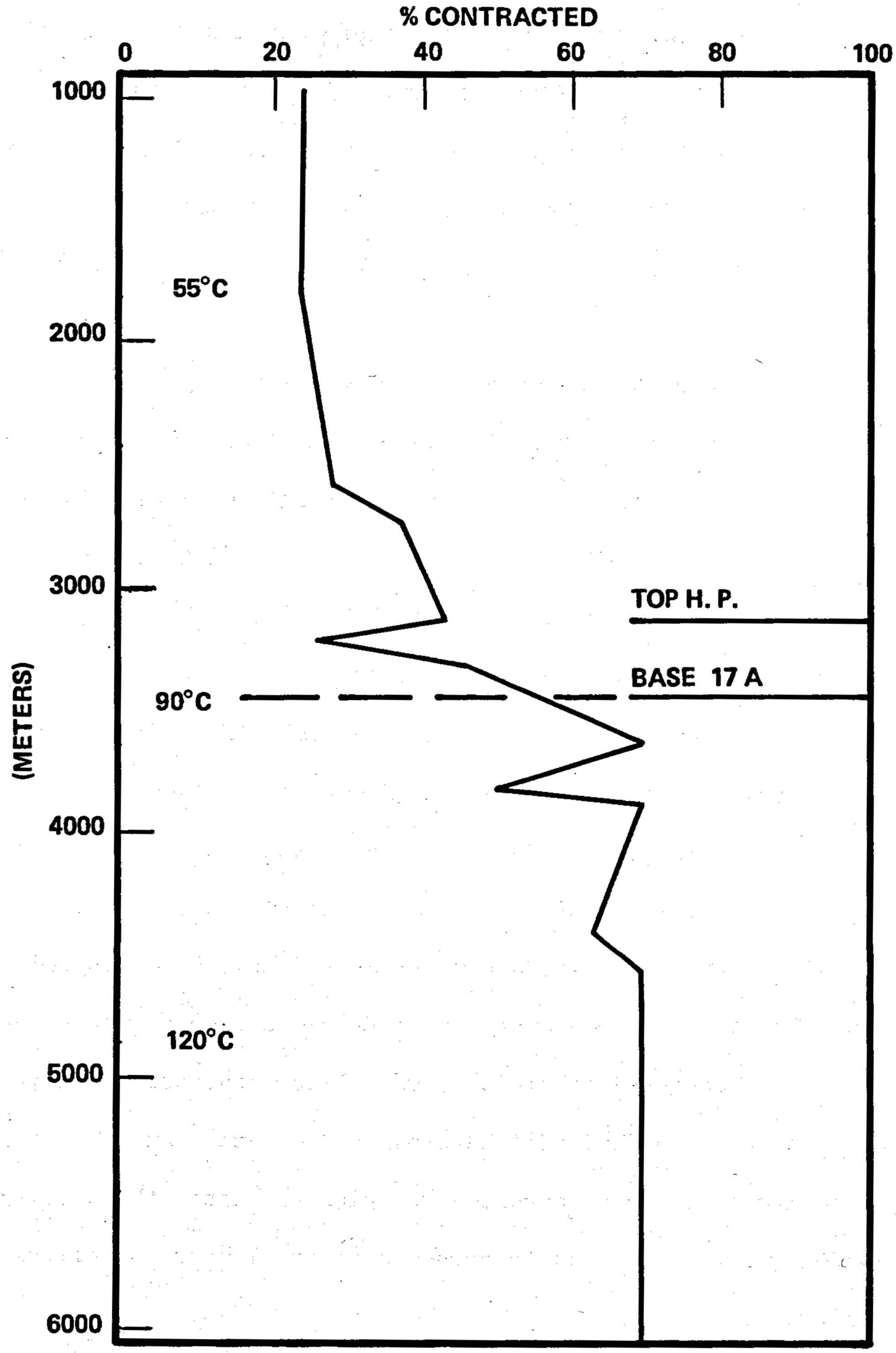


Figure 3. Montmorillonite contraction profile for typical Gulf Coast well (Weaver and Beck, 1971). Reversals appear to be real. Top H.P. indicates top of high-pressure zone. Base 17 A indicates maximum depth of occurrence of 17 A montmorillonite x-ray peak.

made, indicate this is a common feature. A recent study by Boles and Franks (1979) of Lower Eocene (Wilcox) sediments from southwest Texas showed that the stable 20 percent mixed-layer phase was reached at 120°C and remained constant to 150°C. There are numerous reversals, with the proportion of expanded layers being as high as 40 percent. This occurs in both the sandstones and shales, but the clay in the sandstones commonly has more expanded layers. The number of expanded layers in adjacent samples ranges from less than 10 percent to 40 percent.

It appears that some factors other than depth and temperature can effect the contraction of montmorillonite. The aberrations are most likely due to variations in the bulk chemistry of the shale. Eberl and Hower (1977) reported that at temperatures below 300°C Na plus glass of beidellite composition produced a mixed-layer clay similar to that of the K glass. However, at higher temperatures a fully expanded stable phase formed. At even higher temperatures a regular mixed-layer phase developed. The reversals in the increase in the proportion of contracted layers with depth (Figure 3) could conceivably be due to the presence of interlayer Na. Na is at a maximum in the interval where reversals occur. A deficiency of K would also inhibit contraction.

On the basis of variation in ease of expandability, Foscolos and Kodoma (1974) concluded that the mixed-layer clay in the Cretaceous Buckinghouse Formation of Canada consisted of mixtures of illite, montmorillonite, and vermiculite. Weaver and Beck (1971) have presented data that suggest some of the montmorillonite layers are converted to chlorite rather than illite and that the mixed-layer 7:3 is actually composed of equal parts of illite, chlorite, and montmorillonite.

Most recent interpretations of mixed-layer illite-montmorillonite are based on the calculated curves of Reynolds and Hower (1970). Recently

Tettenhorst and Grim (1975 a and b) have challenged some of their interpretations. Among other things, they suggest the following. Variation in background intensity at low angles is due to variations in mean crystallite thickness rather than to interstratification. When the mixed-layer phase contains 90 percent layers with 10 A spacings, the x-ray peaks shift position as the 17 A layer changes from the outside of the crystallite to the middle. When the 17 A layers are imbedded within the crystallites, the calculated x-ray patterns resemble those Reynolds and Hower attribute to ordered interlayering. The presence of one glycol layer on the outer surface of the crystallites produces the same results as the presence of a small percentage of 10 A layers. Some of the expanded layer may adsorb only one layer of ethylene glycol (13.5 A) rather than two (17 A). As little as 10 percent one-layer spacings decreases the resolution in the 7-9°2Θ region, shifts the peak at 9-10°2Θ to lower angles, and broadens the peak between 15-20°2Θ.

In their study of Gulf Coast clays, Perry and Hower (1972) indicated that layer collapse proceeded systematically with depth until 40 percent expanded layers remained. At this point, ordered interstratification is presumed to occur, and the proportion of expanded layers abruptly decreases to 20 percent. Tettenhorst and Grim (1975 b) suggest that the appearance of regularity is caused by the presence of a one-glycol layer complex. The presence of one-glycol layer complexes would cause the amount of 10 A material to be overestimated. My own observations are that layer collapse is usually regular and that no abrupt rate of collapse occurs. In any event, the estimates of rate and amount of layer collapse are not entirely resolved except in a general way.

Tettenhorst and Grim also showed that frayed edges (core and rind) will produce a secondary x-ray peak in the low-angle region (11 to 14 A) similar to that produced as a result of regular mix-layering; however, if a peak is also present with a spacing of 8.5 to 9.8 A ordered interlayering is indicated.

Experimental

Montmorillonite heated under one atmosphere pressure can be dehydrated at from 100° to 120°C. In the presence of K and at relatively high pressures, some layers can be contracted to 10 A at relatively low temperatures, but even at 400°C approximately 25 percent of the layers contain water (Khitarov and Pugin, 1966). Lebedev et al. (1975) heated a montmorillonitic clay at a pressure of 1000 kg/cm^2. They noted no appreciable change at 300°C. At 400° an ordered mixed-layer illite-montmorillonite developed. Hiltabrand et al. (1973) observed no change in the montmorillonite in Gulf Coast muds heated at 200°C under a pressure of 53 kg/cm^2. Hydrothermal studies by Warshaw (1959) showed that it was virtually impossible to produce a pure 10 A mica phase below 400° to 500°C when the composition of the starting material varied much from that of ideal muscovite. "Illites" have been produced at lower temperatures, but the starting compositions were more like that of muscovite than illite.

Eberl and Hower (1976) conducted hydrothermal experiments with synthetic beidellite ($Al_2Si_{3.66}Al_{0.34}O_{10}(OH)_2K_{0.34}$) and Wyoming bentonite (octahedral Mg present). When both were saturated with potassium, mixed-layer illite smectite was formed. The proportion of illite layers increased with increased temperatures (150° to 400°C) and increased run time. An activation energy of 19.6 ± 3.5 kcal/mole was found for conversion of beidellite to mixed-layer illite-smectite. The activation energy and rate constants suggest that the transformation requires the breaking of chemical bonds in the 2:1 layers.

They attempted to determine if the relation between temperature and expandability in the natural system represented chemical equilibrium or reaction kinetics. Their data indicated that if the expandability of buried Gulf Coast clays is a function of the experimentally determined reaction rate, the degree of contraction should be much further advanced. They concluded that expandability is determined by prevailing pressure-temperature conditions rather than the length of time the clay has had to react. The data in Figure 2 tend to support this conclusion.

Further, Eberl and Hower demonstrated that the presence of sodium slows the reaction rate for Wyoming bentonite, though a mixed-layer phase was produced at temperatures as low as 152°C. In their experiments kaolinite was produced (glass → smectite → mixed-layer + kaolinite + quartz). This does not appear to happen during burial diagenesis. They concluded that their kinetic data were consistent with either an equilibrium or a kinetic interpretation of the natural reaction.

In another hydrothermal study of Wyoming montmorillonite, Eberl (1978) found that the rate of collapsed layer formation (rate of increased layer change) was inversely related to the hydration energy of the interlayer cation. He concluded that the greater the hydration energy of the interlayer region, the greater the charge that must develop on the 2:1 layer to cause dehydration and, therefore, the slower the reaction rate. Thus, layer collapse is relatively rapid when Cs, Rb, and K are the interlayer cations and is retarded when Na, Li, and various divalent cations are present.

It is of interest to note that the Li-treated sample, and perhaps the Ba and Ca, produced chloritic layers (tosudite--regularly interstratified dioctahedral chlorite-smectite).

Chemistry

In order for montmorillonite to be converted to illite, K must be added in the interlayer space and the amount of tetrahedral Al must be increased. Studies of the fine, diagenetically formed mixed-layer clay by Weaver and Wampler (1970), Perry (1974), and Aronson and Hower (1976) confirmed that the amount of K increased with depth and temperature as the proportion of illite layers increased. These three studies showed, by K-Ar analysis, that the K moved from the coarse K-feldspar to the montmorillonite as illitic layers formed (thereby decreasing the apparent K-Ar age).

Analyses of the <0.1 μm mixed-layer fraction of a series of samples from a Gulf Coast well (Hower et al., 1976) showed that in addition to K_2O, Al_2O_3 increases with increasing proportion of illite layers. MgO, Fe_2O_3 and SiO_2 decrease with increasing depth. They suggest that the reaction is smectite + Al^{3+} + K^+ = illite + Si^4 + chlorite. The Al and K are believed to come from K feldspar and perhaps mica. The Si released from the smectite is believed to form fine grained quartz. The Mg and Fe released from the smectite are believed to form chlorite. Chlorite was observed to increase with depth. However, an appreciable portion of the chlorite occurs in the >2 μm fraction (and in the >10 μm fraction). The chlorite/kaolinite ratio generally increased with increasing particle size. It is surprising that chlorite should form such large particles. No chlorite was found shallower than 2450 m. This depth coincided approximately with a major formation boundary (Anahuac-Frio). It is possible that, under some conditions, the Mg may be used to form dolomite and the Fe to form siderite or pyrite.

They also found calcite decreasing with depth and believed the decrease was due to dissolution. Weaver and Beck (1971) observed the same trend.

Chemical analysis of the <0.08 μm fraction of mixed-layer clays from the Lower Cretaceous of British Columbia (Foscolos and Kodama, 1974) show the chemical changes that occur with increasing proportion of illite layers:

47 percent illite layers:

$$(Al_{1.52}Fe^{3+}_{0.23}Ti_{0.02}Mg_{0.20})\ (Si_{3.64}Al_{0.36})\ O_{9.80}(OH)_{2.50}K_{0.32}Na_{0.07}Ca_{0.12}\ (94^{\circ}C)$$

82 percent illite layers:

$$(Al_{1.73}Fe^{3+}_{0.05}Ti_{0.02}Mg_{0.17})\ (Si_{3.52}Al_{0.48})\ O_{9.86}(OH)_{2.27}K_{0.60}Na_{0.05}Ca_{0.06}\ (164^{\circ}C)$$

Hoffman and Hower (1978) analyzed shallow and deeply buried bentonite beds from the Cretaceous of Montana and obtained the following average formula for the 0.2 - .5 μm fraction:

15 percent illite layers:

$$(Al_{1.42}Fe^{3+}_{0.22}Mg_{0.40})\ (Si_{3.91}Al_{0.09})\ O_{10}(OH)_2K_{0.08}X^{+}_{0.28}\ (<60^{\circ}C)$$

65 percent illite layers:

$$(Al_{1.67}Fe^{3+}_{0.18}Mg_{0.21})\ (Si_{3.44}Al_{0.56})\ O_{10}(OH)_2K_{0.45}X^{+1}_{0.12}\ (100\text{-}175^{\circ}C)$$

The montmorillonitic shales enclosing the bentonites have mixed-layer illite-montmorillonite ratios similar to those of the bentonite. Both have more chlorite associated with the high illite mixed-layer phase than the low illite mixed-layer phase. Chlorite and mixed-layer chlorite-smectite are common components of the Ordovician K-bentonites (70 to 80 percent illite layers) but are not always present. The chlorite generally increased with increasing depth of burial, but one bed may contain appreciable chlorite and another bed a few feet above or below may have none. Thus, chlorite is not a necessary by-product of the formation of illitic layers from smectite (or volcanic glass).

The source of the K is believed to be the adjacent shales. This does not explain the source of K when the encasing sediments are limestones (Ordovician K-bentonites). Rather than Al being added, it is more likely that Si is removed from the bentonites to the adjacent shales (Weaver, 1953, and Slaughter and Early, 1965).

Analysis by Weaver and Beck (unpublished) of the <0.2 μm fraction of Gulf Coast Pliocene-Miocene clays gives the following results:

20–30 percent illite layers:

$$(Al_{1.24}Fe^{3+}_{0.49}Mg_{0.33})\ (Si_{3.65}Al_{0.35})\ O_{10}(OH)_2K_{0.28}Na_{0.15}Ca_{0.01}\ (50^\circ C)$$

60–70 percent illite layers:

$$(Al_{1.47}Fe_{0.30}Mg_{0.27})\ (Si_{3.53}Al_{0.47})\ O_{10}(OH)_2K_{0.43}Na_{0.09}Ca_{0.13}\ (110^\circ C)$$

Mossbauer and chemical analyses (Weaver and Beck, 1971) of the bulk sample indicate that with depth much of the Fe^{3+} is reduced to Fe^{2+}.

Figure 4 is a graph showing the distribution of the ions in the above structural formulas as a function of percent illite layers. Figure 5 shows the same chemical data plotted in relation to the postulated temperature of formation. Considering the possible variations in the starting material, the relations are good. Both tetrahedral and octahedral Al (and K) increase with increasing proportion of illite layers and temperature. Conversely, octahedral Mg, Fe, and Mg + Fe decrease. Extrapolation of the limited data indicates that a clay with 100 percent illite layers should have the following composition:

$$(Al_{1.80}Fe^{3+}_{0.10}Mg_{0.10})\ (Si_{3.35}Al_{0.65})\ O_{10}(OH)_2K_{0.65}X_{0.10}$$

Extrapolation of the temperature-structural data indicates that this composition should be reached at approximately 190°C. The calculated formula contains only about half the octahedral Mg and Fe found in most illites (Weaver and Pollard, 1973). This could indicate that most illites did not form by burial diagenesis and/or do contain some chlorite or montmorillonite layers.

A plot of tetrahedral Al and octahedral Al versus total Al indicates that as total Al increases the amount of tetrahedral and octahedral Al increases at approximately the same rate. This suggests that rather than Al being added

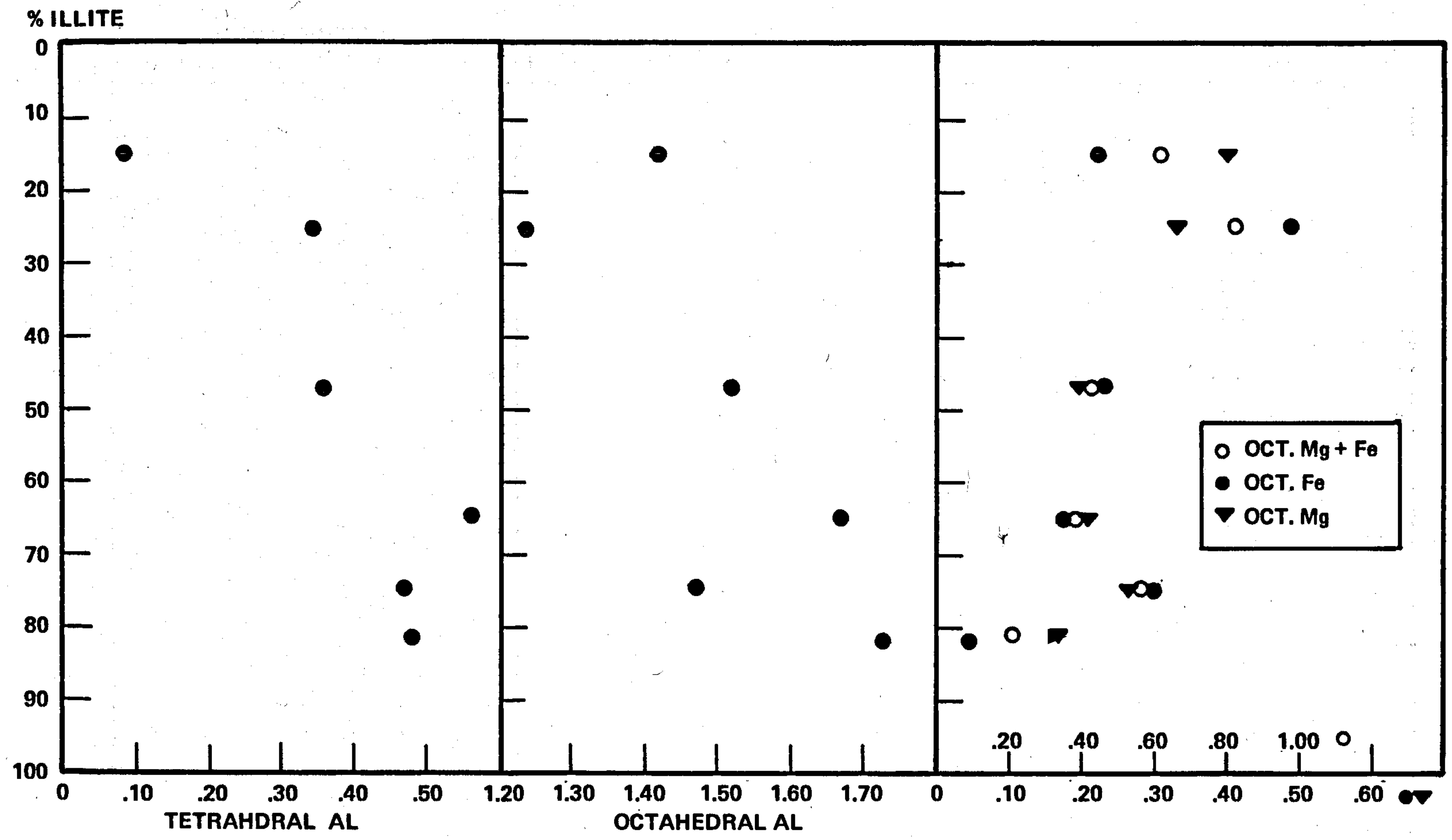


Figure 4. Changes in chemical composition of mixed-layer illite-montmorillonite as a function of percent illite layers.

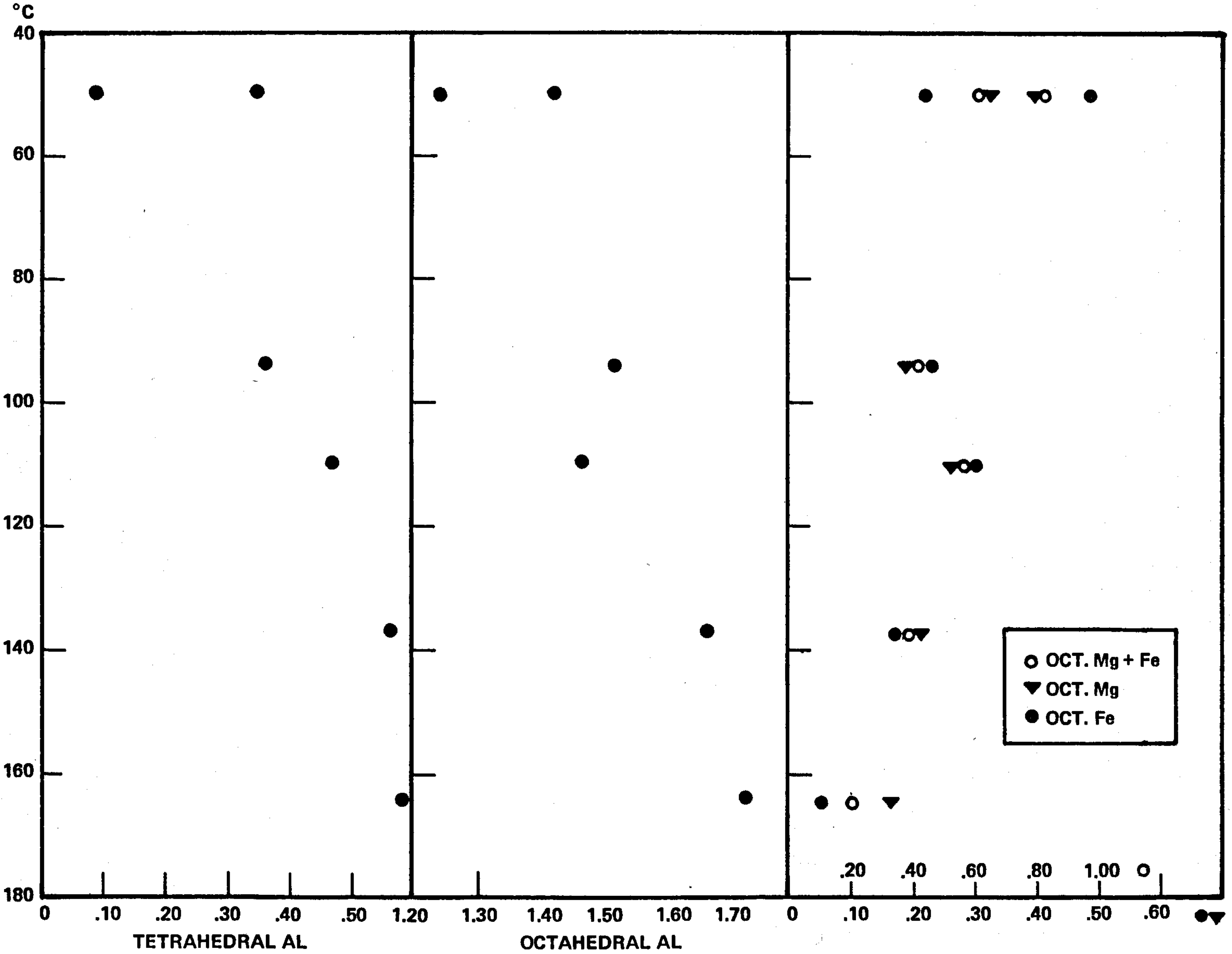


Figure 5. Changes in chemical composition of mixed-layer illite-montmorillonite as a function of temperature.

to the tetrahedral sheet Si is removed from the sheet along with some Mg and Fe from the octahedral sheet. Some of these ions may combine with the Si and Al from the K-feldspar (source of K) to produce a chloritic material.

As the proportion 10 A layers increases, the amount of interlayer K increases. The increase is not linear. When all of the K is assigned to the 10 A layers (x-ray), the amount of K increased linearly, from 0.55 per $O_{10}(OH)_2$ when only 50 percent of the layers are contracted, to 0.8 when 100 percent of the layers are contracted (Weaver and Pollard, 1973). This indicates either that the method of calculating the proportion of expanded and nonexpanded layers is in error, or that the distribution of K is not even and that the last layers contracted contain considerably more K than those that were contracted in the early stages of diagenesis. The interlayer cation suite present during the final stages of diagenesis is different from that present in the earlier stages (the Ca/Na ratio increases with depth). Thus, more charge might be required to produce exchange and contraction in the later stages of diagenesis.

Hower (1967) suggests that the degree of ordering (arrangement of high and low charged layers) will control the proportion of layers that will contract for a given amount of K. He calculated that order interlayering produced more contracted layers (10 A) per amount of K than did random interlayering. As ordering increases with an increase in the proportion of 10 A layers, the amount of K per 10 A layer should decrease with an increasing number of 10 A layers. The trend is exactly the opposite.

Another possibility is that in mixed-layer clays with relatively few 10 A layers, some vermiculitic layers and/or exchangeable K is present and the layers adsorb only one layer of ethylene glycol (rather than two). This would cause the amount of 10 A layers to be overestimated.

Hower's graphs indicating that the amount of interlayer K increases as the number of contracted layers increase are based on data from samples from a wide variety of formations and may not represent a diagenetic trend. Data from individual formations which contain a diagenetic sequence (Weaver and Wampler, 1970; Foscolos and Kodama, 1974; and Hower et al., 1976) do not appear to show such a trend. The K content per layer appears to be nearly constant or may actually decrease as the number of 10 A layers increases.

The chemistry of the bulk samples shows relatively little change with depth, indicating that most of the ions necessary for the formation of the illite layers are generated internally, largely from K-feldspar. Weaver and Beck (1971) demonstrated that most montmorillonitic shales do not have sufficient K, Mg, and Fe relative to Al to be converted to a typical Paleozoic illite-chlorite shale. If the conversion is to occur, they believe that K, Mg, and Fe must be added to the system by migrating upward from the more deeply buried shales. Weaver and Beck's (1971) data show that below 3,330 m K, Mg, and Fe systematically increase relative to Al. Dunoyer de Segonzac's (1969) data for the Cretaceous of North Africa show a similar trend for Mg. Data in Hower et al. (1976) show a decrease in Mg and Fe (where does it go?), and an increase in K relative to Al, with depth. It is difficult to evaluate how much these trends are due to changes in the composition of the detrital material with depth. More data are needed.

Release of Interlayer Fluids

Water

It is not known for certain how many layers of water buried smectites contain. However, the experimental studies of Van Olphen (1963) and Khitarov and Pugin (1966) indicate that water layers in excess of two are removed fairly easily. Studies of buried sediments indicate that the final one or two water layers are removed at temperatures and pressures in the range encountered in the conversion of montmorillonite layers to illite layers (50° to 300°C).

Laboratory experiments involve only temperatures and pressure and do not take into account the increase in layer change which occurs during burial diagenesis. Vermiculites which have a layer charge large enough to allow them to contract to 10 A when K is present contain two water layers. It seems likely that under shallow burial conditions, as the charge in the smectite layers increases, the smectite contains two layers of water until the layers actually collapse. Khitarov and Pugin (1966) found that montmorillonite contained two water layers at 150°C and 5000 atmospheres pressure. One water layer was present at 200°C and 10,000 atmospheres pressure.

An expanded clay with two water layers contains 20 percent water by weight or approximately 33 percent by volume (10 A clay layer, 5 A two water layers). The average shale contains approximately 60 percent clay minerals. If the clay suite contains 80 percent montmorillonite (typical Gulf Coast clay) the amount of interlayer water lost by contraction of all expanded layers would be 9.6 percent. The typical detrital montmorillonite contains 20 percent to 30 percent contracted layers and the mixed-layer phase stabilizes at 70 percent to 80 percent contracted layers at a temperature of 120° to 160°C and persists to 200°C or higher. Thus, through the interval of maximum diagenetic alteration 40 percent to 50 percent of the layers are contracted and 4 percent to 6 percent of interlayer water (by weight) is transferred to the pores. The volume reduction in interlayer space would range from 6 percent to 10 percent. An equivalent increase in pore space and pore water would presumably be created.

Perry and Hower (1972) state that contraction and water loss start abruptly and occur over a relatively short depth-temperature interval. Their data indicates that the collapse rate varies as a function of time and/or temperature. Unfortunately, the two effects could not be separated. In an Oligocene well (geothermal gradient 1.7°C/100 m) the contraction and water release occurred over a depth range of approximately 900 m (40°C); in a Miocene well (1.4°C/100 m) it occurred over a range of 3,000 m (80°C). The data in Figure 2 tend to confirm that most of the water release due to layer contraction occurs over a relatively narrow temperature interval ranging from 40° to 80°C.

The depth-temperature range over which layer collapse occurs is in part a function of the size fraction examined. The data from Hower et al. (1976) indicate that the fine fraction of the original detrital montmorillonite has a higher proportion of illitic layers than the coarser fraction. With increased depth and temperature the proportion of illite layers increases in both size fractions, but not at the same rate. The <0.1 μm and the 0.5 - 2 μm fractions contain 60 percent illite layers at approximately the same depth (3,400 m). Above this depth the proportion of illite layers increases at a faster rate, with depth, in the coarser size fraction; below this depth the situation is reversed. In the <0.1 μm fraction the proportion of illite layers increases from 60 percent to 80 percent over a distance of 500 m and then remains constant for the remaining 1700 m. In the 0.5 - 2 μm fraction, the proportion of illite layers increases from 60 percent to only 70 percent over a distance of 1200 m and then remains constant for the remaining 800 m. The reaction is apparently size dependent. However, with depth the amount of total mixed-layer decreases in the finer size fraction and increases in the coarser size fraction. The data say that as the proportion of illite layers increases in the finest fraction, that portion which has the fewer illite layers becomes coarser and the portion with the most illite layers remains fine. This perhaps could occur if illitization proceeds by dissolution rather than accretion. It is unlikely the data are reliable enough to make such a conclusion. When the whole sample is considered, interlayer water release is spread over a much wider depth-pressure interval than indicated by the published curves. For example, at 170°C the 0.5 - 2 μm fraction (24 percent of the sample) contains 8 percent more expanded layers (32 percent vs. 24 percent) than the less than 0.1 μm fraction (9 percent of the sample) (Hower et al., 1976).

Powers (1967), Burst (1969), and Perry and Hower (1972) have constructed "water escape curves" which are intended to show the contribution of the released interlayer water to the porosity of shales. The meaning of these curves is not entirely clear. The upper portion of the curves, shallow burial, represents the rate of loss of pore water from the mud and the lower part the release of interlayer water to the pores. In addition, the curves are not to scale. Their curves suggest that the released interlayer water is equivalent to one-third to one-half of the original pore water content. Calculations show that the total released interlayer water, over an interval of 1800 m, should amount to approximately 5 percent by weight. Figure 6 contains a curve showing the reduction in pore water content with depth of a typical Gulf Coast shale section. Also shown, approximately to scale, is the contribution of the released interlayer water. Although the contribution of the released interlayer water is not as spectacular as that in the previously published curves, it is probably significant.

Oil

Weaver (1960) established that a relation existed between oil production and the occurrence of expanded clays and suggested that the interlayer water

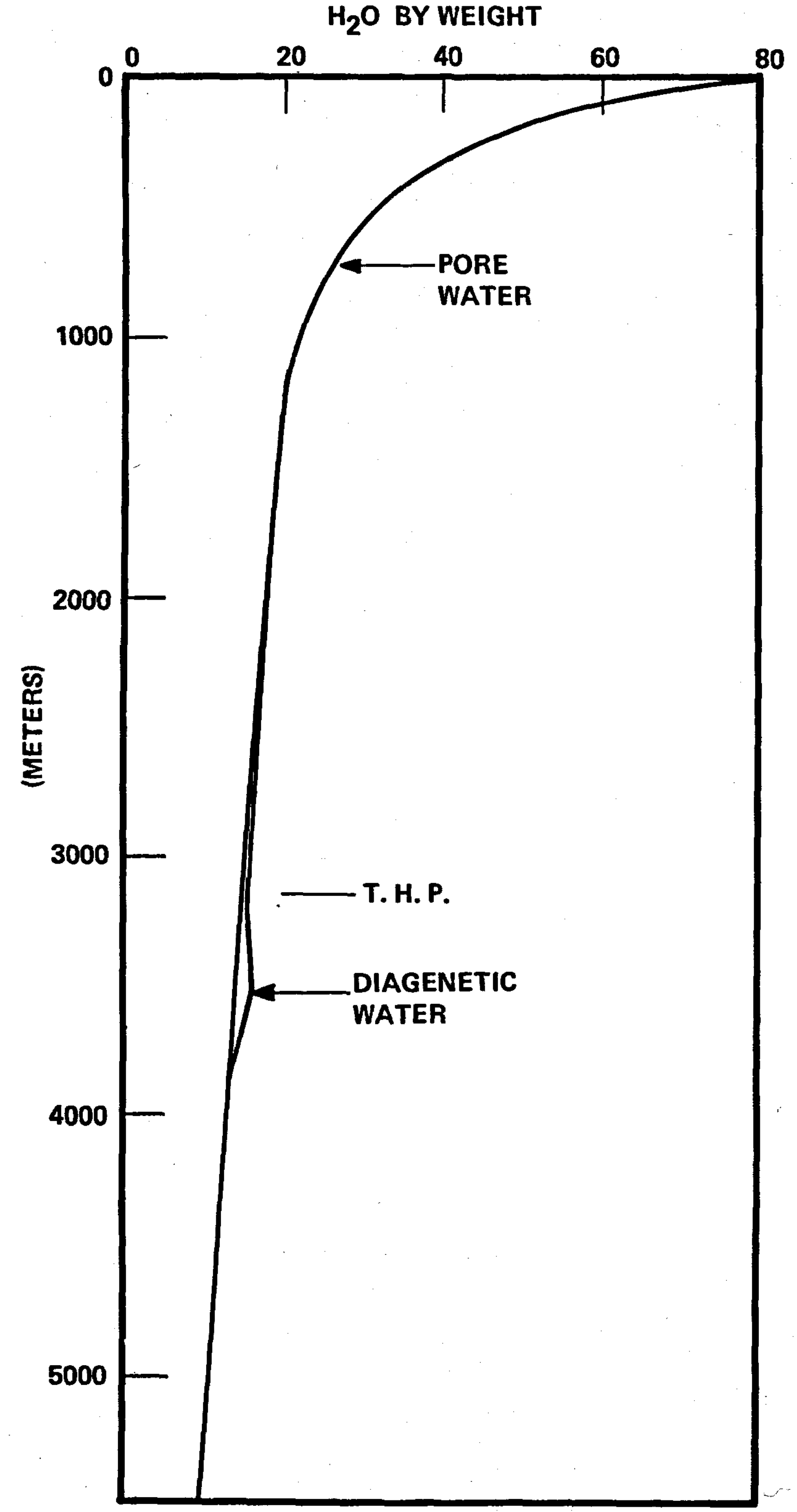


Figure 6. Typical shale pore water curve for early Tertiary Gulf Coast section. Second curve (diagenetic water), between 1,850 m and 4,000 m shows amount of water released by conversion of montmorillonite to illite. Second curve is not cumulative. If all diagenetic water were retained in the shale, the amount of shale pore water below 4,000 m would be increased by 5 percent. T.H.P. indicates general location of the top of the high-pressure zone.

in the expanded clays provided the fluids necessary for the migration of oil after deep burial. Later Burst (1969) constructed a graph showing the vertical distance of Gulf Coast productive zones above and below what he called the second stage dehydration level. Most of the production occurs above this level and is supposed to be related to the upward migration of water released at the second stage dehydration level. His second stage dehydration level is based on the depth or temperature at which the 17 A glycolated montmorillonite x-ray peak "disappears". This disappearance has no particular significance, except that it is relatively easy to observe; however, its identification is highly subjective.

The collapse of montmorillonite starts at a lower temperature and depth than is indicated by the disappearance of the 17 A peak. Depending on the age and geothermal gradient, contraction of montmorillonite layers starts from 600 m to 1500 m above and stops (attains a 4:1 mixed-layer illite-montmorillonite ratio) from 300 m to 1500 m below the depth selected by Burst as the second stage dehydration level. When these limits are plotted on Burst curves for the production-depth distribution (Figure 7), it can be seen that virtually all production comes from the interval between initial collapse of montmorillonite layers and the formation of the stable 7:3 - 4:1 phase. For whatever reason, oil production is concentrated in the interval in which the montmorillonite loses 50 percent to 60 percent of its interlayer water (20 percent to 25 percent of the layers are contracted in the original montmorillonite, and the final 20 percent to 30 percent of layers are not contracted until temperatures of 200° to 250°C). Thus, significant vertical migration of the released interlayer water is not required. Migration need only be local rather than the hundreds of meters indicated by Burst's model.

Connan (1974) discusses the time-temperature dependence of oil genesis and notes that the threshold of intense oil genesis appears at much higher

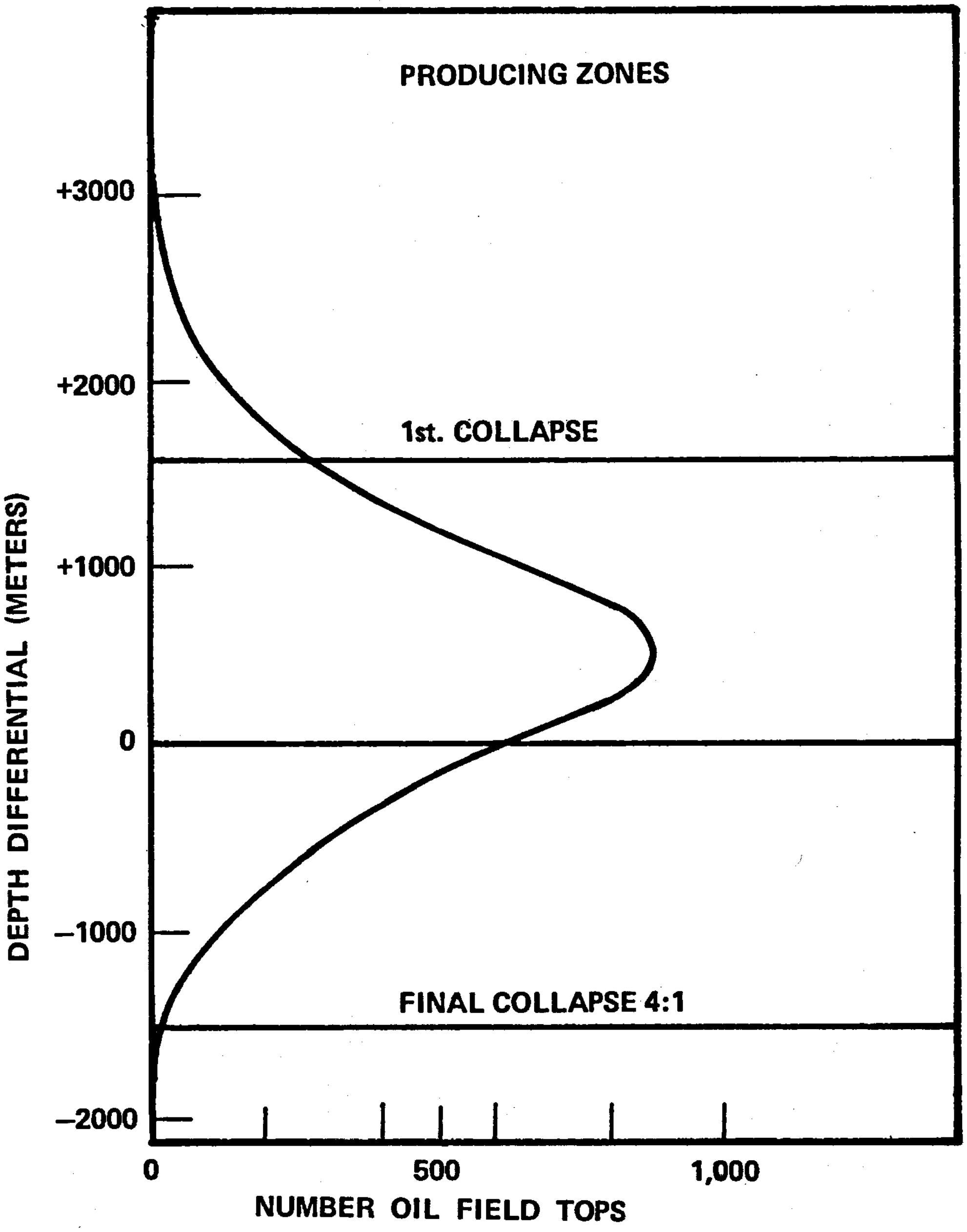


Figure 7. Relation of initial collapse of montmorillonite layers and first occurrence of "stable" mixed-layer phase (4:1) to number of producing fields in the Gulf Coast Tertiary. Production data from Burst (1969). Zero line indicates relative depth at which 17 A x-ray peak can no longer be observed.

temperatures in younger sedimentary series than in old ones. His data indicate that the temperature for the threshold of intense oil genesis decreases from 115° to 120°C for shales 12 m.y. old, to 65° to 80°C for shales 70 m.y. old, to 60° to 62°C for shales 180 to 359 m.y. old. The pseudo-energy of activation is in the range of 11,000 to 14,000 cal/mole. He attributed the low value to the catalytic influence of clay minerals and possible organic matter.

Figure 8 shows the relation of the temperature of the threshold of intense oil generation to the montmorillonite dehydration pattern. For the past 100 m.y., intense oil generation has started near the center of the montmorillonite dehydration zone (1:4-7:3). The data for older sediments are too sparse to be significant. The temperature interval over which the montmorillonite is dehydrated (50° to 150°C) is similar to the temperature interval over which oil is generated (Hood et al., 1975).

To go one step further, it may well be that layer contraction aids in the generation of hydrocarbons. When two or more water layers are present, organic material in the interlayer position may not be in direct contact with the clay surface. When layer dehydration starts, the organic material is brought in closer proximity to the silica tetrahedral surface, and the necessary catalytic reactions can occur to convert the organic material to hydrocarbons. Another important factor may be that the concentration of interlayer cations is increased considerably during the final stages of layer dehydration.

Among other things, the conversion of organic material to hydrocarbons requires a decrease in the size of the molecules and an increase in volatility, mobility, and hydrogen content. Thomas (1949) established that catalytic cracking by Si-Al compounds is caused by the presence of hydrogen ions in the catalysts. The acidity, or exchange capacity, is created by Al^{3+} substituting for Si^{4+} in the tetrahedral oxygen network. Acidity increases with increase

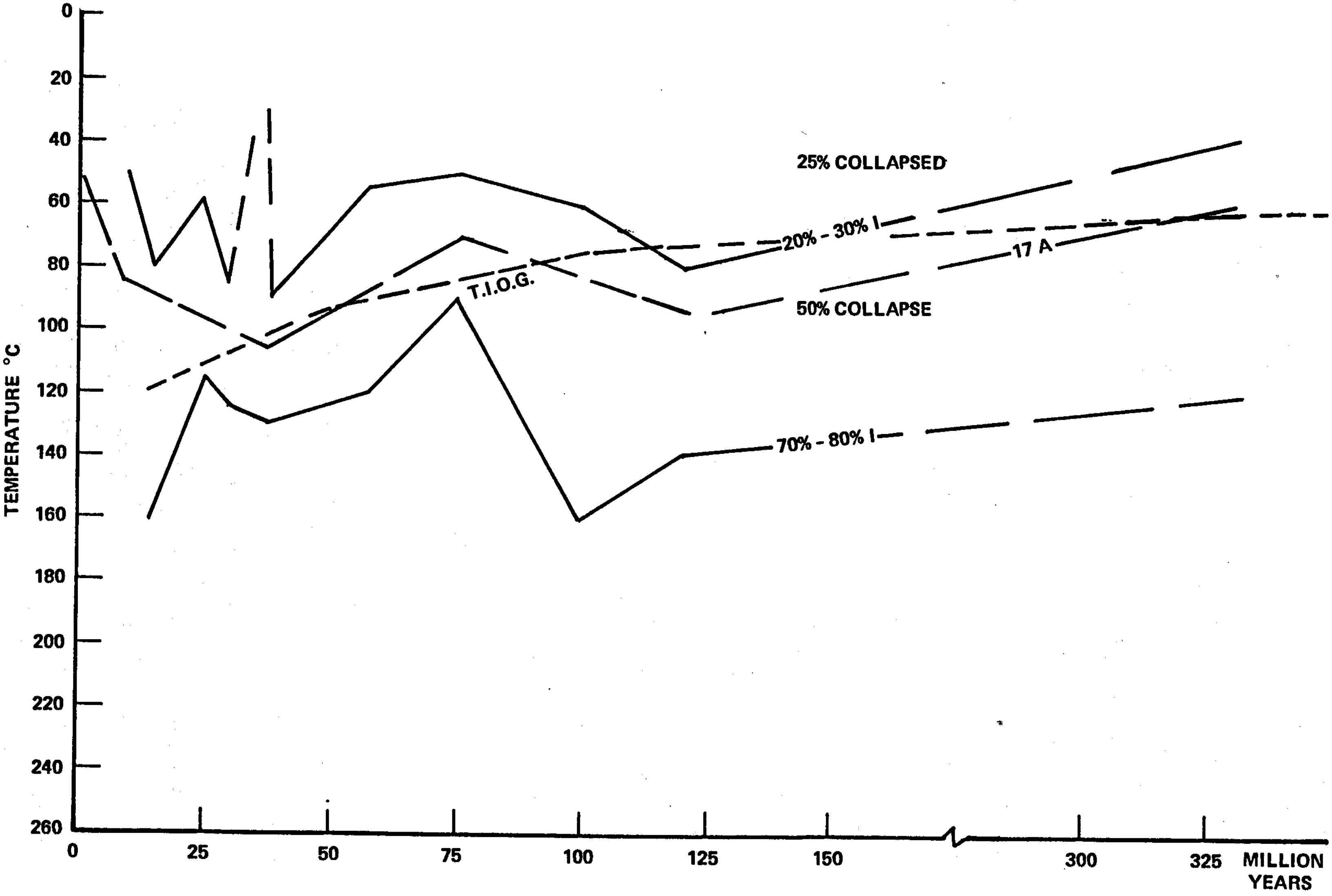


Figure 8. Relation of temperature of intense oil generation (T.I.O.G.) (Connan, 1974) to smectite conversion to mixed-layer illite-smectite. See Figure 2.

in Al^{3+} substitution until the Al/Si ratio reaches one. Mortland et al. (1963), Fripiat et al. (1965), and Mortland (1968) showed that the acidic properties of interlayer water are considerably greater than in normal water. Proton donation increases with the decreasing content of interlayer water. The production of protons from water molecules is related to the electronegativity of the cation. As the electrons are displaced towards the metal ion, the proton is more easily removed. As the water content decreases, the polarization forces are less diluted, and the remaining water molecules become more polarized and better proton donors. The extent of proton donation by residual water in montmorillonite as a function of the type of metal ion increases as follows: $Fe^{3+} > Al^{3+} > Mg > Ca > Na$. Johns and Shimoyama (1972) noted these relations and suggested that preceding the contraction of montmorillonite layers, adsorbed fatty acids undergo progressive decarboxylation and long chain alkanes are produced. With increasing temperature, as the water content of the expanded layers is reduced and proton donating capabilities are increased, alkane cracking occurs.

Tissot (1969) and Tissot et al. (1974) established that there were three basic groups of organic matter in sediments. The three types were characterized by their potential to produce hydrocarbons as burial depth and temperature increased. Ishiwatari et al. (1977) suggested that Tissot's three groups of organic matter were lipid, humic acid, and kerogen. Their studies support the earlier suggestions of Tissot (1969) that the pathway for hydrocarbon production from kerogen is through the formation of liquid products which were preferentially altered to aromatic and aliphatic hydrocarbons. This liquid product would presumably be the material that is adsorbed between the layers of expanded clay, as it is unlikely that much of the original organic material was present in the interlayer position. When humic material is heated, only a minor amount of liquid product is formed. It should be noted that the water between the montmorillonite layers is not, for each layer, reduced systematically from two layers to one layer to a partial layer. This sequence may take place, but on a layer-by-layer basis. Initially, layers with the higher charge contract and lose all interlayer water; the lower charge layers still contain two layers of water. Thus, cracking can occur as the first layers are contracted (50° to 80°C) and can continue until the final layers are contracted. The increase in layer charge required for the layers to contract is largely caused by increasing the Si/Al ratio. The increased charge causes an increase in the concentration of interlayer cations. Both factors should enhance the cracking capabilities of the interlayer region.

Montmorillonite may aid in cracking by providing a source of readily available H ions. A reciprocal action may occur. It is conceivable that by removing H ions the organic material aids in the conversion of montmorillonite to illite. A number of possibilities exist. Mortland et al. (1963) found in their study of the interaction between ammonia and expanding lattices that there was some exchange between the lattice hydroxyls and the adsorbed water. Thus, it is possible that as H^+ is complexed by the organic material in the interlayer material, H^+ from the octahedral OH^- moves to the interlayer position. This would increase the layer charge and facilitate contraction. Essentially, the organic material would act as a pump to remove H^+ from the montmorillonite layers.

Hydrocarbons can apparently form when expanded clays are not present or are present in only minor amounts. The surface or edge of the clay plates may act as a catalyst. However, when the interlayer water is not present, migration should be restricted. The availability of expressed interlayer water for migration may be more important than the catalytic activity of the clay in the formation of commercial deposits of hydrocarbons. Hydrocarbons are present in many shales, but appear to be concentrated in reservoirs primarily in those sediments which contain or contained an appreciable amount of expandable clay (Weaver, 1960). Cordell (1972) made an excellent review of the factors controlling the origin and migration of hydrocarbon.

High Pressure

In some Gulf Coast wells the normal decrease in shale density and porosity with depth is interrupted by a relatively abrupt reversal of trend. After a relatively short interval (150 to 300 m) the normal trend continues (Kerr and Barrington, 1961; Myers and Van Siclen, 1964; Powers, 1967; Weaver and Beck, 1971; Schmidt, 1973). Most of these authors suggest, in one way or another, that the released interlayer water is a factor in causing the density reversal and the abnormally high pressures associated with the reversal. Powers (1967) and Burst (1976) have suggested that the interlayer water has a higher density than pore water and when released to the pores expands, creating high pressures. It has not been established that interlayer water has a higher density than unconfined water.

Changes in water density are not necessary for the formation of high pressures. Bredehoeft and Hanshaw (1968), Fertl and Timko (1970 a and b), Weaver and Beck (1971), Chapman (1972), and others have indicated that high pressures are created by low permeability or low hydraulic conductivity in sections of thick shales. Bradley (1975) has reviewed the many processes which could contribute to the formation of abnormal pressures and concluded that the primary requirement was the formation of a seal and that temperature was the principal source of pressure. He pointed out that porosity loss is not due to overburden stress but is due to a group of interrelated chemical processes which are dependent on reactivity, temperature, surface area, and pressure. The development of high pressures may be dependent on the rate of chemical changes in the shales and on the timing and effectiveness of some forms of seal. This seal need not be a pressure seal at inception. The preseal could restrict water flow and delay chemical process with increases in density. Porosity values in high-pressure zones are similar to those 1500 m to 2000 m higher in the section (Weaver and Beck, 1971, and Schmidt, 1973) suggesting the preseal developed at these depths. Initial layer collapse starts in this same depth range and may be a factor in its development. However, Chapman (1972) calculated that the abnormally high pressures encountered at 3000 m to 3700 m acquire their abnormality at depths of burial on the order of 600 m to 800 m. In any event, once diagenetic reactions are sufficient to cause layer collapse, some of the released Si and Ca can migrate to the barrier zone, where crystallization of quartz (opal) and calcite will further decrease the permeability.

Magara (1975) also concluded that low permeability rather than differences in water density is probably the main cause of high pressures. He pointed out that during burial where a normally compacted shale of relatively low porosity reached the depth-temperature where porosity increased (under-compaction), there would have to be a rebound or volume increase of at least 6 percent. The volume increase due to the proposed difference in water density would be considerably less than this (2 percent). Weaver and Beck (1971) calculated that the abrupt change from low porosity shales to high porosity shales would require the release of six layers of water. This is an unacceptable value at this depth. Barker (1972) used the pressure-temperature-density values of water to show that during burial the heating of entrapped water can create large excess pressure (aquathermal pressuring).

Release of interlayer water to the pores should have no effect on bulk density (Magara, 1975), though it should increase porosity. It is difficult, using heating techniques, to differentiate between pore water and interlayer waters. The major effect of the released interlayer water should be on the chemistry of the pore water; however, because some of the released ions and water are apparently lost from the pores, a direct assessment of the role of the released water is difficult.

Hedberg (1978) suggested that methane, generated thermochemically at depth, is the major cause of overpressuring in shales. Methane is undoubtedly a factor in the formation of many mud diapirs.

As Nagara (1975) has suggested, once the seal has formed and abnormal porosities are developed (compaction disequilibrium), the resulting increase in temperature gradient will accelerate the increase in layer contraction and the release of the interlayer water. Earlier, Lewis and Rose (1970) had noted that as water is a threefold greater insulator than rock, over-pressured zones should act as insulators causing an increase in the temperature gradient. In an interval of 1600 m, the temperatures can increase by 50° to 60°C more than what it would be in the absence of abnormal water content (Timko and Fertl, 1972). The temperature increase is certainly enough to cause a significant increase in the amount of interlayer water released. Thus, the presence or absence of high-pressure water can be responsible for the variations in the depth at which layer collapse starts. Rather than released interlayer water causing high pressure, high-pressured water can accelerate the release of interlayer water.

Montmorillonite is commonly, if not always, abundant in high-pressure shales. The role of montmorillonite may have little or nothing to do with its alteration to illite. Montmorillonite is the only clay that can retain a high pore water content to a sufficient depth and temperature to allow a permeability seal to form and trap a significant amount of fluid.

It is generally assumed that the interlayer water completely fills the entire volume of interlayer space. This need not be. Martin (1960) noted that x-ray patterns can indicate the presence of two water layers (15 A) when there is actually not enough water present to form one complete water layer. Walker (1956) found that vermiculite is fully hydrated (all potential water sites occupied) only when immersed in water or at very high relative pressures. As the vermiculite is dehydrated, the water is lost molecule-by-molecule rather than layer-to-layer, and during most stages of dehydration complete water layers are not present. Though it may well be that when a swelling clay is buried the interlayer space is completely filled with water, this situation need not exist during all stages of burial. It is conceivable that at some stage water is released from the interlayer space to the pores with no accompanying decrease in interlayer volume. If an expanded clay layer containing less than its full component of interlayer water is collapsed to 10 A, the increase in void area without a concomitant increase in pore water would cause overcompaction. It is not clear whether these phenomena are significant, but they may need to be considered.

When montmorillonite layers are converted to illite, there should be a volume reduction of the layers, exclusive of interlayer volume. As Al^{3+} is substituted in the octahedral sheet and the large Mg^{2+} and Fe^{3+} ions are removed, there is a decrease in size in the b-axis direction. As Al substitutes in the tetrahedral sheet, it increases in size; however, when the layer charge is large enough, the tetrahedral rotates, decreasing the size of the b-axis, and locks the K^+ into position (Weaver and Pollard, 1973). These changes should result in a decrease in layer volume. The released Si^{4+}, Fe^{3+}, and Mg^{2+} may react to form chlorite and quartz and compensate for the reduction in the size of the 2:1 layers. These new minerals would presumably form some distance from the site where the ions were taken into solution. Thus, local inequities would result. In one area the pore volume would be increased and in another decreased. It is unlikely that all of these ions would migrate to the zone where the seal is formed, but some evidently do.

Heat generated by high-level radioactive waste will likely cause similar chemical reactions and cause ions to be mobilized in the high-temperature zone and migrate to lower temperature areas, where they could precipitate to form a permeability barrier.

Water Chemistry

The salinity of the interstitial water in sandstones normally increases with depth (De Sitter, 1947; Dickey, 1969, 1972; Fertl, 1976), reaching values ten times that of seawater. Some investigators (Timm and Maricelli, 1953, and Myers, 1963) found that in sandstones associated with thick shale sections the waters have lower salinities than that of seawater. This is believed to be due to the influx of fresher water from the shales. Dickey et al. (1972) demonstrated that in southwestern Louisiana high-pressure formation waters from sands enclosed in undercompacted shales have the composition of waters that normally are 500 m to 1000 m shallower.

Various studies (Sukharev and Krumbul'dt, 1962; Rieke et al., 1964; Fertl and Timko, 1970a; Schmidt, 1973) have shown that the salinity of interstitial fluids in shales is considerably lower than salinity in associated sandstones. Schmidt found that the difference was less in the high-pressure zone.

In normal-pressured sections, the salinity of the interstitial water in shales tends to increase with increasing depth; however, in high-pressure zones the salinity decreases (and porosity increases). The decrease is commonly abrupt and can be observed by a decrease in shale resistivity. The decrease in resistivity is commonly used to give a forewarning of the presence of overpressures. (For a detailed review of the phenomenon, see Fertl, 1976).

Most experimental compactions studies of clays and natural muds (for review, see Fertl, 1976) indicate that the solutions squeezed out at the beginning of compaction have higher concentrations of ions than the interstitial solutions initially present and that with increasing pressure the electrolyte content in the expressed water decreases. However, other studies (Manheim, 1966, and Shishkina, 1968) found no appreciable change in the composition of extracted water during squeezing.

Fertl (1976) suggested that the laboratory experiments which indicate that the salinity of squeezed-out solutions progressively decreases with increasing pressure may explain why the interstitial water in shales is less than that of water in associated sandstones.

Aside from the fact that the laboratory results are conflicting, it is unlikely that the results obtained from the short-term application of pressure can be used as a model for long-term burial. In the natural system, water chemistry and diagenesis go hand-in-hand. Diagenetic reactions, which affect the chemistry of the pore water, cannot be duplicated in short-term laboratory experiments. Laboratory squeeze studies may give an indication of what happens during the earliest stages of burial. There is little doubt that the salinity of brines in sandstones is determined in part by the water in the enclosing shales. Some of the processes that are believed to control the migration of shale pore water and ions into sand are: compaction, osmosis, reverse osmosis, ion filtration, diffusion, montmorillonite dehydration, and probably others (for review see Rieke and Chilingarian, 1974; Bradley, 1975, Burst, 1976). As Bradley (1975) points out, there is no consistent relation between salinity and depth, salinity and pressures, and shale density (porosity) and abnormal pressures. Thus, it is unlikely there is a simple answer.

Most of the people concerned with the problem consider that the release of interlayer water is a significant factor in controlling the composition of subsurface waters. However, they all seem to assume, based on the statements of Powers (1967) and Burst (1969), that the released water is fresh. This is only partially correct. Water released in excess of the final water layer is fresh. Thus, at shallow depth some fresh water is released. When the final water is released, some cations must be released with it. This release starts at burial temperatures of 50° to 80°C and at depths of 1500 m to 2000 m.

The exchangeable interlayer cations are largely Na, Mg, Ca, and H. These are exchanged for K, which is obtained largely from K-feldspar. Thus, the concentration of cations in the pore water should increase unless the exchanged cations replace the K in the feldspar, which is unlikely. Hydrogen ions presumably replace the K in the feldspar. The data of Weaver and Wampler (1970) show that from the beginning of layer collapse until the 7:3 mixed-layer phase is reached, approximately 0.5 percent K (of dried sample) is moved from the K-feldspar to the montmorillonite. Presumably an equivalent amount of Na, Mg, and Ca is released. In the Gulf Coast Tertiary shales, water soluble cations (largely interstitial) comprise 0.4 to 0.5 percent by weight of the dried bulk sample (Weaver and Beck, 1971). The interlayer cations released from the montmorillonite are a significant factor in determining the chemistry of subsurface pore waters.

The interlayer water is rich in cations. The concentration of cations (half Na, half Mg) in a typical montmorillonite (cation exchange capacity 100 meq/100 g) containing two layers of water is approximately seven times that in seawater (assuming 20 percent of cations are adsorbed on the edges of the clay flakes). Analyses (Weaver and Beck, 1971) indicate that a typical shallow buried Gulf Coast Tertiary clay contains approximately 60 percent clay minerals, of which 80 percent is montmorillonite containing 80 percent expanded layers. Approximately 40 percent of the solid component consists of expanded layers. The amount of interlayer water present, based on two water layers, is 7 percent by weight of the dry sample. Interlayer exchangeable cations comprise approximately 0.65 percent of the bulk sample. The amount of cations in the interstitial water, 20 percent by weight, would be 0.2 percent, assuming the pore water was seawater. Thus, after the muds are buried a few hundred meters the weight of exchangeable cations is about three times that of the cations in the interstitial water.

In a typical Gulf Coast well the proportion of expanded layers is reduced from 20 percent to 70 percent (50 percent of total expanded layers) within an interval of approximately 1500 m and the released cations comprise 0.3 percent by weight of dried sample. Within this 1500 m interval approximately 2,040 g of exchange cations have to be released from 150,000 cm^3 of sediment (assuming 20 percent porosity). The total amount of cations in the interstitial water (assuming seawater composition) in this volume is 600 g. Within this interval the released interlayer cations should dominate the pore water chemistry.

Weaver and Beck's (1971) data for a Gulf Coast well indicate that within the interval (approximately 1800 m) where the expanded layers are reduced from 20 to 70 percent there is a loss of 0.3 percent (1.0 to 0.70 percent) of exchangeable cations, based on dry weight of sample (Figure 9). The value is essentially the same as the calculated value and is slightly less than the amount of K that is transferred from the K-feldspar and mica to the montmorillonite (Weaver and Wampler, 1970). Because the layer charge must be increased in order for K to be fixed between the layers, the K value should be larger than the value for exchangeable cations. Within approximately this same interval the amount of cations in the interstitial water increases by approximately 0.2 percent by weight (Figure 9). Most of the released interlayer cations appear to remain in the shale in this interval. Though Weaver and Beck's values for the various cation species may not be accurate, the total values for the exchange and interstitial ions should be reasonably correct.

In normal-pressured muds and shales, as interlayer water and exchange cations are added to the pore water, compaction pressures forces much of the pore water, released interlayer water, and some cations (and Cl) from the shales. As the porosity decreases, more and more cations are retained in the pore water, and the cation concentration increases.

When a permeability barrier develops, a relatively high proportion of the released interlayer water as well as the cations are trapped beneath the barrier. Figure 9 shows the relation of layer contraction and decrease in cation exchange capacity to the increase in the amount of cation in the interstitial water. The increase in interstitial cation concentration coincides with the increase in layer collapse, suggesting that the exchange cations are the source of the interstitial cations. The formation of a permeability barrier traps both the released interlayer cations and interlayer water causing a relative increase in the cation concentration of the interstitial water. In the well studied by Schmidt (1973), the increase in cation concentration occurs immediately above the top of the high-pressure interval. The underlying permeability barrier may inhibit the flushing of the overlying shales.

In the wells studied by Weaver and Beck (1971) and Schmidt (1973) the salinity maximum is followed by decrease in salinity with depth; however, the salinity values are higher than those above the salinity maximum and are not

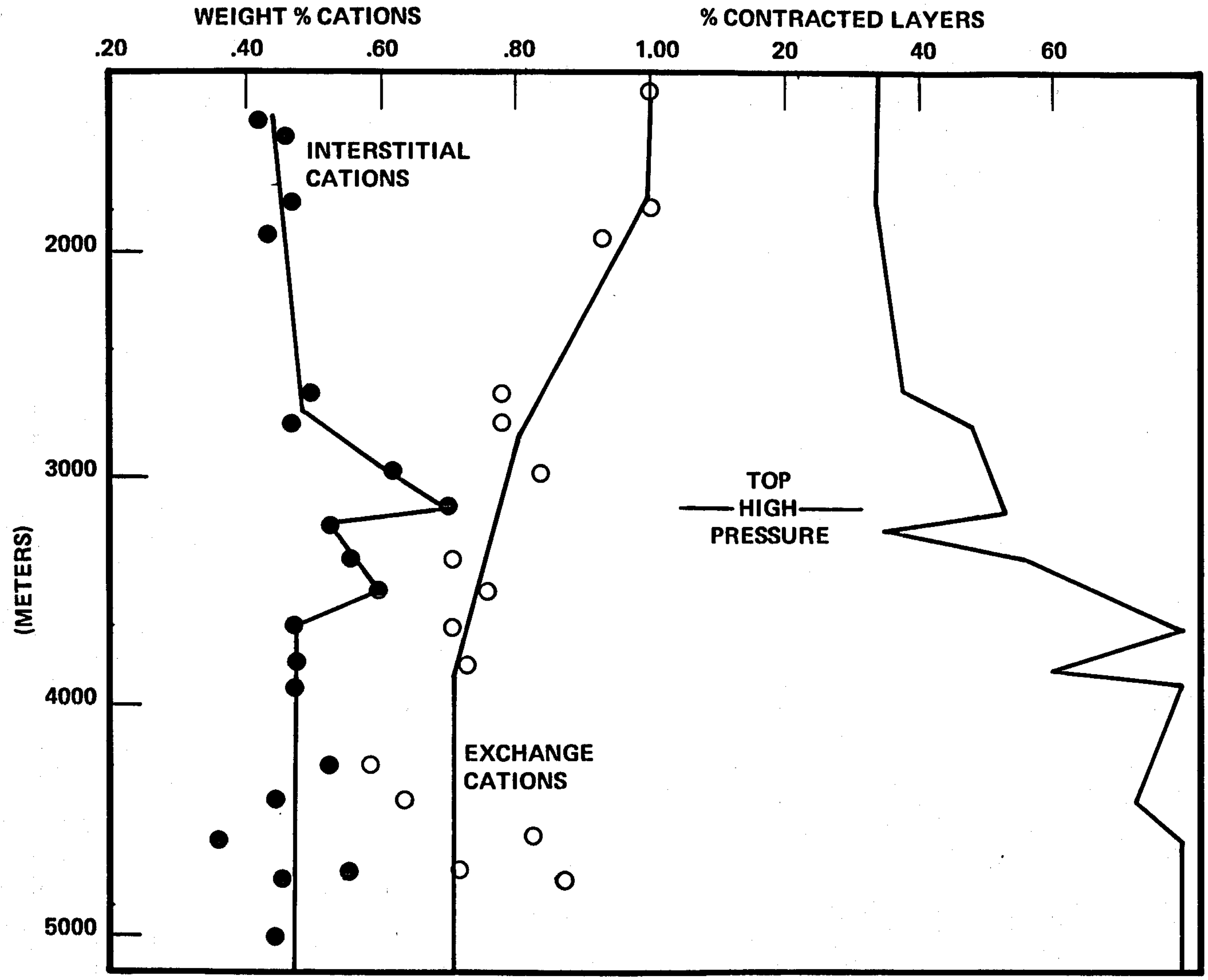


Figure 9. Percentage (dry weight of sample) of cations in the interstitial water and exchange cations as related to increase in percent of contracted layers. Gulf Coast early Tertiary well. After Weaver and Beck (1971).

truly fresh. The relatively low salinity values in the deeper portions of the wells suggest that layer contraction occurred in these shales before a permeability barrier formed and many of the released interlayer cations (and hydrocarbons?) were able to migrate.

Presumably there is no Cl in the interlayer space, and the Cl distribution should give some idea of the effect of layer collapse on the composition of interstitial water. The Cl concentration and weight percent Cl show a general decrease with depth (Weaver and Beck, 1971). As should be expected, the Cl concentration decreases rapidly through the interval where there is a maximum release of interlayer water.

ILLITE

Hydrothermal studies by Yoder and Eugster (1954) and Velde (1965 a) established that the stable high temperature muscovite is the 2M polytype. The one-layer monoclinic disordered (1Md) polytype is formed at the lowest temperature and the one-layer monoclinic (1M) polytype at intermediate temperatures. The sequence with increasing temperature is 1Md → 1M → 2M; however, in nature the sequence appears to be 1 Md → 2M. Most hydrothermal experiments have been conducted using compositions similar to muscovite rather than illite. Velde (1965 a and b) concluded that 1Md and 1M polymorphs are either metastable muscovite forms or are micas with a composition differing from muscovite, e.g. glauconite, celadonite, and illite. A relatively rare three-layer triclinic (3T) polytype also exists.

Low-temperature illites form by the weathering of K-feldspar and possibly by direct precipitation; however, most illite apparently forms by the burial diagenesis of montmorillonite and volcanic material.

Many illites are detrital and derived from low-grade metamorphic rocks. The metamorphic rocks have presumably gone through the burial diagenesis stage. Whether the precursor was commonly montmorillonite is not known.

"Pure illite" should consist entirely of contracted 10 A layers; however, many illites have a relatively broad 10 A reflection. The 10 A broadens in the direction of the low angle spacing and the 5 A peak in the direction of the high angle spacing. Weaver (1965) and Weaver and Beck (1971) have interpreted this to indicate that the illite contains some interlayered 14 A layers. These layers may be either montmorillonite or chlorite (possibly dioctahedral). On the basis of chemical data, Raman and Jackson (1966) concluded that many illites contain 20 percent to 30 percent chlorite layers along with varying amounts of montmorillonite and vermiculite. These authors suggest that the "true 10 A" layers in illite are close to muscovite in composition and that the high Mg and Fe and low Al and K is due to the presence of other layers. Others (Velde, 1965 a; Hower and Mowatt, 1966; Reesman and Keller, 1967) believe illite is a single-phase mineral. The truth is probably somewhere in between. The 10 A layers likely have a composition different from muscovite, but other types of layers are almost certainly present in many illites.

Chemistry

X-ray analyses of illite samples indicate that they commonly contain 10 percent to 30 percent expanded layers. Other illites, usually deeply buried Paleozoic and Precambrian, have no expanded layers and appear to be composed entirely of 10 A layers.

Both "impure" and "pure" illites commonly contain an abundance of Fe and Mg which is assigned to the octahedral sheet. A typical illite would have the following structural formula:

$$(Al_{1.50}Fe^{3+}_{.20}Mg_{.32})\ (Si_{3.50}Al_{.55})\ O_{10}(OH)_2K_{.76}Na_{.01}Ca_{.02}$$

There is a tendency for the octahedral Fe/Mg ratio to be smaller in the well-crystallized 2M illites.

Phengites average formula: $(Al_{1.37}Fe^{3+}_{.19}Fe^{2+}_{.11}Mg_{.38}\ (Si_{3.33}Al_{.67})\ O_{10}OH_2\ (K_{.80}Na_{.10}Ca_{.05})$ are mica-like minerals that occur in the low grade metamorphic blueschist and greenschist facies (Ernst, 1963). Their formation is favored by high pressures and relatively low temperatures (Velde, 1965 b). Phengites have a layer charge of approximately 1.00 (Ernst, 1963; Ernst, 1964; Velde, 1965 b); illites have layer charges ranging from 0.60 to 1.00, with most having a value less than 1.00. Phengites have a tetrahedral charge ranging from 0.50 to 0.95, with an average value of 0.65 to 0.70. Some illites have a charge this high, but most have a lower tetrahedral charge (0.45 to 0.60). The average octahedral charge for phengites (0.36) is slightly larger than the value for illites (0.32).

The average illite data are misleading, as many of the illites included are really mixed-layer clays. The structural formula of two of the better-crystallized illites are:

Belt -100 percent 10 Å layers (Weaver and Pollard, 1973):

$$(Al_{1.51}Fe^{3+}_{.03}Fe^{2+}_{.03}Mg_{.43})\ (Si_{3.43}Al_{.57})\ O_{10}(OH)_2K_{.89}Na_{.02}Ca_{.045}$$

Marblehead -~95 percent 10 Å layers (Gaudette, 1965):

$$(Al_{1.51}Fe^{3+}_{.04}Fe^{2+}_{.07}Mg_{.36})\ (Si_{3.54}Al_{.46})\ O_{10}(OH)_2K_{.70}Na_{.03}Ca_{.05}$$

The better-crystallized illites can have a layer charge of 1.0. They have less tetrahedral and more octahedral charge than the typical phengite. Most of these illites have less octahedral Fe than phengites (and less than well-crystallized illites).

Figure 10 shows the distribution of tetrahedral and octahedral Al relative to total Al for montmorillonite-beidillites, mixed-layer illite-montmorillonites, illites, and phengites. Tetrahedral and octahedral Al decreases in the sequence montmorillonite, mixed-layer clay, illite, phengite. This should be accompanied by an increase in width of both the tetrahedral and octahedral sheets and should cause no significant change in the amount of tetrahedral rotation. It seems unlikely that this evolutionary mineral sequence develops with the Al content remaining constant.

The same figure shows that as total Al increases for a given mineral both tetrahedral and octahedral Al increases. As the total Al increases it is equally divided between the tetrahedral and octahedral layers, and layer charge does not show a major increase except for the mixed-layer clays (slope of

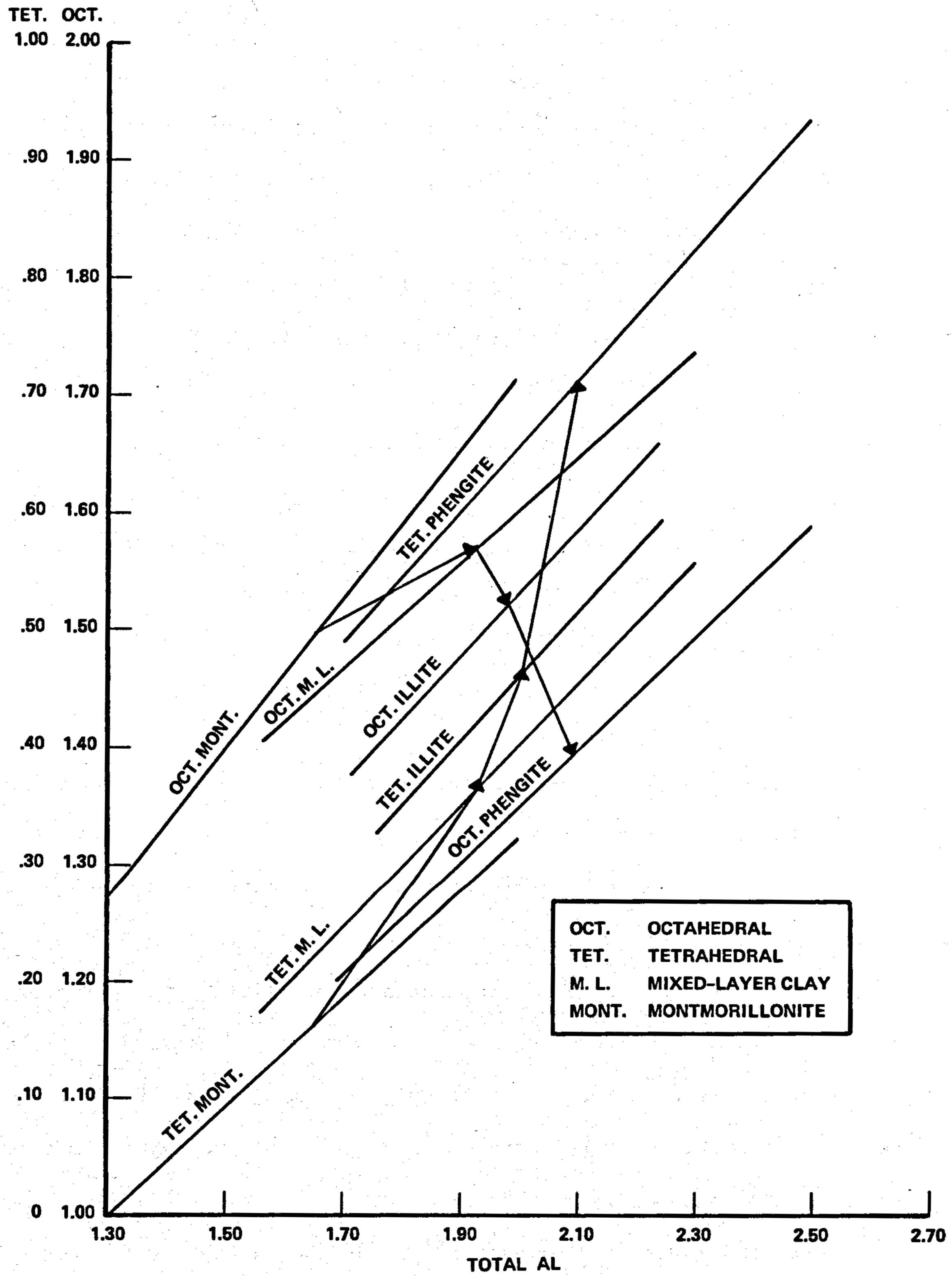


Figure 10. Aluminum distribution in dioctahedral 2:1 clay minerals. Lines indicate range of values. Arrows indicate midpoint of range and indicate direction of increased grade of diagenesis-metamorphism.

octahedral Al graph does not parallel tetrahedral Al). The width of the tetrahedral layer should increase and the octahedral layer decrease. This favors the fixation of K.

The maximum total Al increases from 2.0 for montmorillonite to 2.30 for mixed-layer clay and illite to 2.50 for phengite. For values less than the maximum there is considerable overlap, but total Al generally increases as the temperature at which the minerals formed increases. The median tetrahedral Al content increases from 0.16 for montmorillonite to 0.71 for phengite. Octahedral Al decreases slightly, from 1.50 for montmorillonite to 1.40 for phengite. The size of the tetrahedral layer should increase relative to the octahedral layer favoring the development of K-locked micaceous layers. These changes in Al content can be caused by adding Al to the mineral or removing Si. Laboratory experiments indicate that under some conditions Si is removed from the 2:1 layers.

H_2O

Chemical analyses of muscovites show that they contain approximately 4.5 percent to 4.7 percent H_2O. Phengites commonly contain 4.4 percent to 4.7 percent H_2O, which suggest they do not contain interlayers of chlorite. In contrast illites contain from 4.6 percent to 8.0 percent H_2O with an average of approximately 7 percent. X-ray patterns of illite have a broader 10 A reflection than those for phengite and muscovite. The broadening shows as a less steep slope on the low-angle (high A) side of the 10 A peak. The material accounting for this change in slope is presumably the material containing the excess H_2O.

Hower and Mowatt (1966) suggested that the excess H_2O is present as neutral H_2O trapped in nonexpanded layers. Not only is the 10 A peak broadened on the low-angle side, but the 5 A peak is broadened on the high-angle side. The nature of the 5 A peak indicates that either the illite contains some 14 A interlayers (which would require two layers of trapped water) or the chlorite contains a large percentage of 10 A layers. Raman and Jackson (1966) and Weaver and Beck (1971) have suggested that the broadening of the illite peak, and the excess H_2O are caused by the presence of chlorite layers, probably dioctahedral, in the illite; however, this does not account for the high Si content of illites. It seems likely that some montmorillonite or vermiculite layers are present.

The fact that phengites, with no excess H_2O, have an octahedral layer with a significantly higher R^{2+} content than muscovites indicates that mica-like minerals (illite) can exist with this composition; however, phengites have a layer charge of 1.0 as opposed to a value of 0.7 to 0.8 for illites. As Hower and Mowatt (1966) suggested, because a value of 1.0 is an upper limit does not mean it is also a lower limit.

In any event many, if not most, illites have not been subjected to high enough temperatures and/or pressures for all of the illite to form a single phase. In most cases the second phase is an expanded layer. The base of the 10 A x-ray peak of "typical" Paleozoic illites is asymetrical, being flared slightly towards the larger A values. These illites are commonly considered to be "pure" illites. When the samples are treated with ethylene glycol, the low-angle shoulder decreases and there is a slight increase in the sharpness ratio. When the samples are heated to 300°C there is a further increase in the sharpness ratio and a significant increase in peak height. Calculations based on the increased peak height after heating indicate illites commonly contain 10 percent to 30 percent mixed-layer illite-expanded clay (probably montmorillonite or beidellite). The mixed-layer phase contains 5 percent to 20 percent expanded layers.

It should be noted that for those samples with the larger amounts of calculated mixed-layer clay the 7 A chlorite peak decreases when the samples are heated to 300°C. It may be that some poorly crystalline chloritic layers are present in the mixed-layer phase.

Illite-Phengite Relation

Plots of data for illites and mixed-layer illite-montmorillonites versus number of contracted layers (Hower and Mowatt, 1966, and Weaver and Pollard, 1973) indicate that as the total layer charge increases most of the increase occurs in the tetrahedral sheet and there is relatively little change in the octahedral sheet; however, graphs of chemical changes versus burial temperature (Figure 4) suggest that with increasing temperature the octahedral charge and octahedral Mg and Fe decrease and octahedral Al increases to a value of 1.80. Phengites commonly contain three times as much octahedral Mg and Fe.

If there is a trend for the Al content of the octahedral layer to increase with increasing temperature, then the phengites must be considered a separate phase rather than a part of the montmorillonite → illite → phengite diagenetic sequence. Phengites are formed at high pressures and relatively low temperatures (Velde, 1965 b). Velde has suggested that illites (low R^{2+}), chlorite, K-feldspar, and water react to form phengite (high R^{2+}), chlorite (low R^{2+}) and quartz. A typical illite (high R^{2+}) plus K-feldspar should produce a phengite and require relatively little recrystallization.

Thus, during diagenesis and metamorphism montmorillonite plus K-feldspar can take two routes. First a mixed-layer phase is formed. If this phase is subjected to high pressures and relatively low temperatures, the octahedral sheet is not "cleaned up" and phengite (low octahedral Al) plus quartz is formed. If the mixed-layer phase is subjected to high temperatures and relatively low pressures, the octahedral layer is "cleaned up" and a sericite- or muscovite-type (high octahedral Al) mineral plus chlorite is formed. This dual evolutionary sequence is also indicated by the average MgO values: montmorillonite 3.6 percent → illite 2.8 percent → sericite 1.7 percent → muscovite 0.6 percent. The MgO content decreases as the formation temperature increases. In contrast, phengites have essentially the same average MgO value (3.8 percent) as the montmorillonites.

Guven (1970) states that illites are sometimes subjected to deep burial with the resulting greater pressure increase relative to temperature; he concludes that illites are therefore environmentally closer to phengites than to muscovites; however, in areas like the Gulf Coast and other montmorillonite-rich areas where undercompacted shales exist and where the excess water acts as a heat storage reservoir, temperature may be more important than pressure.

Hydrothermal Studies

Hydrothermal experiments (300° to 450°C) with natural mixed-layer illite-montmorillonite (Velde and Bystrom-Brusewitz, 1972) showed that the initial transformation is the crystallization of quartz and a decrease in the percentage of mixed-layer material and expanded layers. This is followed by the exsolution of chlorite (kaolinite, if Mg and Fe are not present) and the continued decrease in the proportion of expanded layers. The mixed-layer phase becomes ordered when the expanded layers decrease to 25-30 percent. Illite may start to form at this time. The next stage is the destruction of the mixed-layer phase and formation of additional illite and chlorite (or kaolinite). Eventually the illite breaks down to form 2M muscovite and chlorite (greenschist facies).

Hydrothermal experiments (Velde, 1977) with a number of natural clays and clay mixtures showed that with increasing temperature montmorillonite developed a mixed-layer illite-montmorillonite phase. The proportion of illite layers increased with increasing temperature; at the same time corrensite (high R^{2+}) developed. With increased temperature, quartz and chlorite (high R^{3+}) exsolved (near 300°C) from illite, and the illite gradually developed a better set of 2M reflections as more chlorite was exsolved. Chlorite first developed when an ordered IMII (illite-montmorillonite-illite-illite) phase developed and persisted as a muscovite-type mica developed.

He also noted that Na, K, and Ca are present in most natural materials and found that the Na and K will enter into mixed layers and mica phases with increased temperature, but the Ca will be released into the aqueous solution, possibly to produce calcite where the $P(CO_2)$ is sufficiently high. The Weaver and Beck (1971) study of natural clays indicated that Ca is preferentially retained in the expanded layers and that Ca ions are the last interlayer ions to be released during diagenesis. This is compatible with the results of Velde.

Polymorphic Forms of Illite

The most common illite polytypes are the 2M and 1Md forms. Other than for glauconite and celadonite the 1M variety is relatively rare. Velde and Hower (1963) and Maxwell and Hower (1967) proposed peak-height ratios, 2.74 A/2.58 A and 2.80 A/2.58 A respectively, which can be used to measure the 2M/1Md ratio. Experimental curves were constructed using mixtures of 2M muscovite and 1Md illite. The physical forces necessary to reduce the muscovite to one micron in size should disrupt the 2M arrangement and lead to high estimated 1Md values. Their data tend to confirm this, as they found that the 3.74 A/2.58 A ratio was larger, for a given amount of 2M mica, for the >1 μm fraction than for the <1 μm fraction. These peak-height ratios can be considered to be only a rough estimate of the relative amounts of 2M and 1Md forms; however, trends can be assumed to be reliable.

Most shales contain both 2M and 1Md illites. Velde and Hower (1963) x-rayed various size fractions of 74 Paleozoic shale samples. Their analysis indicated that the >10 µm fraction usually contained only 2M illite. The proportion of 1Md increases with decreasing grain size, commonly comprising 100 percent of the <0.2 µm fraction; however the lower limit of detection for the 2M polymorph is believed to be 24 percent (Maxwell and Hower, 1967). The <1 µm fraction of most samples contain less than 50 percent 2M illite. The amount of 2M illite in the >1 µm fraction ranges from 0 to 100 percent with no modal concentration. Their data suggest that the illite in Paleozoic shales consists of an average of approximately 30 percent 2M and 70 percent 1Md illite. All errors would cause an increase in the 1Md values. It is almost certain that the 2M polytype is more abundant than indicated by these data; however, it does decrease with decreasing grain size. The grain size of illite is a rough measure of the relative amount of the two polytypes. The major problem is to determine how much of the 2M illite is detrital and how much has formed during burial diagenesis. It should also be noted that 1Md illite can also be detrital. When 1Md illite is present, many authors assume that it had an authigenic origin.

Several studies have demonstrated an increase in the 2M/1Md ratio with increasing degree of metamorphism (temperature). Reynolds (1963) found that in the Precambrian Belt limestones the 2M/1Md ratio increased as the metamorphic grade increased. Reynolds concluded, on the basis of the K/Rb ratio, that the 2M illites formed from K-feldspar rather than from 1Md illite. In limestones the availability of K may be the most important factor that influences the formation of 2M illites.

The Maxwell and Hower (1967) study of the Belt shales showed that the 2M/1Md ratio systematically increased from 25 to 100 percent as the depth of burial increased. They noted that there was a general trend of increasing grain size with depth. In addition, the fabric changes from one showing excellent foliation parallel to the bedding at the top of the section, to one showing an increasing disorientation of the layer silicates at the bottom of the section. Biotite was present in samples containing 2M/1Md ratios larger than 7/3. Thus, it appears that 1Md illite can persist to relatively high temperatures (greenschist facies).

O^{18}/O^{16} studies (Eslinger and Savin, 1973 a and b) of some of these same sediments (<0.5 μm fraction) suggested that burial temperatures ranged from 225°C for a shale having a 2M/1Md ratio 1/3 and 310°C for one with a ratio of 3/2. Extrapolation indicated that a temperature of 400°C would be required to obtain 100 percent 2M illite. These results will be discussed in more detail in a later section.

Foscolos and Kodama (1974) studied the Lower Cretaceous shales of British Columbia and established the following relations.

Percent 2M Illite	Crystallinity Index (mm)	Sharpness Ratio	Percent Illite In ML Phase	Temperature
<25	>20	<1.5	<25	77°C
35	19	-	40-50	94°C
50	17	1.9	70-80	141°C
65	15	2.3	80-90	164°C

These values do not jibe with the data obtained on the Precambriam Belt (Maxwell and Hower, 1967; Eslinger and Savin, 1973). The Belt shales only have 25 percent 2M illite at a temperature of 225°C and only 60 percent at 310°C (O^{18}/O^{16}). In part, the difference is due to the fine grain size (<0.5 μm) analyzed by Eslinger and Savin (1973) as compared to the less than 2 μm fraction analyzed by Foscolos and Kodama (1974). However, Maxwell and

Hower (1967) found similar percent 2M values for the less than 2 μm fraction of Belt samples from the same section. Maxwell and Hower report that even the most shallow buried illites, which contain no detectable 2M polytype, are completely collapsed and contain no expanded layers (though their x-ray patterns suggest this may not be so).

The question is whether montmorillonite completely converts to a non-expanded 1Md illite before any 2M material is formed, or whether the 2M polytype systematically increases through the mixed-layer stage of diagenesis, as suggested by Foscolos and Kodama (1974). A reexamination of the <0.2 μm fraction of Gulf Coast Miocene samples (Weaver and Beck, 1971) indicates that there are no 2M reflections present in the samples with a mixed-layer ratio ranging from 1/4 to 7/3. It seems unlikely that any 2M illite reflections should develop until all the layers are contracted to 10 A; however, once a 10 A phase develops it should become coarser and may develop a 2M structure, whereas the mixed-layer phase would remain in the fine fraction.

In the Jurassic of the Durance basin of France, Dunoyer de Segonzac (1969) found the 2M/1Md ratio systematically increased with depth.

Crystallinity (Sharpness)

In a study of low-grade metamorphic shales, Weaver (1961) showed that the "sharpness" of the 10 A illite peak increased with increased metamorphism. Weaver observed that the 10 A peak became narrower and the low-angle shoulder decreased with increasing degree of metamorphism. He proposed that the ratio of the peak height at 10.5 A to that at 10.0 A (sharpness ratio) could be used as a measure of degree of metamorphism. He demonstrated that in the shales fringing the Ouachita Mountains the sharpness ratio increased with increasing degree of metamorphism. Later, Kubler (1966 a and b) introduced the crystallinity index (peak width, in mm, at half-height). Kubler believes that the peak width is a measure of crystallinity. The 10 A peak becomes narrower as the proportion of interstratified montmorillonite, vermiculite, and chlorite layers decreases. Thus, any measure of peak width is a measure of illite purification and does not necessarily have anything to do with crystallinity. Weaver originally rejected the peak width at half-height measure because it did not include the low-angle tail in the measurement. Further, an absolute measurement is dependent upon machine settings. Lydka (1974) has suggested a measurement wherein the 10 A peak height is divided by the quartz peak width at half-height.

Weber (1972) suggested using the peak width at half-height of quartz as an internal standard,

$$Hh_{rel} = \frac{\text{Hh illite (mm)}}{\text{Hh quartz (mm)}} \times (100)$$

He found that the illite crystallinity in a series of slates showed regional variations which could be related to different burial depths and variable heat flow rates. He conducted experiments that showed that the peak width of the 10 A peak increased as the thickness of the clay layer on the x-ray slide increased. This is because during the preparation of slides the finer fraction (wider peak) occurs on the surface of the slides. He further noted that the 10 A peak patterns from the sedimented slides were wider than those produced from polished slabs of the slate and that the divergence increased as the grain size decreased. Thus, as expected, grain size must be taken into account when determining the significance of the "degree of crystallinity".

Weber et al. (1976) proposed a measure of "crystallinity" called "apparent-thickness". It is based on the Scherrer formula relating peak width to crystal size.

Weaver (1965) presented data to indicate that the K content of illites increased linearly as the 10 A/5 A ratio decreased. The K increase also relates to the sharpness ratio and peak width at half-height. Later, Weaver and Pollard (1973) showed that there was a linear negative relation between the K_2O and Fe_2O_3 values of illites. The Fe_2O_3 content decreases from 12 percent to 1 percent as the K_2O content increases from 5 percent to 8-11 percent. Both K and Fe affect the relative intensity of the 10 A/5 A ratio but with opposite effects. An increase in K causes a decrease in the 10 A /5 A ratio; an increase in Fe causes an increase in the 10 A/5 A ratio.

A plot of Hower and Mowatt's (1966) Fe and K values for a number of illites and mixed-layer illite-montmorillonites indicates two separate trends. The samples with less than 20 percent expanded layers and those with more than 20 percent expanded layers show separate trends. In both cases the K content increases as the Fe content decreases. There is considerable scatter. Both series of samples show a decrease in Fe with a decrease in the percentage of expanded layers. Contrary to the general trend (decrease in Fe with decrease in expanded layers), the samples with more than 20 percent expanded layers average less Fe than those with fewer expanded layers. This is because most of the samples with a high content of expanded layers are K-bentonites derived from low-Fe volcanic ash. The data indicate that most illites developed from material that had a higher Fe content than rhyolitic volcanics.

Klingebiel and Latouche (1962) related the 5 A/10 A ratio of illites to the Fe content. Esquevin (1969), Duyoyer de Segonzac (1969), and others have related the (002)/(001) ratio of illite to crystallinity, and have suggested that the (002)/(001) ratio increases as "crystallinity" increases, and have related these trends to the degree of metamorphism (diagenesis, achizone, and epizone). Gill et al. (1977) found that a broad general relation existed for illites in sandstones, siltstones, and argillaceous rocks but not for carbonate rocks. Though the peak width at half-height and sharpness ratio do increase with increasing metamorphism, most analyses show only a very general or no increase in the (002)/(001) ratio with increasing metamorphism. This is presumably due to the fact that K, Mg and Fe affect the ratio. Though an increase in K usually occurs (increasing the (002)/(001) ratio) during increased diagenesis, the Mg + Fe content may or may not (phengite) decrease. Analyses of a series of anchizone samples from the Basque mountains (Dunoyer de Segonzac and Heddebaut, 1971) showed that there was no relation between the Al/Mg + Fe ratio of the octahedral layer and the (002)/(001) ratio of the illite peaks.

A plot of the data used to obtain the results reported by Weaver (1965) shows that not only does the 10 A/5 A ratio decrease as K_2O increases but the sharpness ratio increases (Figure 11) and the half-width decreases (Figure 12).

Thus, with increasing degree of diagnesis and metamorphism the K content of illites increases, as would be expected. The Mg + Fe content generally decreases. One question is whether external K is added to the illite or whether the K remains constant and an appreciable amount of Mg and Fe are lost from the illite. Data presented earlier suggest that external K is added to the illite and that Fe, Mg, and Si are lost during the earlier stages of diagenesis. With increasing temperature these processes appear to continue; with increased pressure (phengite) the latter process apparently is modified (Fe and Mg remain).

Both the crystallinity index and the sharpness ratio depend on measurements relatively high up on the 10 A peak and do not fully take into account the low-angle tail often present on 10 A peaks. Another measurement is proposed that should correct this deficiency and give a better description of

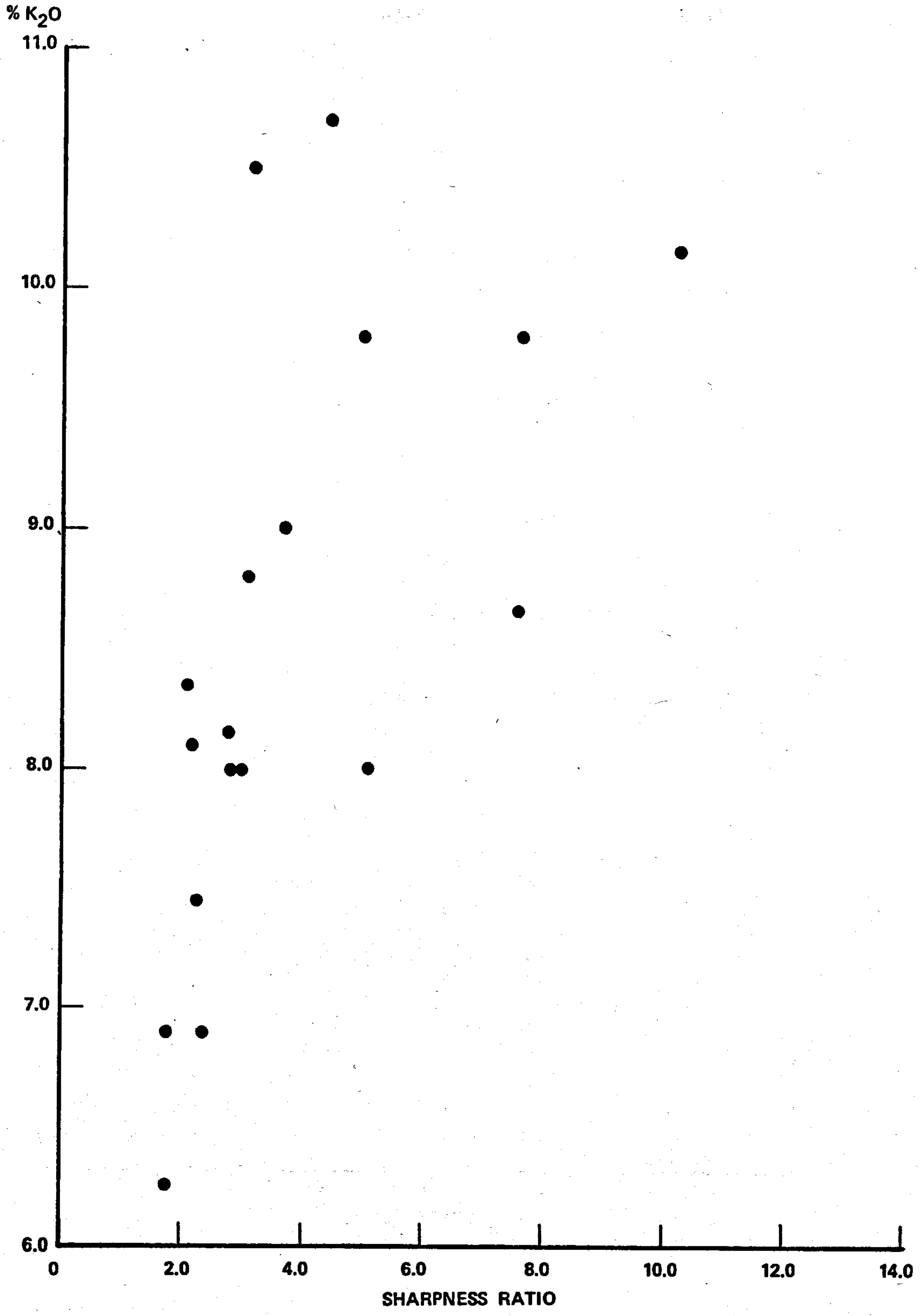


Figure 11. Relation of K_2O content of "illites" to sharpness ratio of 10 A x-ray peak.

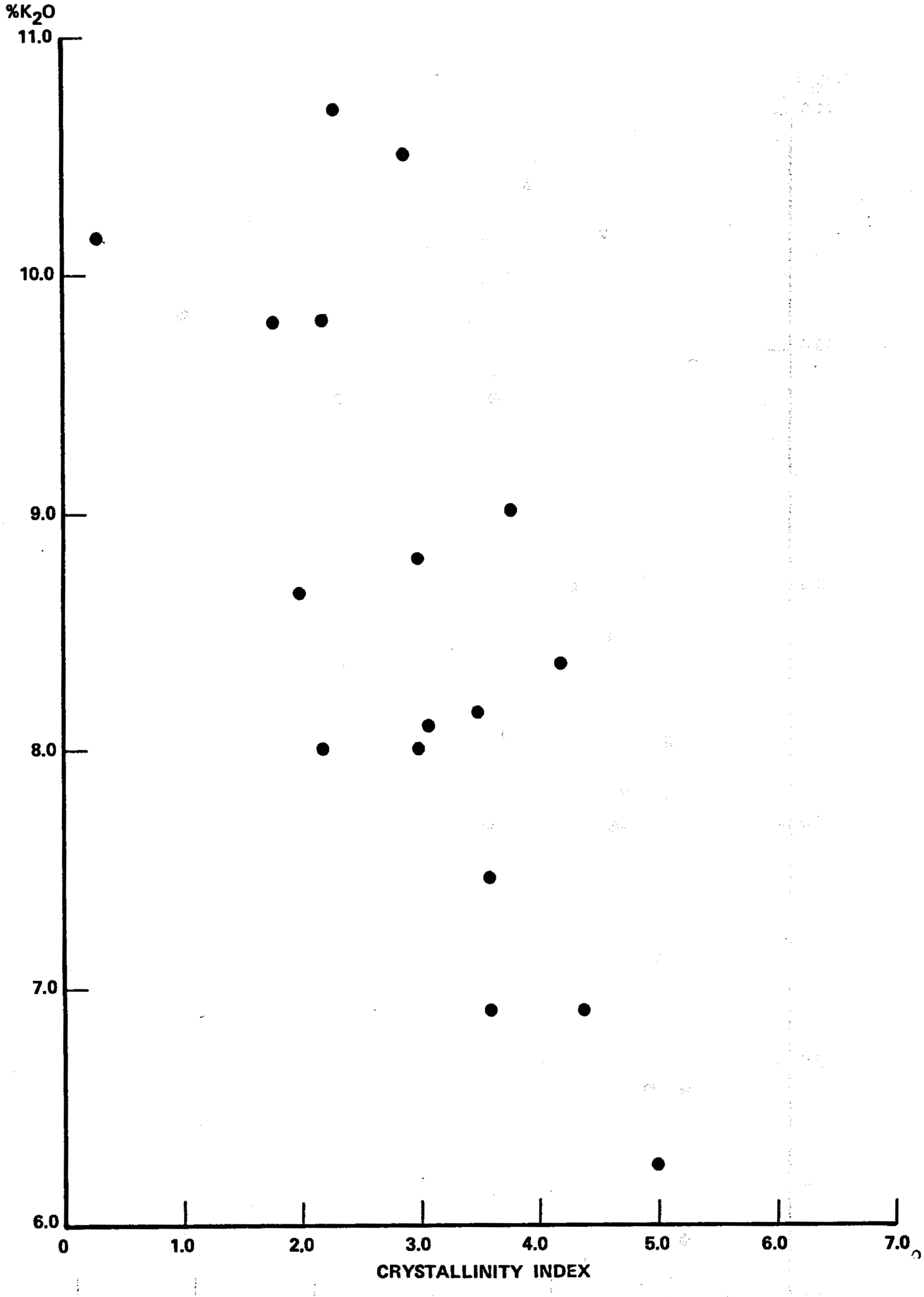


Figure 12. Relation of K_2O content of "illites" to crystallinity index of 10 A x-ray peak.

the peak. The measurement is called the "asymmetry ratio". A line is drawn from the apex of the 10 A peak perpendicular to the lower edge of the chart paper. From near the base of the 10 A peak, slightly above the base line and background noise, the distance from the center line to each side of the 10 A peak is measured. The width of the right portion (low-angle side) is divided by the width of the left portion. The width of the left portion of the base of the peak is relatively constant. Thus, the ratio is largely a measure of the flare-out of the low-angle portion of the 10 A peak.

Figure 13 shows the relation of the asymmetry ratio to the K_2O content (samples described by Weaver, 1965). Samples were dispersed with calgon, air dried, and x-rayed without further treatment. There is a good linear relation, with the asymmetry ratio decreasing as the K_2O content increases. This measurement suggests that peak asymmetry is related to the K_2O content. The 10 A/5 A ratio increases as the asymmetry ratio increases indicating that whatever is affecting the 10 A peak is affecting the height of the 5 A peak even more. This, plus the relation to the K content, suggest that both ratios measure the amount of non-10 A layers present. Heat treatments suggest that these layers are either montmorillonite or vermiculate (which would have a high Mg and Fe content). It is difficult to see how randomly trapped interlayer water molecules (Hower and Mowatt, 1966) can account for these systematic variations in the peak intensity of width of the 10 A and 5 A peak.

The factors affecting the crystallinity index and the (001)/(002) ratio are not as simple as suggested, because the data for most formations do not show a linear relation to these two values.

Numerous studies have shown that the sharpness ratio and/or crystallinity index vary as a function of depth of burial (temperature) and degree of metamorphism (Weaver, 1960; Kubler, 1964, 1966 a and b, 1967, 1968; Dunoyer de

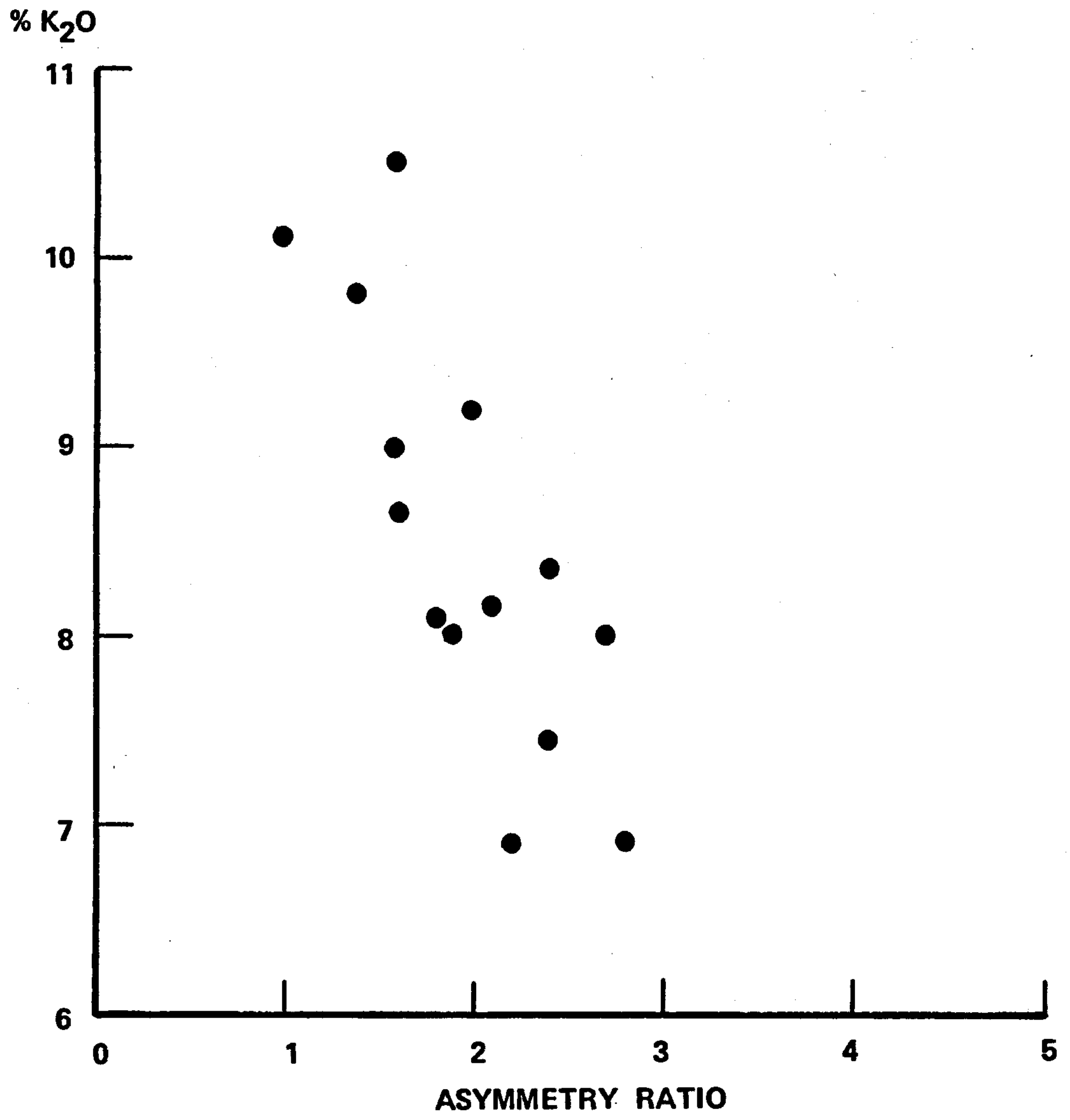


Figure 13. Relation of K_2O content of "illites" to asymmetry ratio of 10 A x-ray peak.

Segonzac and Kubler, 1966; Dunoyer de Segonzac, 1969; Esquevin, 1969; Foscolos and Kodama, 1974; Dunoyer de Segonzac and Bernoulli, 1976; Dunoyer de Segonzac, 1976; Rowsell and Deswardt, 1976; Gill et al., 1977). Jackson (1977) determined the crystallinity index of 24 samples ranging in age from 0.016 to 3.3 x 10^9 years B.P. The values show little variation with age except for an increase in the interval 0.8-1.05 x 10^9 years B.P. Jackson believes this increase is significant. The number of samples seems somewhat limited for such a conclusion.

Various authors (Kubler, 1968; Dunoyer de Segonzac, 1969; Frey and Hunziker, 1973; and Foscolos and Scott, 1975) have assigned specific illite crystallinity values to the boundaries between the zone of diagenesis, the anchizone, and the epizone. The value assigned to these boundaries is not consistent, in part because of the variation in the x-ray equipment and the various settings used. The boundary between the anchizone and the epizone has been based on 2.5, 4.0, and 7.8 mm peak widths (and the development of pyrophyllite and allevardite); the boundary between the diagenesis zone and the anchizone has been based on peak widths of 4.0, 7.5, and 12.8 mm. The equivalent boundaries based on the sharpness ratio (S.R.) are 12.1 and 2.3. The latter values are independent of machine settings and can better be standardized. Foscolos and Scott (1975) have proposed separating the diagenesis zone into three subzones on the basis of crystallinity index values. Because most clays in this zone are mixed-layers, pretreatment and the nature of the starting material limit the usefulness of this classification. Gill et al. (1977) suggested that there was a transition stage between the late diagenetic zone and the anchizone and that it be called the metadiagenetic zone (S.R. 2.0 to 3.0).

Dunoyer de Segonzac and Abbas (1976) studied a diagenetic sequence in the Alps and found that as the crystallinity index decreased from 7 to 3 there was an increase in albite, chlorite (5 to 50 percent) and paragonite. Chemical analyses (66) show a large variation for a given degree of metamorphism. Average values indicate an increase of total layer charge from 0.695 in the zone of diagenesis to 0.735 in the anchizone to 0.76 in the epizone. The differences are small and, in view of the large variations within zones, of questionable significance. The average data further indicate that with increasing metamorphism there is a slight increase in tetrahedral Al and octahedral Mg and a decrease in octahedral Fe. K increases from 0.66 to 0.71. It is somewhat surprising that the chemical differences are so small. There appears to be an increase in the octahedral Al/Fe+Mg ratio with increasing metamorphism but the data were not plotted and it is not clear whether such a trend exists.

Trace element analyses of the <2 μm fraction of these same samples (Besnus et al., 1976) show considerable scatter but, in general, Ga, Ti, Co, Cr, Ba, Sn, and Pb increase and Si, Fe, and Cu decrease as the degree of metamorphism increases.

Hydrothermal experiments by Smykatz-Kloss and Althaus (1974) confirmed that "crystallinity" increased with increasing temperature; however, they were unable to establish any absolute relation between temperature and crystallinity and suggested that the crystallinity index should be applied very cautiously. It should also be mentioned that the results of hydrothermal experiments should be applied with caution. Gill et al. (1977) found that crystallinity changes were controlled to some extent by lithology. Sandstones were the most susceptible to change, siltstones less so, and argillaceous rock the least.

Though the crystallinity index, sharpness ratio, assymetry ratio, and (002)/(001) ratio in general measure the relative temperature to which the 2:1 clay has been exposed, the reason for the peak modifications is not well understood. The most significant variable would appear to be the grain size x-rayed and the amount and type of interstratification. These various measurements probably should not be applied to mixed-layer clays containing more than 10 to 20 percent expanded layers. The peak width and shape are strongly influenced by the regularity of the interlayering and by variations in the types of nonexpanded (illite and chlorite) and expanded (montmorillonite and vermiculite) layers. At more advanced stages of diagenesis these measurements to a large extent reflect the relative amount of coarse (10 A layers) and fine (mixed-layer phase) material. Only when all the 2:1 layers are completely collapsed is the half-width a measure of crystallinity and (002)/(001) a strict measure of chemistry.

Illite in Sandstones

Authigenic illite commonly forms in porous sandstones during burial. In some instances it appears that the illite is probably formed at temperatures lower than those at which it is formed in shales. These authigenic clay minerals commonly decrease the porosity and permeability of the sandstones.

Millot (1970) observed kaolinite altering to illite in the Cambrian sandstones of Algeria. In equivalent age sandstones from the same area, Triplehorn (1967) found authigenic 1M illite at depths of 2,873 to 3,070 m. In the shallow buried Upper Carboniferous sandstones of northern Germany (Füchtbauer, 1967), the detrital feldspar has been altered to kaolinite; at depths on the order of 6,000 m the feldspar is sericitized. It is suggested that an acid environment is created by the release of CO_2 and humic acids during the early stages of coalification. During the second stage of coalification methane is released, causing an increase in pH which favors the formation of micaceous minerals. The alkaline conditions also cause carbonate minerals to form and replace a variety of other minerals.

Wilson and Pittman (1977), in their review of the literature on the occurrence of authigenic clay minerals in sandstones, show a number of scanning electron micrographs of authigenic illite. Illite generally occurs as irregular flakes with lath-like projections. Occasionally the long lath-like projections are curled and up to 30 μm long.

Paragonite

Paragonite is a common mineral in highly aluminous pelitic schists of low-to-medium grade of metamorphism (Zen and Albee, 1964; Guidotti, 1968). It is most common in medium grades of metamorphism and is related to a relative enrichment in Al_2O_3 and/or $NaAlO_2$ (Guidotti, 1968). Winkler (1976) states that paragonite makes its first appearance at very-low-grade metamorphic conditions (200° to 400°C). Frey (1970, 1974) described the distribution of paragonite in anchizone rocks of the Alps and suggested the following origin. Mixed-layer illite-montmorillonite → regular mixed-layer mica-montmorillonite → mixed-layer paragonite-phengite → paragonite. In the lower Paleozoic shales of the southern Appalachian, I have found paragonite in anchizone shales exposed to high pressures (fault zones), but not in those exposed to high temperatures (deep burial).

The (002) spacings of muscovite and paragonite are affected by the K/Na ratio. Zen and Albee (1964) found that the (002) spacing of both minerals closely reflects the metamorphic grade. In rocks from the biotite and chlorite zone, paragonite has the smallest spacings and muscovite the largest spacings. Spacings approach each other as the metamorphic grade increases.

Feldspar

Weaver and Wampler (1970) found that in the Gulf Coast Tertiary the K-feldspar/Na-feldspar ratio decreased with depth. Hower et al. (1976) reported a decrease in K-feldspar in sediments from the same general area. It is apparent that the K-feldspar is being destroyed as the K is used to convert montmorillonite layers to illitic layers. It is not known whether the amount of Na-feldspar increases. Though secondary orthoclase is abundant in some sediments (Müller, 1967; Fairbridge, 1967) much of it appears to have formed from volcanic material at a relatively low temperature.

Some studies of metamorphosed argillaceous rocks (Weaver, 1961; Dunoyer de Segonzac and Abbas, 1976) have shown that Na-feldspar can be more abundant than K-feldspar, and Winkler (1976) notes that phyllites may contain as much as 20 percent albite.

The paragenesis of Na and K feldspar in the temperature range of 100° to 400°C is bound to be complex but the general trend appears to favor an increase Na-feldspar/K-feldspar ratio.

KAOLINITE

Shales

There is little question that kaolinite in shales disappears during deep burial, but there is little firm information on what happens to it. The depth and temperature at which it disappears vary widely and the factors which determine at what temperature it is destroyed or transformed are not well known.

A review by Dunoyer de Segonzac (1970) indicates that kaolinite in shales disappears at temperatures ranging from 80° to 190°C. The persistence of kaolinite to a temperature of 180°C at Pierrefeu he ascribed to a very low rock porosity and the relatively young age (Oligocene) of the formation. In the Paleozoic of the Polignac Basin, kaolinite persists to a temperature of at least 120°C. This he believed was due to a high organic content. The persistence of kaolinite up to a temperature of 190°C in the Salton Trough geothermal area might also be due to the young age of the sediments. In the latter case kaolinite starts to decrease in abundance at 165°C. In the Cretaceous Logbaba section kaolinite starts to decrease at 70°C and is gone by 90°C; however the loss of kaolinite coincides with a formation boundary and may never have been present in the underlying section.

In the Oligocene of the Upper Rhine Graben, kaolinite is present to total depth in a well with a bottom hole temperature of 169°C (Doebl et al., 1974). In Oligocene sediments of the Gulf Coast (Hower et al., 1976), kaolinite content decreases abruptly at 90°C and then remains constant to 174°C (total depth).

In a study of Carboniferous "kaolinite-coal-claystones" of the Ruhr district, Eckhardt (1965) found that the b-axis disorder of kaolinite decreased with an increasing temperature (increased coal rank). At temperatures less than 130°C there was little change in the crystallinity of the kaolinite (in claystones). No b-axis disorder was found in kaolinite exposed to temperatures above 200°C. In the Low Pennsylvanian-Upper Mississippian Springer shales of Oklahoma, kaolinite persists to a temperature of at least 220°C (Weaver and Beck, 1971, and Hood et al., 1975). The kaolinite content starts to decrease at a temperature of approximately 180°C.

Kossovskaya et al. (1964) reported that only chlorite and illite are present in the floors of semianthracite coal seams. In areas where the coal is lower rank, kaolinite is present. In Queensland, Australia, kaolinite is present in Permian tonsteins associated with medium-volatile bituminous coal (Kisch, 1966 b). Demaison (1974) has shown that equivalent rank Permian coals in Australia have been exposed to maximum temperatures of 130°C to 155°C. Semianthracite coals of equivalent age contain only chlorite and illite. The temperature for the formation of coals of this rank coal is approximately 200°C (Demaison, 1974). K, Mg, and/or Fe must be present to convert kaolinite to illite and chlorite. The source of the ions is not known. The presence of kaolinite on the shallow flanks of a basin does not mean it was once present in the central, more deeply buried portions of the basin. A study of Pennsylvanian underclays of the Mid-Continent-Appalachian area (Schultz, 1958) established that there was a regional variation in the clay mineral suite, with kaolinite being more abundant in the shelf underclays than in those in the geosyncline; however, this pattern could be due to variations in burial depth.

In a study of regionally metamorphosed shales in the Quachita Mountains, Weaver (1960) found that kaolinite was destroyed before the mixed-layer illite-montmorillonite was completely converted to illite.

With increased depth and temperature, kaolinite in shales is commonly observed to decrease and chlorite to increase. It is frequently suggested that this pattern indicates that kaolinite alters to chlorite. There is no direct evidence to indicate that this transformation occurs. Weaver and Beck (1971) suggested that the Al from the kaolinite may be incorporated in montmorillonite layers in mixed-layer illite-montmorillonite to form layers of dioctahedral chlorite.

Grim (1953) and Weaver (1959) found that kaolinite was less abundant in older shales than in younger (Cenozoic and Mesozoic) ones. A similar situation apparently occurs in Europe (Dunoyer de Segonzac, 1970, and Stark, 1968) and in Russia (Vinogradov and Ronov, 1956; Kossovskaya and Shutov, 1970). Grim suggested that kaolinite was destroyed during burial. Weaver (1960) suggested that the increase in kaolinite was due, in part, to the development of land plants and the creation of more acid conditions in more recent times.

Studies in other areas indicate that kaolinite is abundant in the Devonian of the Param Basin of Uraguay (Sanford and Lange, 1960) and in the Cambrian to Carboniferous shales of North Africa (Dunoyer de Segonzac, 1969). In Africa the present maximum depth of burial of the Paleozoic sediments is 3,000 m and present maximum well temperatures are less than 120°C. These data suggest that kaolinite was probably as abundant in the Paleozoic (but because of continental drift it formed in different areas) as in younger sediments, and that in much of North America, Europe, and Russia many of the Paleozoic sediments have been exposed to temperatures high enough (greater than 120°C) to destroy the kaolinite.

Sandstones

In interbedded shales and sandstones the sandstone units commonly contain more kaolinite than the surrounding shales. This is the case even when sand layers are only 1 mm thick (Weaver, 1967). Most studies indicate that the kaolinite was formed during shallow burial by acid waters that formed from organic material. The acid altered feldspar or other clay minerals to kaolinite. Bucke and Mankin (1971) reported a similar relation in Desmoinesian sand-shale pairs. They noted that in addition to organic material (low pH) and feldspar as a source of Si and Al, it was necessary to have degraded illite to adsorb potassium released from K-feldspar. This latter requirement is necessary only if the movement of water is restricted.

There are many examples of the formation of kaolinite in sandstones after burial; some examples from the United States are described by Glass (1958), Weaver (1967), and Wilson and Pittman (1977).

In salt-water-bearing Cambrian sandstones from the Sahara, Kulbicki and Millot (1961) found that kaolinite altered to illite.

Füchtbauer (1967) found authigenic well-crystallized kaolinite in clean Jurassic sandstones of Germany. The degree of crystallinity decreases with increasing clay content. The enclosing shales contain poorly crystallized kaolinite. Some of the kaolinite was formed from feldspar in an acid environment. The acid environment was created by CO_2 released during the early stages of coalification. With depth, kaolinite is believed to be converted to chlorite. Silica is liberated to form quartz overgrowths. In the Cretaceous of Alberta, Ghent and Miller (1974) found that in quartz-rich sandstones authigenic kaolinite formed later than quartz cement. In feldspar-rich sandstones it was associated with authigenic chlorite, calcite, and quartz. Sarkisyan (1972) reported that when pore waters are acid, regeneration of detrital kaolinite and kaolinization of clay cements occur at depths of 1,000 to 2,000 m. At depths of 2,000 to 3,000 m kaolinite can form from SiO_2 (dissolution of quartz) and Al_2O_3 (dissolution of feldspar).

Shutov et al. (1970) reviewed the Russian studies and reported that during transportation kaolinite becomes disordered. With burial there is a gradual transformation of kaolinite to dickite through the stage of mixed-layer growths. During deep burial, veins of dickite are formed. Under strong stress conditions, dickite is transformed to nacrite.

In the Cretaceous sandstones of the Cameroon, dickite is formed in the temperature range of 70°C to 90°C (Dunoyer de Segonzac, 1969). Though "elevated" or diagenetic temperatures are required to produce dickite, the temperature of formation appears to vary in response to varying chemical and physical conditions.

In a study of porous Pennsylvanian carbonate rocks of Kansas, Schroeder and Hayes (1968) found that dickite had been deposited from waters heated by Tertiary intrusive igneous rocks. At a distance of tens of miles from the intrusions, the water temperature had cooled sufficiently that well-crystallized kaolinite precipitated. The crystallinity of both the dickite and kaolinite is in part controlled by the porosity and permeability of the limestone. Poorly crystallized dickite and disordered kaolinite occur in the smaller voids in the less porous rocks. This is believed to indicate that the water moving through the restricted paths cooled more than that in the more porous rocks. These lateral changes in the kaolin minerals are similar to those observed in thick vertical sections.

Kossovskaya and Shutov (1963) reported that in quartz-kaolinite sandstones the kaolinite is converted to dickite when the pressure-temperature reaches the stage of deep-seated epigenesis, and to pyrophyllite at the metagenesis stage (anchizone). The pH is acid to neutral. They suggest that time influences the transformation temperature. Dickite was observed in lower Paleozoic rocks at 1,000-1,500 m and in Mesozoic rocks at 2,500 m.

Winkler (1976) reported that in rocks composed largely of kaolinite and quartz (and containing only minor amounts of K and Mg) the kaolinite can persist to temperatures in the range of 325° to 375°C. At higher temperatures it can be converted to pyrophyllite. The temperature of transformation decreases as the H_2O pressure decreases. When kaolinite occurs as a minor constituent in shales (less than 30-50 percent of the clay suite), it is usually destroyed or converted to some mineral other than pyrophyllite at an appreciably lower temperature.

In addition to massive pyrophyllite, solutions can be mobilized and pyrophyllite deposited in fissures produced during dynamometamorphism (Anton, 1975).

Pyrophyllite is abundant in shallow buried (deeper than 1500 m) Devonian and Silurian sediments of the Sahara where it replaces mica, kaolinite, and quartz. Associated minerals are calcite, dolomite, halite, and gypsum (Dunoyer de Segonzac, 1969). The associated mineralogy would appear to be a factor in the low-temperature formation of pyrophyllite.

Kubler (1966 b) and Kisch (1974) show pyrophyllite to be present in the anchizone and early metamorphic stages (illite crystallinity 7.5 to 2.0), which probably indicates a minimum temperature of formation of approximately 200°C. Frey (1970) found pyrophyllite in sediments which had been exposed to a maximum temperature of about 200°C.

Experimental

Henley (1959) established the stability fields of kaolinite, pyrophyllite, mica, and K-feldspar in terms of temperature and $\{K^+\}/\{H^+\}$. If the K^+ concentration and pH are sufficiently high, kaolinite can convert to illite at temperatures encountered at moderate depth. Such a transformation occurs in porous rock but does not appear to occur in shales.

In an investigation of the alteration of clay minerals under hydrothermal conditions, Frank-Kamenetzky et al. (1971) found that in the presence of KCl, kaolinite first is converted to montmorillonite and disordered kaolinite (∿225° C) and then to a K-hydromica at 250° C. K-hydromica is the only phase present at a temperature higher than 400° C. In the presence of NaCl the sequence is similar, except Na-hydromica develops and minor amounts of montmorillonite persist to a temperature of 500° C. In the presence of $MgCl_2$, kaolinite persists to 375° C. In the absence of quartz and in the presence of K and Na, kaolinite is converted to micaceous minerals. Laboratory studies by Lagache et al. (1963) established that illite alters to kaolinite at relatively low temperatures (<200° C) in the presence of CO_2. Kaolinite in Gulf Coast muds was destroyed at 100° C when the mud was heated in reactor bombs (Hiltabrand et al., 1973). The sediment-seawater ratio was 1:5, which does not duplicate natural conditions.

In nature, kaolinite may be destroyed or modified at temperatures as low as 70° C or may persist to 375° C. The temperature at which it is destroyed or transformed depends on the pH, chemistry, and porosity. The temperature at which changes occur appears to decrease as pH and/or porosity increase. In porous rocks containing acid water the crystallinity of kaolinite increases with increasing temperature, the kaolinite eventually being transformed to dickite. It is not clear whether the formation of pyrophyllite is necessarily preceded by this sequence of transformation.

When the solutions are alkaline, the kaolinite is destroyed; if K is abundant, it can be converted to illite.

In shales, kaolinite disappears over a wide temperature range, approximately 70° to more than 200° C. The temperature at which it is destroyed is in part dependent on the length of time it is exposed to these temperatures. The chemistry of the associated clay minerals and organic content (pH) are also factors. It is not definitely established what happens to the kaolinite in shales. In all likelihood the released Al and Si are reorganized to form layers of dioctahedral chlorite, or, where K is abundant, perhaps illite. In situations where kaolinite is essentially the only clay mineral present, the amount of b-axis disorder decreases in the temperature range of 130° to 200°C. It is not known if at higher temperatures the kaolinite is transformed to dickite. This appears unlikely because dickite is rare in shales. Where kaolinite is abundant, it can be altered to pyrophyllite at temperatures as low as 200°C (upper portion of anchizone).

CHLORITE

Less is known about the chlorite minerals in shales than about any other type of clay mineral. Chlorite is present in most shales but is seldom the dominant mineral. Thus, it is difficult to obtain direct chemical analyses or to determine the polytype. Most of the chemical information is obtained by x-ray analysis (Brindley, 1961). However, there is considerable information available about metamorphic chlorites and chlorites in sandstones, limestones, and evaporites, where chlorite is often the dominant clay mineral.

Polytypes and Composition

The structural variations of the chlorites have been discussed by Brindley (1961), Brown and Bailey (1962 and 1963), Shirozu and Bailey (1965), Lister and Bailey (1967), and Eggleston and Bailey (1967). Taking into account the bonding restrictions imposed by the superposition of the 2:1 layers and the hydroxide sheets of ideal hexagonal geometry, Brown and Bailey (1962) showed that four different arrangements of the brucite sheet relative to the initial 2:1 layer were possible. For each of the four chlorite layer types, the hexagonal rings in the repeating 2:1 layer may be superimposed in six different orientations. Six ideal systems with semirandom stacking are possible, two (Ib and IIa) based on an orthorhombic-shaped cell and four (Ia, Ib, IIa, IIb) based on a monoclinic-shaped cell.

Brown and Bailey (1962) examined 300 chlorites from different localities and found that approximately 80 percent had the IIb structure but found examples of the orthorhombic Ib, monoclinic Ib, and Ia structural types. The relative abundance of the polytypes was related to structural stability. To some extent, composition influences the stability of the chlorites through its effect on the cation charge and amount of distortion of the hexagonal network caused by size adjustments. Increasing tetrahedral Al substitution is accompanied by an increase in octahedral Fe to maintain a reasonable degree of fit between the two types of layers.

There is considerable overlap in the compositions of the various structural polytypes. The Ia and Ib chlorites have relatively distinct compositions, both being low in tetrahedral Al.

The IIb chlorite is the stable polytype in normal chlorite-grade metamorphic rocks and in medium- and high-temperature ore deposits. Brown and Bailey suggest that when sufficient energy is available the most stable polytype (IIb) will form. They found that the orthohexagonal and monoclinic Ib types were the ones most likely to be considered diagenetic chlorites. These are the chlorites with the lowest amount of tetrahedral Al. The Ib type readily converts to the more stable IIb type during metamorphism.

Hayes (1970) confirmed that the type I chlorites are formed by diagenetic processes. He proposed the following diagenetic stability sequence: Ib_d (disordered) to Ib (B = 90°) to IIb. He found that the type I chlorites occurred largely in sandstone and limestones, where they filled or lined voids and replaced such minerals as feldspar, biotite, volcanic material, calcite, and probably montmorillonite. The studies of Brown and Bailey (1962) and Hayes (1970) indicate that there is no significant difference in composition between type I and IIb chlorites. Hayes (1970) found that type I contained from 1.03 to 1.65 tetrahedral Al (per four positions). Octahedral Fe^{2+} ranged from 0.36 to 3.55 (per 6 positions). The ratio Fe^{2+}/Fe^{2+} + Mg ranged from 0 to approximately 0.8 and averaged approximately 0.4. Thus, most chlorites of both types contain more Mg than Fe. The source of the Mg and Fe was not considered in any detail.

Velde (1977) reports that in rocks containing chlorite and phengite the chlorite tends to be 50 to 100 percent more Fe-rich (relative to Mg) than the phengite. The higher the Fe content of the rock, the higher the Fe content of the chlorite.

Bradley (1955) has suggested that the silica-rich tetrahedral sheet is more temperature sensitive than the octahedral sheet and that at high temperatures the tetrahedral sheet has the potential for more lateral extension than the octahedral sheet. Macrocrystals which have structural regularity are formed at relatively high temperatures and have a strain-free fit between sheets. Such macrocrystals would be put under strain upon reversion to ordinary temperatures. Chlorites with a relatively high Fe content have a poor fit between sheets and do not form crystals as large as those with a more favorable composition. They exhibit diffraction effects which could be considered as departures from the ideal chlorite structure. Bradley believes that in both cases the strain is dissipated by the formation of faults which form by the periodic reversal of groups of silica tetrahedra similar to that which occurs in the palygorskite structures. This irregular distribution of faults would tend to diffuse the odd order x-ray reflections which alternate with the sharper even order reflections.

Foster (1962) calculated the structural formulas for 150 selected trioctahedral chlorites. These formulas indicate that the Si content ranges from 2.34 to 3.45 per four tetrahedral positions, the distribution being highly skewed toward the higher Si values. Most chlorites tend to have a much higher tetrahedral Al content than the 2:1 clays. Octahedral occupancy ranges from 5.46 to 6.05. R^{3+} octahedral occupancy ranges from approximately 10 to 47 percent of the filled positions with most of the values ranging from 15 to 35 percent.

A classification of the chlorites was devised by Foster (1962) based on ionic replacement of Al by Si in the tetrahedral sheet and Mg by Fe^{2+} in the octahedral sheet. The dividing lines are arbitrary and imply no genetic significance; in fact, they probably have some.

Experimental hydrothermal studies in a portion of the system $MgO - Al_2O_3 - SiO_2 - H_2O$ (Nelson and Roy, 1958) showed that a complete sequence of 14 A chlorites could be synthesized ranging in composition from amesite $(Mg_4Al_2)(Si_2Al_2)O_{10}(OH)_8$, to penninite $(Mg_{5.5}Al_{0.5})(Si_{3.5}Al_{0.5})O_{10}(OH)_8$. A certain minimum amount of R^{3+} substitution is necessary in order to provide sufficient layer charge to bind the various layers. The chlorite structure is not stable with more than one-third of the octahedral positions filled with Al; if more Al is present, a three-phase assemblage is produced, containing a chlorite of the amesite composition.

The same compositions, but at lower temperatures (below 400-500°C), produce a 7 A structure of the kaolin type. Nelson and Roy (1958) called these materials septechlorites. It was not established whether the 7 A phase was metastable or not.

Relatively few dioctahedral chlorites have been described but they may be more abundant than past studies indicate. In order to maintain electrical neutrality, the octahedral sheets must contain more than 4 Al per $O_{10}(OH)_8$. The excess octahedral charge should equal the amount of negative tetrahedral charge if no exchange cations are present. Reported tetrahedral charges range from 0.60 to 1.30. These charges are fully satisfied by excess octahedral occupation in hydrothermal samples but not in the sedimentary samples. The sedimentary specimens have a much higher tetrahedral Al content (1.20 and 1.30) than the hydrothermal clay, which would suggest that the basic 2:1 layers were not originally stripped illite or montmorillonite. It may be that the starting material was stripped biotite or chlorite from which much of the octahedral Mg and Fe was removed and, in part, replaced by Al (Weaver and Pollard, 1973).

Mode of Formation

Chlorite forms under a wide variety of conditions and temperatures. Present data indicate little relation between composition and temperatures, but some relation between composition and the environmental conditions in which authigenic chlorite forms.

Soils

Chlorites weather easily and are rare in soils except in relatively cold climates. Ball (1966) has described a chlorite-rich soil from the mountainous region of North Wales. The chlorite (IIb, Hayes, 1970) is residual and concentrated by the weathering of chloritic tuffs. Tetrahedral Al ranges from 1.0 to 1.7. The $Fe^{2+}/Fe^{2+} + Mg$ ratio ranges from 0.17 to 0.53, with 20 of the 26 samples having value less than 0.34. These "volcanic" chlorites have a higher Mg content than most of those found in sedimentary rocks.

In soils, smectites and vermiculite are frequently partially "chloritized" by the precipitation of hydroxy-Al, Fe, or Mg between the expanded layers (for review see Rich, 1968). "Chloritization" is seldom complete and the hydroxy material occurs as islands. The original clay is most often dioctahedral and hydroxy-Al is the most common interlayer material. Al and Fe hydroxides are precipitated under acid conditions and Mg hydroxide under basic conditions. Weaver and Beck (1977) have observed Fe-rich chlorite forming from kaolinite and Fe oxides in the soils of the southeast U.S.

Marine

Under marine conditions some hydroxy-Mg precipitates between montmorillonite layers causing partial chloritization (Grim and Johns, 1954). Rex (1967) describes hydroxy-Fe precipitating between montmorillonite layers in Pacific Ocean clays.

Bonatti and Arrhenius (1965) found Fe chlorite (Ib_d, Hayes, 1970) forming in the Pacific Ocean from Fe-Al oxide hydrate coatings (desert varnish) on silt grains, and Swindale and Fan (1967) described chlorite forming from sand- and silt-size gibbsite grains off the coast of Hawaii. Conversely, Berry and Johns (1966) and Heath (1969) found that detrital chlorite was being degraded in the bottom muds of the Atlantic and Pacific Oceans. Studies of sediments from the Mid-Atlantic ridge (Siever and Kastner, 1967, and Copeland et al., 1971) indicate that Fe chlorites from the outcropping greenstones are slowly changed, through contact with seawater, to Mg chlorite. It appears that either Fe or Mg chlorites can form in the marine environment.

Evaporites

Authigenic chlorite is commonly present in salty clays associated with salt deposits (Füchtbauer and Goldschmidt, 1959; Braitsch, 1971; Nelson, 1973), but is relatively rare in the dolomites associated with these deposits. These chlorites are reported to be Mg-rich, typically having a $Fe^{2+}/Fe + Mg$ ratio less than 0.1. Microprobe analysis (80) of authigenic chlorite from the Silurian salts of New York (Bodine and Standaert, 1977) shows they are also Mg-rich:

$$(Mg_{4.51}Fe^{2+}_{0.23}Al_{1.21})\ (Al_{1.06}Si_{2.91})\ O_{10}(OH)_8$$

Chlorite tends to be predominant in the strand line deposits of the German Zechstein deposits (Braitsch, 1971). In a survey of evaporite deposits of North America, Droste (1963) found that chlorite and corrensite were commonly present, though illite was the predominant clay in most deposits. Illite is present in most evaporite deposits. Corrensite or various forms of mixed-layer chlorite-vermiculite and chlorite-montmorillonite is a common component of evaporitic salt and sulfate beds (Kubler, 1973).

Carbonates

Chlorite and mixed-layer chlorite-montmorillonite are relatively abundant in Paleozoic and Mesozoic carbonate rocks (Weaver and Beck, 1977). These two minerals are the most abundant clay minerals in Lower Ordovician and Upper Mississippian carbonate rocks extending over thousands of square kilometers in the eastern United States. Limited data suggest these are mostly tidal deposits and the chloritic material has a high Mg/Fe ratio (Weaver, 1961, and Peterson, 1961). Ephemeral hypersaline conditions are believed to have existed in the tidal flat environments in which these clays formed (Weaver, 1961).

The data from the evaporite and carbonate rocks strongly suggest that Mg-rich chlorites form under hypersaline conditions; however, it is not known whether all of these chloritic clays are authigenic or whether some are formed after burial. Chlorites of similar composition are also common in metamorphic rocks.

Ironstones

Fe-rich clays are abundant in many sedimentary iron deposits (Berg, 1944; Chilingar, 1956; Schoen, 1964; Hunter, 1970). Most of the clay minerals are the 7 A variety (chamosite, septechlorite, greenalite, and cronstedtite), but chlorite is also present. Schoen (1964) calculated from x-ray data that the chlorite in the Clinton ironstones had the following composition:

$$(MgAl)_{2.5}(Fe)_{3.5}(Si_{2.65}Al_{1.35})O_{10}(OH)_8$$

The 2:1 layer had more Fe than the hydroxide sheet. Coexisting, primary 7 A chamosite from which much of the chlorite formed has a similar composition. Schoen further concluded that the Fe/Mg ratio of the chlorite had increased during diagenesis. He believed this was caused by an increase in Fe/Mg activity ratio in the solution rather than by temperatures.

Sandstones

Nondetrital chlorite commonly occurs as pore fillings and grain coatings in sandstones. As most of this chlorite appears to have formed after burial, it will be discussed in detail in another section.

Shales

There are few, if any, chemical analyses of chlorites in shales. X-ray analyses by Weaver (Weaver and Pollard, 1973) and Hayes (1970) indicate that the chlorites in Paleozoic shales typically contain 1.0 to 1.6 tetrahedral Al and have an $Fe^{2+}/F^{2+}+Mg$ ratio ranging from 0.25 to 0.67. The range of composition is similar to that for metamorphic chlorites except for those with either a very high Fe or Mg content (Brown and Bailey, 1963). It is likely that most of the chlorites in shales are detrital metamorphic chlorites. This is by no means certain, as it is likely that appreciable chlorite is formed during the transformation of montmorillonite to illite.

Diagenesis

Diagenetic chlorite forms in nearly all, if not all, the major rock types during burial. The composition is quite variable and appears to be more dependent on the composition of the solid phase and the solution than on temperature.

Sandstone

The presence of diagenetic chlorite in sandstones has been described by numerous people (reviewed by Weaver, 1967; Hayes, 1970; and Wilson and Pittman, 1977). There has been some controversy as to whether the chlorite-rich matrix in graywacke was primary or diagenetic. Recent studies (Lovell, 1972; Reimer, 1972; and Galloway, 1974) indicate that much of the matrix is formed by the diagenetic decomposition of unstable components.

The development of chlorite in sandstones during diagenesis and metamorphism has been described by Kossovskaya and Shutov (1958 and 1963). They point out that the stable mineral assemblages formed during diagenesis and low-grade metamorphism are dependent on the bulk composition of the original rock. Femic minerals are necessary for the formation of chlorite. The chlorite (and illite) first develops as a cement. With increasing depth, temperature, and lateral stress, chlorite aggregates form. At the slate stage of metamorphism, chlorite has a perpendicular orientation and penetrates into regenerated quartz and feldspar grains. In slate, chlorite lepidoblasts develop. Segregation takes place both on the surface bedding and along cleavage planes.

In a study of Tertiary sedimentary arc-related basins along the Pacific continental margin, Galloway (1974) found that at depths greater than 300 m authigenic chlorite and montmorillonite formed as coatings around detrital grains. With increasing depth (900 to 3,000 m) and temperature, open pore spaces are filled with authigenic zeolite, chlorite, or montmorillonite. Volcanic rock fragments, plagioclase feldspar, and mafic heavy minerals were the source material for the clays and zeolites. In advanced stages of burial, replacement of feldspar and rock fragments by chlorite and other minerals occur, and the matrix is recrystallized and partially replaced by chert and micas.

Karpova (1969) found Ib chlorite cement formed from volcanic fragments in continental and deltaic sandstones from the Upper and Middle Carboniferous of the Russian Platform. With depth IIb chlorite becomes predominant. Mg is more abundant in IIb than in the Ib chlorite. Sarkisyan (1972) reports that below a depth of 3,500 m chlorite cement forms in sandstones, siltstones, and silty shales. The chlorite content increases as the proportion of sand and silt increases. In a Permian basin in Russia, corrensite and Mg chlorite (in lagoonal sediments) and Fe-Mg chlorite (in marine sediments) are believed to have formed after burial in both shales and sandstones (Kossovskaya, 1969).

Almon et al. (1976) described the occurrence of authigenic corrensite in Upper Cretaceous volcaniclastic deltaic sands. Authigenic montmorillonite occurred in the associated marine sands. They suggested that the corrensite formed in a hyposaline rather than a hypersaline environment. It is of interest to note that their corrensite contains more Fe than Mg, whereas corrensite associated with evaporite deposits is Mg-rich. The limited chemical data indicate that corrensites have a range of compositions and that the composition appears to be at least partially related to salinity.

In the Eocene sandstones of southwest Texas the disappearance of kaolinite at 150-200°C is accompanied by an increase in chlorite. Calcite cement is replaced by ankerite at about 117-120°C. K-feldspar is destroyed at a temperature interval of between 199°and 120°C (Boles and Franks, 1979).

From x-ray analyses of diagenetic chlorites, largely from sandstones, Hayes (1970) found that IIb chlorites (detrital) tend to have more Mg and Si than type I chlorites, which definitely have higher Fe and Al contents. However, he concluded that composition alone is unimportant in determining the stability ranges of the different polytypes. Chemical composition is influenced by the bulk composition of reactants in the diagenetic environments. Hayes suggests that 150°C may be about the temperature at which Ib converts to IIb chlorite.

Wilson and Pittman (1977) noted that the concentration of Fe in secondary chlorites varied with morphology. The relative concentrations of Fe were plates and rosettes > honeycomb > cabbagehead.

In the Cretaceous arenites and calcarenites of northeastern Algeria, globular 14 A chlorites occur as shell fillings. It is believed that these pellets originally formed as 7 A chlorites and were converted to 14 A chlorite when exposed to burial temperatures of 25°C to somewhat above 100°C (Velde et al., 1974).

Shales

Hower et al. (1976) observed in a Gulf Coast Tertiary well that an increase in chlorite coincided with an increase in the illite layers in the mixed-layer illite-montmorillonite. They believe the chlorite is a by-product of the transformation of montmorillonite to illite. Chlorite is first observed at a well temperature of 70°C. It increases to a depth where the temperature is 100°C, then remains constant to total depth (174°C).

A reexamination of the data obtained by Weaver and Beck (1971) from a study of a Gulf Coast Miocene section indicates that at a temperature of 80°C the <0.2 μm fraction contained a mixed-layer illite-chlorite-montmorillonite. Below this depth-temperature, there is a slight increase in the amount of discrete chlorite. In the Pennsylvania Springer shales of Oklahoma, heat treatments indicate that the crystallinity of chlorite increases with depth and that the amount of expanded layers (mixed-layer chlorite-vermiculite) decreases with depth (Weaver, 1958).

Füchtbauer and Goldschmidt (1963), Dunoyer de Segonzac (1969), and others have observed that in thick sedimentary sections kaolinite decreases and trioctahedral chlorite increases with depth and temperature, and they suggest that kaolinite alters to chlorite. In the Jurassic shales of Lower Saxony, Füchtbauer (1967) found that chlorite increased at the expense of kaolinite and suggested that Si was liberated to form quartz cement in sandstones. In the Upper Carboniferous sandstones biotite flakes are chloritized below 3400 m. Weaver and Beck (1971) showed that as kaolinite decreased with depth in the Springer shales a dioctahedral chlorite developed. Minor amounts of kaolinite persist to depths where the present temperature is near 220°C. At 220°C only dioctahedral chlorite is present.

Sarkisyan (1972) reported that in the Caucasus corrensite (50 percent expanded layers) coexists with mixed-layer illite-montmorillonite containing 25 to 30 percent expanded layers. This suggests that the temperature to which the rocks were exposed was at least 120°C. In the Lower and Middle Ordovician shales and shaley limestones of Newfoundland, corrensite is believed to have formed diagenetically from volcanic detritus (Suchecki et al., 1977). The associated mixed-layer illite-montmorillonite contains only 10 to 15 percent expanded layers. This suggests that the temperature to which these sediments have been exposed is in the range of 170°to 220°C.

In metamorphosed Alpine rocks corrensite is present in rocks containing well-crystallized illite (Kubler, 1968).

The thermal stability range of corrensite exceeds that of illite-montmorillonite and appears to range from approximately 90°C to temperatures in excess of 200°C, perhaps as high as 300°C. Suchecki et al. (1977) suggest that this is due to the trioctahedral character of the chlorite-montmorillonite. The hydrogen bonds of the octahedral OH ions are oriented perpendicular to the clay layer, allowing for greater electrostatic repulsion between interlayer cations and the layer.

On the southwestern border of the Russian Platform (Karpova, 1969), Ib chlorites occur in the Upper and Middle Carboniferous sandstones. Deeper in the section the IIb polytype is present and contains more Mg than the Ib type. It is not known whether the IIb polytype was formed from the Ib polytype by Mg-metasomatism or after the Ib polytype was dissolved.

In felsic tuffs in the Neogene of Japan (Iijima and Utada, 1971, montmorillonite changes to corrensite at approximately 100°C (analcime zone) which in turn alters to chlorite at approximately 120°C (albite zone).

Kossovskaya et al. (1964) report that diagenetic chlorite and illite are abundant in the floor of semianthracite coal seams in the Petchora Basin. In Australia, Kisch (1966b) reported the presence of abundant Fe- and Al-rich diagenetic chlorite (along with mixed-layer illite-montmorillonite-chlorite) in tonsteins associated with coal of semianthracite rank (90-91.5 percent carbon). The chlorite is believed to form from kaolinite when Mg and Fe are present. The Fe is believed to come from siderite which through the loss of Fe is converted to ankerite (Kisch, 1968 a). When Mg and Fe are not present, the kaolinite becomes better crystallized or converts to dickite. Semianthracite coal is believed to have been subjected to temperatures on the order of 200°C (Demaison, 1974). A minor amount of chlorite is present in tonsteins associated with coals having 89 percent carbon (∿150°C). The presence of mixed-layer illite-montmorillonite with (001) spacings ranging from 10.2 to 12 A confirms that the rocks were probably not exposed to temperatures much greater than 200°C, and further demonstrates that diagenetic chlorites form at lower temperatures than pure illite (100 percent 10 A layers).

Dunoyer de Segonzac and Bernoulli (1976) observed that in the Upper Triassic of the Southern Alps chlorite and corrensite are present in the deeply buried Generoso Basin but not in the shallow buried sediments in the Lugarro Swell. Only illite and chlorite are present in the Austro-alpine maps.

Analysis of chlorite from metamorphic and igneous rocks (Albee, 1962) shows that their composition depends on the total composition of the rock and minerals associated with it. Thus, chlorites with a high Al content are usually associated with high-Al minerals (muscovite, margarite, spinel, etc.). Chlorites may have any proportion of Fe to Mg. The proportion depends on the Fe/Mg ratio of the bulk rock and the nature of the other minerals among which the Fe and Mg are partitioned. In general, chlorites are more Mg-rich in higher grades of metamorphic rocks. This has been demonstrated by the experimental studies of Nelson and Roy (1958) which showed the maximum stability temperature of Mg-chlorite to be higher than that of Fe-chlorite.

The composition of chlorite formed from montmorillonite and illite during diagenesis would presumably be determined by Fe and Mg content of the octahedral sheet of these two clays. However, it cannot be assumed that the Fe and Mg are released on the same proportion in which they occur in the octahedral sheet. Data compiled by Weaver and Pollard (1973) showed that there is a negative relation between K_2O and Fe_2O_3 for both illite and mixed-layer illite-montmorillonite; MgO is not related to K_2O. This suggests that Fe may leave the octahedral sheet more easily than Mg. During diagenesis, octahedral Fe^{3+} tends to be reduced to Fe^{2+}. The dioctahedral clays can accommodate only a relatively small amount (0.20 per $O_{10}OH_2$) of the large ferrous ion and it must leave the structure. Actually it may help disrupt the structure and facilitate the diagenetic reactions. Thus, chlorites formed during diagenesis should have a larger Fe/Mg ratio than the mixed-layer clay or illite from which they were derived.

In the Karroo shales of South Africa chlorite is first encountered close to the boundary between anchi- and epimetamorphism at a suggested temperature of 280°C (Rowsell and Deswardt (1976). The Fe and Mg were believed to have been derived from illite during recrystallization. Some of the chlorite occurs as porphyroblasts, as veinlets, and intergrown with muscovite. Crystallinity values range from 2.7 to 3.3.

Dunoyer de Segonzac and Abbas (1976) found that in a dolomite series in the Alps the thermal stability of chlorite increased with increasing degree of diagenesis and metamorphism. Thermal stability was measured with the following ratio:

$$R = \frac{\text{Intensity 7 A, unheated}}{\text{Intensity 7 A, heated}}$$

Chlorite can be formed in shales, sandstones and limestones at relatively low temperatures. Conversely, in the laboratory, many chlorites formed at low temperatures can be destroyed at temperatures as low as 300°C when they are heated in the absence of water.

K-Bentonites

A study of the K-bentonite beds of Sweden (Bystrom, 1957) indicates that the content of chloritic material increases as the tectonic deformation of the beds increases. In the Appalachian region, K-bentonites commonly contain chlorite or mixed-layer chlorite-montmorillonite. At least some of the chlorite is dioctahedral (Weaver, 1959). Chloritic material has not been reported in the equivalent age K-bentonite beds from the mid-content. These data suggest that the formation of chlorite is related to the depth of burial or temperatures. However, in the Appalachians chlorite may be present in one K-bentonite bed and not in another a few feet away in the same outcrop (Weaver, 1953). Something other than temperature must be involved. A chemical analysis of one of the chlorites from the Appalachian region indicates that it contains less than 2 percent Fe_2O_3.

Hydrothermal

In the Salton Sea hydrothermal area, Muffler and White (1969) observed that Mg-rich chlorite starts to form at temperatures of 130° to 165° C. In the Wairakei thermal area (Steiner, 1967), Fe-chlorite starts forming from montmorillonite at temperatures of less than 100° C. Eslinger and Savin (1973) found that the chlorite stage was preceded by a corrensite stage. Corrensite was observed at 112° C (shallowest sample examined) and chlorite at 140° C. Chlorite and mixed-layer chlorite-montmorillonite are commonly formed in wall rock altered by hydrothermal fluids or intrusions (Bundy and Murray, 1959; Naboko and Berkhin, 1970; Sudo et al., 1957; Chen, 1972; Harvey and Beck, 1960; Blatter et al., 1973). The chlorite is generally at the outer (cooler) rim of the alteration halo. In the low-grade metamorphic portion of the Ouachita System, thin veins of pure-Mg-rich chlorite are abundant (Weaver, 1961). Kubler (1973) concluded that under normal diagenetic conditions corrensite forms at temperatures of approximately 90° to 100° C and persists to at least 150° C.

Hydrothermally altered pillow basalts from the Mid-Atlantic Ridge consist predominantly of chlorite-rich greenstones (Humphris and Thompson, 1978). The chlorite MgO/FeO ratio is approximately one. Much of the Mg is obtained from seawater. Temperatures range from ambient bottom water temperatures to a few hundred degrees centigrade.

Corrensite and swelling chlorite are present in the basaltic rocks of the geothermal area on Reykjanes, Iceland, at temperatures ranging from 150° to 280° C. At lower temperatures, only montmorillonite is present. Normal chlorite was found in one well in the temperature range of 220° C to 290° C. Mixed-layer chlorite-smectite dominates at 200° to 230° C (Thomasson and Kristannsdottir, 1972).

ORGANIC MATERIAL

The scientists studying coal have established a relation between coal rank and temperature. Following these early studies, the petroleum scientists have established that the organic material in shales was temperature sensitive and that the type of hydrocarbon generated was dependent on temperature. Recent studies have demonstrated that time is as important as temperature.

The book "Stach's Textbook of Coal Petrology" (Stach et al., 1975) provides an up-to-date review of coalification. Much of the first part of this discussion is taken from their review.

Coalification Process

The development from peat through lignite, subbituminous coals, and bituminous coals to anthracites and meta-antracites is termed coalification. The chemical and physical changes that take place during coalification indicate that only the processes that operate up through the stage of lignite (soft brown coal) can be classed as diagenetic. The alterations that occur from the beginning of the subbituminous (hard brown coal) stage are so severe that they are regarded as metamorphism.

Coals react so much more sensitively to temperature than do minerals that the temperature, time, and pressure necessary for the formation of bituminous coals cause only minor diagenetic changes in associated sediments. Thus, the degree of coalification is perhaps the best method of determining the temperatures that existed during the early stages of sediment diagenesis. I believe the clay minerals are as sensitive to temperature as are coals. The clay minerals have the advantage of being present in nearly all sediments.

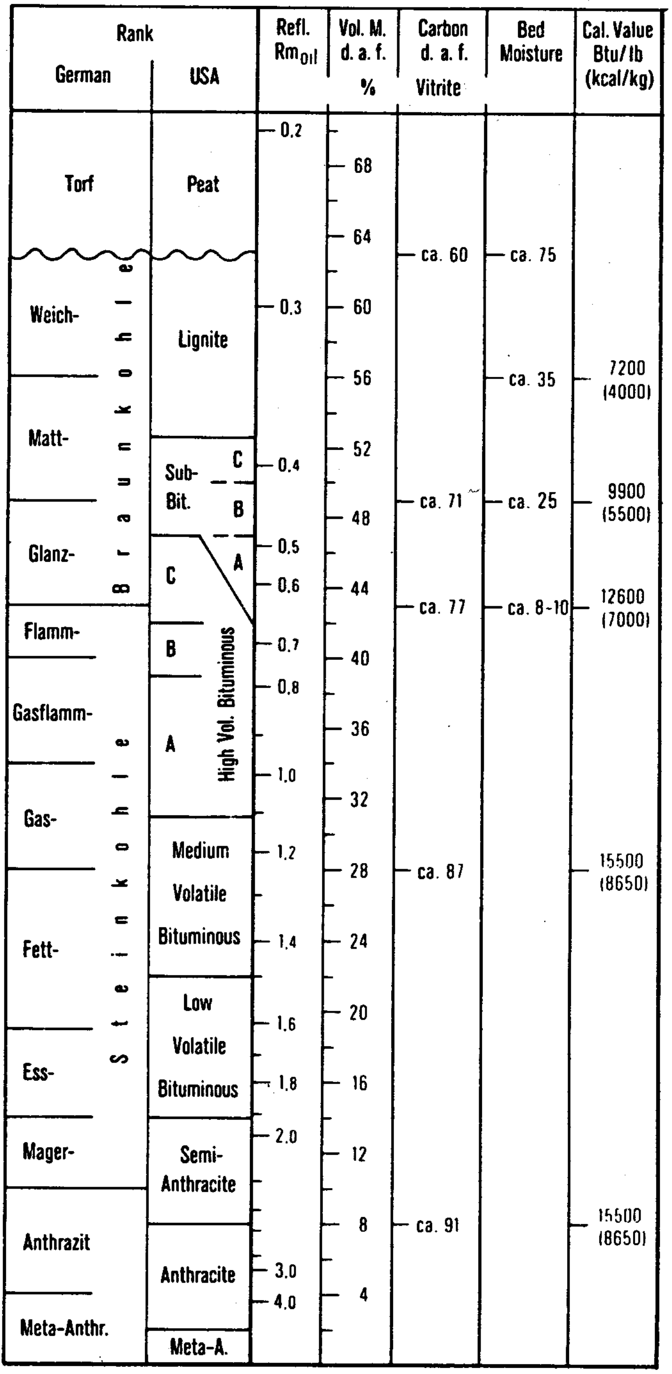
Both chemical and physico-structural changes occur during coalification. Decreases in porosity, moisture content, and optical anisotropy parallel to the bedding planes occur during the early stages of diagenesis (peats and brown coals). More advanced stages of diagenesis and metamorphism cause changes predominantly in chemical properties and optical properties (dependent on chemical composition).

As the moisture content decreases, the calorific value of the coal increases. The loss of moisture depends on a decrease in porosity and on the decomposition of hydrophylic functional groups, particularly OH-groups. Also, carboxyl, methoxyl, and carbonyl groups are split off, increasing the carbon content. During the lignite to subbituminous stage the last remnants of lignin and cellulose are transformed into humic materials. The humic acids condense to larger molecules, losing their acid character to form alkali-insoluble "humins". The most striking changes at this stage are petrographic. Geochemical gelification (vitrinitization) of the humic substances occur and the coal becomes black and lustrous.

During the bituminous stage the volatile matter (V.M.) systematically decreases and reflectivity rises. About equal amounts of CH_4 and CO_2 are released (Jüntgen and Karweil, 1966). The anthracite stage is characterized by a rapid fall of hydrogen content and of atomic H/C ratio, and a strong increase in reflectivity and optical anisotropy. Large quantities of methane only are released. Increasing graphitization occurs, especially during the meta-anthracite stage. These changes are summarized in Table 1.

The coalification process is controlled primarily by temperature and time. Pressure retards chemical reaction during coalification by inhibiting the release of gas. Chemical rank normally increases with depth. The rate of

Table 1. The different stages of coalification and their distinction on the basis of different physical and chemical rank parameters. After Stach et al. (1975). D.A.F. = Dry Ash Free.



Rank			Refl. Rm_{oil}	Vol. M. d. a. f. %	Carbon d. a. f. Vitrite	Bed Moisture	Cal. Value Btu/lb (kcal/kg)
German		USA					
Torf		Peat	0.2	68 64	ca. 60	ca. 75	
Weich-	Braunkohle	Lignite	0.3	60 56		ca. 35	7200 (4000)
Matt-		Lignite Sub-Bit. C	0.4	52	ca. 71	ca. 25	9900 (5500)
Glanz-		Sub-Bit. B Sub-Bit. A High Vol. Bituminous C	0.5 0.6	48 44	ca. 77	ca. 8-10	12600 (7000)
Flamm-	Steinkohle	High Vol. Bituminous B	0.7	40			
Gasflamm-		High Vol. Bituminous B High Vol. Bituminous A	0.8	36			
Gas-		High Vol. Bituminous A Medium Volatile Bituminous	1.0 1.2	32 28	ca. 87		15500 (8650)
Fett-		Medium Volatile Bituminous Low Volatile Bituminous	1.4 1.6	24 20			
Ess-		Low Volatile Bituminous	1.8	16			
Mager-		Semi-Anthracite	2.0	12			
Anthrazit		Semi-Anthracite Anthracite	3.0	8	ca. 91		15500 (8650)
Meta-Anthr.		Anthracite Meta-A.	4.0	4			

rank increase is dependent on the geothermal gradient and on the heat conductivity of the rocks. Studies in folded regions indicate that pressure has little effect on coalification. In most instances the coalification rank was obtained during burial and before folding. Adjacent to faults along which movement has been rapid, the coal rank may be increased due to the creation of frictional heat. Generally, movement is so slow that frictional heat is lost before it affects the coal.

Temperatures on the order of 100° - 150°C will normally produce a bituminous coal and temperatures on the order of 300°C (200°C is a more common value) will produce anthracite. Numerous examples indicate that for samples buried to similar depths those that have been buried for a longer time will have a more advanced degree of coalification. The influence of time is greater the higher the temperature.

Demaison (1974) has compiled data showing the relation of maximum paleotemperature to coal rank (Table 2). Presumably much of the variation is due to the influence of length of exposure to heat. Demaison believes that the influence of time is minor past about 200 m.y. of exposure to maximum heat effects.

Calculations have been made showing how coal rank is related to temperature and time (Huck and Karweil, 1955; Karweil, 1956; Lopatin, 1971; Lopatin and Bostick, 1973). Lopatin (1971) notes that it is necessary to sum the time a coal was in the various thermal zones in order to properly evaluate the time-temperature effects (sum of the adjusted durations of the process).

Lopatin and Bostick (1973) reviewed some examples. Temperatures below 50°C have little effect regardless of time. Lower Carboniferous coals of the Moscow Basin have not been subjected to temperatures higher than 25°C and

Table 2. Relation of coal rank to burial temperature. D.A.F. = Dry Ash Free. After Demaison (1974). For references see original paper.

COLOUR OF EXINITE CHANGES ARE TRANSITIONAL	VITRINITE REFLECTANCE R_o MAX.	CARBON CONTENT C % D.A.F.	COAL RANK (ASTM)	VOLATILE MATTER VOL. % D.A.F.	FRANCE PARIS BASIN CORREIA 1969	GERMANY UPPER RHINE GRABEN TEICHMÜLLER 1970	U.S.S.R U.S.S.R KARTSEV VASSOEVICH ETAL 1971	U.S.A U.S.A BOSTICK 1971	CANADA WEST CANADA STAPLIN ETAL 1973	AUSTRALIA COOPER GIPPSLAND SOUTH. PERTH DEMAISON (THIS PAPER) 1973
YELLOW 2	Ca 0.5	76	SUB. BITUM.	45	60°		60°	Ca 55°	65°	Ca 60°
ORANGE	Ca 0.7	82	HIGH VOL. BITUM.	40		Ca 80°	80°	Ca 75°		100°
3	Ca 0.9	84		36	90°	Ca 115°	115°	Ca 90°		115°
	1.12	86		31				Ca 100°		130°
BROWN			MEDIUM VOL. BITUM.				135°		140°	
3.5	1.51	90		22			150°	Ca 120°	170°	Ca 155°
DARK BROWN TO BLACK			LOW VOL. BITUM.							
	1.92	91	SEMI ANTHRAC.	14			165°			
4 OPAQUE	2.50		ANTHRACITE.	8			210°		200°	

remain lignites. In contrast, a temperature of 100°C has produced anthracite in the Upper Carboniferous, Oklahoma (270 m.y.); about 175°C was required to convert coaly material to anthracite in Jurassic (160 m.y.); and in the Salton Geothermal Field (Late Pliocene-Early Pleistocene), temperatures of 290° to 300°C were required to produce anthracite coal. Diagenetic changes of clay minerals are much less time dependent (Figure 8).

Damberger (1974) determined the coalification patterns of the Pennsylvanian coal basins of the eastern United States and noted that though they generally reflect the depth of burial during later Pennsylvanian and Permian times there is a superimposed pattern due to regional thermal disturbances. From Permian to recent times high heat flow apparently existed in the Rhode Island Meta-anthracite region, in the Pennsylvania anthracite region extending westward into the low- and medium-volatile bituminous coals of Pennsylvania and West Virginia, and in the high-rank bituminous coals in southern West Virginia.

Shales

Finely divided coaly particles are present in most shales and siltstones. Bostick (1974) coined the term phytoclasts for detrital plant material in sediments which has a composition similar to coal (others use the term kerogen). He concluded that 90 to 95 percent of the organic matter in sediments is phytoclasts rather than compounds soluble in organic solvents. Most of the phytoclasts consist of plant spores and pollen, leaf cuticles, and fragments that have bordered pits, ribs, fibers, or cellular structure. Some consist of insoluble humate and flocculant masses that may be of algal origin.

Rank measurements can be made with the microscope on these organic particles. Untreated rock samples are more satisfactory than concentrates prepared by chemical or physical methods. However, separation is often necessary because many rocks have an extremely low content of organic material.

One of the simplest methods of determining the degree of thermal alteration is through the use of a color index (Staplin, 1969; Hood et al., 1975; Epstein et al., 1976). The color of kerogen generally changes from yellow to brownish yellow to various shades of brown and finally to black as the degree of alteration increases. A yellow color indicates that the kerogen has been subjected to temperatures of less than 60°C; yellow to brown, temperatures 60° to 125°C; and black, temperatures greater than 125°C. More quantitative measurements include vitrinite reflectance (deVries et al., 1968, and Bostick, 1974), carbon content, and electron spin resonance.

Castaño and Sparks (1974) found little difference in vitrinite reflectance of coal-shale pairs except when the shales contained small amounts of vitrinite. Palynomorphs in limestones have significantly lower reflectance values than associated coals (Epstein et al., 1976). The reflectance of vitrinite in sandstones is less than that in mudstones (Chichua, 1964).

Hydrocarbons and Temperature

Coalification and bituminization are diagenetic processes during which mobile products (gas or crude oil) are evolved and aromatization and condenstion of the solid residual products (coal or kerogen of petroleum source rocks) take place. In general, the parent substance and the initial decomposition soon after deposition will determine whether coal or petroleum forms. Coals are formed primarily from lignin and cellulose from higher plants, and petroleum from lower organisms (algae, animal plankton, and bacteria). These latter organisms decompose anaerobically to produce lipids, the most important progenitors of hydrocarbons. During the geochemical bituminization process, the lipids become incorporated into kerogen.

Thermal degradation of organic matter is required to produce petroleum (Philippi, 1965). Degradation forms smaller molecules of increasing volatility, mobility, and hydrogen content (with methane as the end product). The carbonaceous residue (condensation) loses hydrogen, with graphitic carbon being the end product (Dobryansky, 1963).

The results of studies relating hydrocarbon occurrence to rank of associated coaly matter in various oil provinces were tabulated by Bostvick and Danberger (1971). Oil and associated gas occurs mainly in rocks in which the coaly material has reached subbituminous to high-volatile bituminous rank. Dry gas (methane) is formed during the medium-volatile bituminous coal through the anthracite stage. The base of the oil zone also coincides with 65 to 70 percent fixed carbon and vitrinite reflectance values of 0.8-1.1. A comparison of Table 1 with Table 2 (coal rank to temperature relations) indicates that the base of the oil zone occurs at 100°-140°C.

The effects of time on hydrocarbon generation were demonstrated by Laplante (1972). In the Gulf Coast Tertiary he found the level of carbonization necessary for hydrocarbon generation increased from 80°C for Oligocene sediments to 86 C for lower Miocene and 97°C for Upper Miocene.

Pusey (1973 b) introduced the concept of a liquid window. He noted that thermal "cracking" of kerogen and hydrocarbon generation starts at 65°C, and that liquid hydrocarbon destruction becomes dominant at temperatures greater than 150°C. This temperature interval he termed liquid window. Of the 266 known giant oil fields, 262 occur in this temperature range.

Pusey (1973) used electron spin resonance (ESR) data as a geothermometer. The number of free radicals increases as kerogen is subjected to increasing temperature. ESR provides a measure of the number of free electrons per gram of kerogen and of spin density (the number of free electrons per gram of sample).

The maximum paleotemperature determined by ESR was only 205°C. Pusey made no correction for effective heating time. Earlier Binder (1965), Crelling and Dutcher (1968), and Retcofsky and Friedel (1968) used ESR to rank coals.

The various coal-ranking properties (calorific value, moisture content, volatile content, hydrogen content, and vitrinite reflectance) are not applicable over a wide temperature range. Hood et al. (1975) suggested a scale which is continuous over the temperature range of approximately 50°C to 300°C and which can be correlated with coal-rank parameters. Though temperature is the major defining factor in the process of organic metamorphism, the effect of time is important enough that a temperature scale cannot be used as a general measure of organic metamorphism.

They call their scale "Level of Organic Metamorphism" or "LOM". The scale is a linear subdivision of a type-section (Tertiary-Cretaceous of New Zealand) or organic-rich sediments which was buried at essentially a constant rate and a constant temperature. Their scale is arbitrary and they note that the coal rank of a Carboniferous relative-depth column compiled by Bostick and Danberger (1971) does not coincide with the one they chose to use.

Lopatin (1971) and others concluded that doubling the reaction rate with each increase in temperature of 10°C provided a model of the relative effects of temperature and time in subsurface organic metamorphism. Hood et al. (1975) combined maximum temperature (T_{max}) with an effective heating time (t_{eff}) to develop a simplified method of predicting LOM for petroleum source rocks. Using a variety of burial histories and a wide range of activation energies (8.4 to 55 kcal/mole), they concluded that the effective heating time during which a rock has been within 15°C of its maximum temperature represents a suitable definition of effective heating time. Thus, if a sediment deposited

150 m.y. ago required 100 m.y. to reach a temperature of 120°C, and if during the remaining 50 m.y. reached a maximum temperature of 135°C and did not drop below 120°C, the last 50 million years is counted as the effective heating time.

Figure 14 shows the suggested relation of LOM and other parameters to the principal stage of petroleum generation. Diagenetic methane is formed in the lowest LOM stages. This is followed, with increasing LOM, by the generation of oil, condensate plus wet gas, and high-temperature katagenetic methane.

LOM values obtained from shale from two wells indicate that the values are not linear with depth. Shallower samples have higher LOM values than those defined by linear relations of LOM to depth. They believe this is mainly a result of an increase in apparent activation energy with increasing LOM. The lower activation energies, at low LOM values, indicate a greater importance of time with respect to temperature. Thus, for low LOM values the deviation from linearity is larger for Paleozoic than Mesozoic and Cenozoic rocks.

The published data (Hood et al., 1975, and Pusey, 1973 a) indicate that, regardless of age, the depth-temperature relations are linear at temperatures higher than approximately 150°-160°C. LOM and ESR parameters are linearly related to both at these higher temperatures. Between 75° and 150°-160°C the same relations are nearly linear, but the LOM and ESR parameters increase at a slower rate as a function of increased temperature.

In the Tertiary sediments of the Upper Rhine Graben (Doebl et al., 1974), reflectance of huminites/vitrinites increases from 0.20 (40°C) to 0.86 (169°C) in the well with the higher geothermal gradient and from 0.20 (40°C) to 0.73 (130°C) in a well with a lower gradient and containing a thicker section.

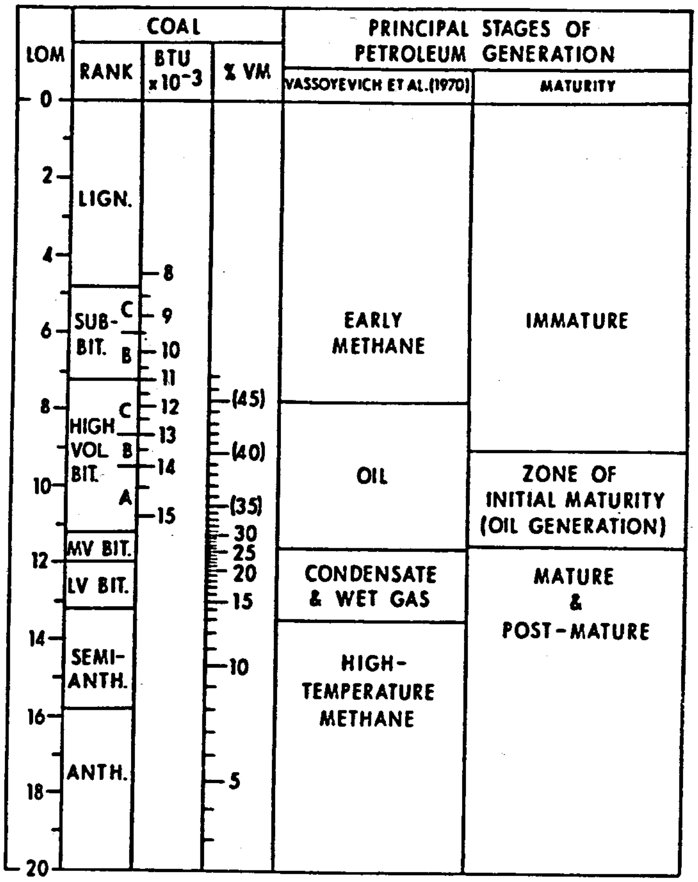


Figure 14. Organic metamorphic stages of petroleum generation. LOM = Level of Organic Metamorphism; VM = Volatile matter. After Hood, et al. (1975).

The transition from lignite to hard coal, corresponding to a reflectance value of 0.6, occurs at 130°C. High volatile bituminous coal was found only in the deepest sample, 169°C. These temperatures are considerably higher than those reported for equivalent reflectance values for coal (Demaison, 1974). The relatively low reflectance values for the measured temperatures may be due to the young age of the sediments, largely Oligocene and Miocene, and a recent increase in the geothermal gradient.

In the well with the higher geothermal gradient (7.7°C/100 m) the first formation of petroleum hydrocarbons was observed at a depth of 700 m (65°C); in the well with the lower gradient (7.2°C/100 m) they were first observed at 2600 m (118°C). This study further emphasizes the role of time and temporal variations in the geothermal gradient in determining the extent of mineral and organic transformation.

Conodonts

In a recent study, Epstein et al. (1976) related the color alteration of conodonts to an index of organic metamorphism. Conodonts are the hard parts, 0.1 to 1 mm in size, of an unknown organic group and are composed largely of carbonate apatite. They established a color alteration index (CAI) by heating conodonts at various temperatures till they obtained a stable color (Table 3).

Table 3. Munsell soil colors of conodont color alteration indexes (Epstein et al., 1976)

CAI	Munsell Soil Color
1	Pale yellow (2.5YR7/4 to 8/4)
1½	Very pale brown (10YR7/3 to 10YR8/4)
2	Brown to dark brown (10YR4/2 to 7.5YR3/2)
3	Very dark grayish brown (10YR4/2) to dark reddish brown (5YR2.5/2), to black (10YR2.5/1)
4	Black (5YR2.5/1) to black (10YR2.5/1)
5	Black (7.5YR2.5/0) to black (2.5YR2.5/0)

An Arrhenius plot of the data from conodont open-air heating runs was made to allow for the effects of time. The maximum heating time was 1000 hours and trends were extended to 5 x 10^8 years. Confined pressure during heating had no effect on carbonization; however, pressure in the presence of water retarded carbonization. Using the Arrhenius plots, they concluded that time had relatively little effect on the CAI beyond durations of about 50 million years. They point out that various studies, including theirs, have shown that coalification is a function of depth of burial, and tectonism influences it only where it increases depth of burial.

The CAI and temperature data (from Arrhenius plot) were compared with the translucency index and with vitrinite reflectance (Table 4).

Figure 15. Map showing conocont color alteration index (CAI) in Ordovician rocks in the Appalachian basin. After Epstein, et al. (1976).

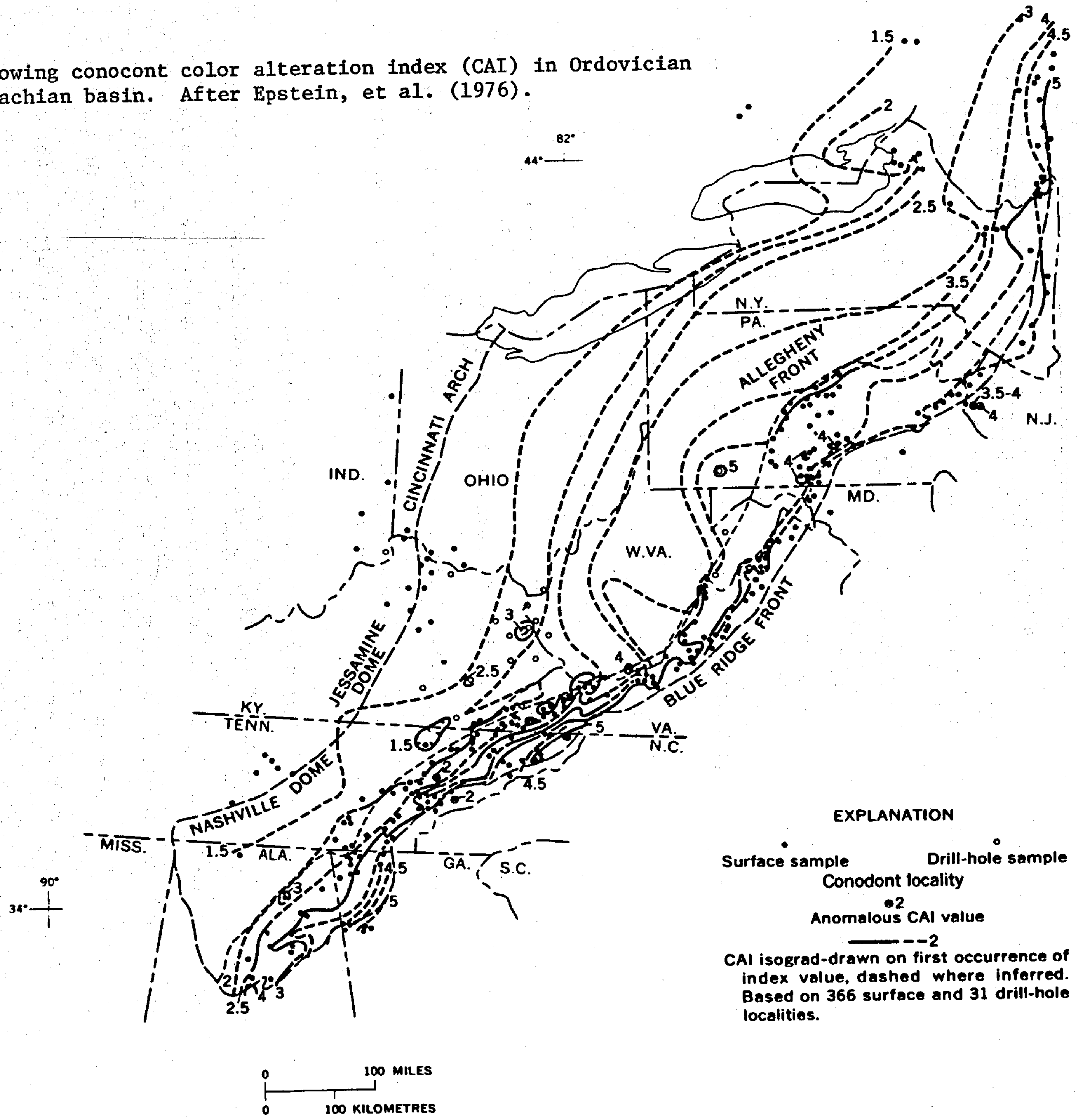


Table 4. Organic metamorphism indices (Epstein et al., 1976)

Conodonts		Palynomorphs		Vitrinite	
CAI	Temperature °C	Translucency Index (Amoco)	Weight Percent Carbon in Kerogen	Reflectance	Percent Fixed Carbon
1	<50-80	1-5	<82	<0.8	<60
1½	50-90	5-up.5	81-84	0.7-0.85	60-65
2	60-140	5-6	81-87	0.85-1.3	65-73
3	110-200	up.5-6	83-89	1.4-1.95	74-84
4	190-300	6	84-90	1.95-3.6	84-95
5	300-400	up.6-7	+90	+3.6	+95

The translucency index is most sensitive at lower temperatures (less than 160°C), and CAI and vitrinite reflectance at higher temperatures. There is a considerable temperature range for each CAI value. The reflectance data and the CAI show similar trends. Comparison with published data (Demaison, 1974) indicates that temperature values are in reasonably good accord, though for a given measurement there is considerable spread for both sets of temperature values.

Epstein et al. (1976) determined the CAI of conodonts from 705 limestone samples from the Appalachian Basin. They constructed CAI isograd maps for the Ordovician, mainly Middle Ordovician, Silurian through Middle Devonian, and Upper Devonian through Pennsylvania. Figure 15 is a map showing CAI isograds for the Ordovician. An isopach map of Middle Ordovician through Permian rocks was constructed to determine if the CAI values were related to the maximum depth of burial. Unloading is believed to have begun in the Triassic. Throughout most of the basin, CAI isograd and isopach trends are conformable.

The CAI values generally decrease from east to west. CAI = 1.5 begins at 1,220 m of overburden and persist to 2,440 m; CAI = 2 persists from 2,440 to 3,660 m of overburden; CAI = 3 persists from 3,660 to 5,490 m of overburden; CAI = 4 persists from 5,490 to 7,625 m of overburden; CAI = 5 begins at about 7,625 to 9,150 m of overburden. By assuming that the present-day geothermal gradient (3.3° per 100 m) persisted throughout post-Ordovician time, they calculated the temperature range for the various overburden depth intervals. The calculated values compared well with the experimental (heated conodonts) values.

In some areas CAI values are anomalously low. These values are for rocks that occur as windows in thrust sheets. Anomalously high values are found for conodonts in rocks near Cenozoic intrusions. The CAI isograd patterns of the younger sediments show similar relations, though the CAI values are generally lower. The oil fields are west of the 2 isograd. A CAI of 2 is equivalent to a vitrinite reflectance range of 0.85-1.3. Gas production extends into areas where surface rocks have CAI values as high as 4 (equivalent vitrinite reflectance range is 1.95-3.6).

Figure 16 is a map of a portion of the eastern United States showing the relation of oil and gas occurrence to the 70 percent fixed carbon line (100° - 140°C) in Upper Paleozoic strata. Equivalent strata to the east of this line were exposed to higher temperatures (Bostick and Danberger, 1971).

Relation of Mineral Diagenesis to Organic Metamorphism

Coal petrologists use the term "metamorphism" to refer to changes that occur in the temperature range which includes both the zones of "diagenesis" and "metamorphism". In the following section the literature is reviewed which shows the relation of mineral diagenesis and metamorphism to organic metamorphism.

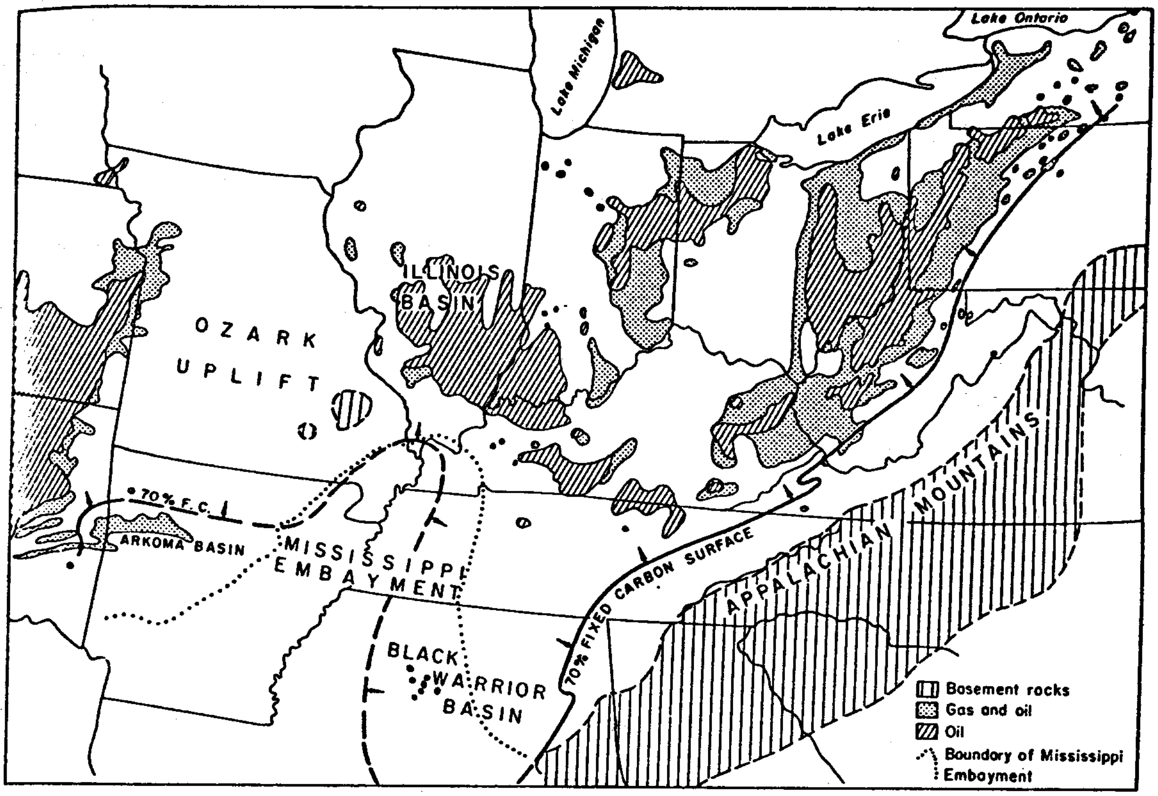


Figure 16. Regional relation of oil and gas occurrence to coal rank in Upper Paleozoic strata of the eastern United States. After Bostick and Danberger (1971).

Clay Minerals

Kisch (1968 a and 1974) reviewed the relation between coal rank and burial metamorphic mineral facies. He notes that minerals formed during burial are commonly metastable and that mineral composition, CO_2, H_2O, pore salinity, and pressure have an effect on progressive coalification.

Figure 17 summarizes Kisch's (1974) conclusions. He compared the data of the Russian authors to those of the French and Swiss and concluded that the zone of diagenesis is equivalent to the epigenesis zone; the anchimetamorphic zone is equivalent to the early metagenesis zone; and the epizone is equivalent to the stage of late metagenesis. The diagenesis-anchizone boundary coincides with the change from lean coal to anthracite (V.M. 8 percent, V.R. 2.5). This change in coal rank occurs at a temperature of approximately 200°C (Demaison, 1974, and Hood et al., 1975). The boundaries of the anchizone are based on crystallinity values for illite, upper 7.5 - lower 4.0. Dunoyer de Segonzac (1970) uses values of 4.0 and 2.5 for these boundaries.

Coal rank-mineral data on the Carboniferous of the Karaganda Basin and the Permian of the Petchora-Vorkuta Basin are given by Kossovskaya et al. (1964); Botscharnikowa (1965); Kossovskaya and Shutov (1970). Their data are tabulated in Table 5. I have estimated the temperatures, using the values of Demaison (1974) and Hood et al. (1975).

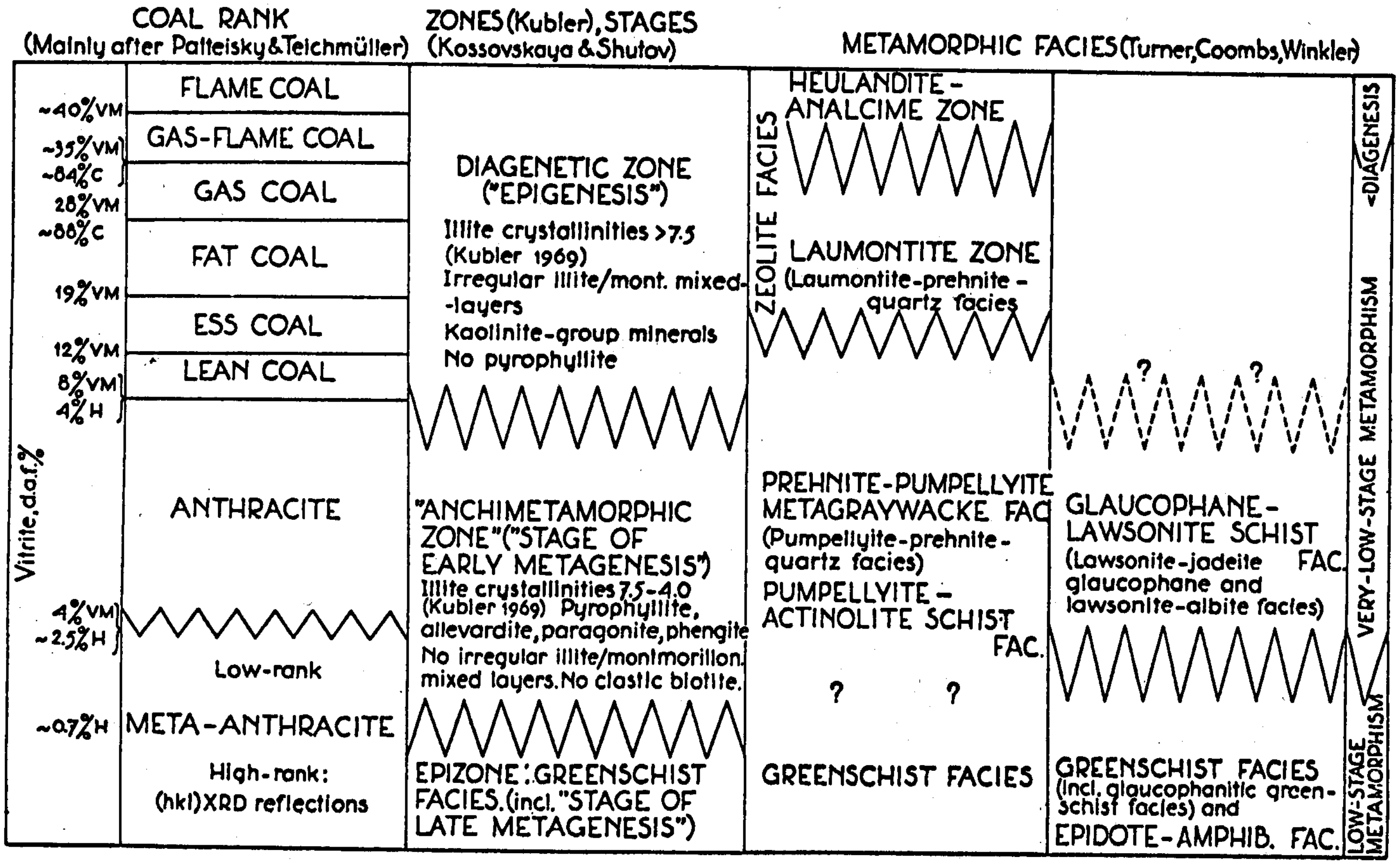


Figure 17. Schematic relation of diagenetic-metamorphic stages to coal rank. After Kisch (1974). For references see original publication.

Table 5. Relation of coal rank to shale mineralogy and temperature in some russian paleozoic sediments (Kossovskaya et al., 1964)

Rank	V.M.%	Clay Minerals	Possible Temp., ° C
High volatile bituminous	35-30	Montmorillonite (probably containing <50% illite layers)	90-115
Medium and low volatile bituminous	30-18	Mixed-layer, 20-50% expanded layers	100-170
Low volatile bituminous and semi-anthracite	18-10	IM illite (1MD?)	150-180
Anthracite	<6%	2M illite, chlorite	>200

In a detailed study of the Tertiary clays of the Upper Rhine Graben, Doebl et al. (1974) related the transformation of organic matter and clay minerals to various geothermal gradients. They established from a study of numerous wells that smectite persists to temperatures in the range of 68° to 76°C, though in young, rapidly buried sediments it persists to temperatures as high as 115°C. The absence of smectite presumably refers to the absence of a 17 A reflection and the formation of a mixed-layer illite-smectite with less than 40 percent expanded layers.

The maximum temperature they reported was 169°C (2063 m). Though void ratio and pore radii decrease with increasing temperature, and reflectance of huminites and vitrinites increase, there is no major change in the clay mineral suite (smectite, mixed-layer illite-smectite, illite, kaolinite, and chlorite), other than the conversion of smectite to mixed-layer clay, with depth and temperature. There is some suggestion that in the temperature range of 130° to 169°C kaolinite decreases and chlorite increases. Approximately 20 percent calcite is present and does not decrease with increased depth and temperature. Kaolinite disappears from sandstones at a depth of 3000 m in the Upper Namur C. The associated coal is an anthracite (7 percent V.M.).

Kisch (1974) has compiled the data on the coal ranks associated with anchizone minerals (illite crystallinity 7.5 to 4, allevardite, paragonite pyrophyllite). He points out the problem of measuring illite crystallinity when pyrophyllite (9.2 A) or paragonite (9.7 A) are present. The coals associated with the anchizone minerals listed above are anthracites (8 to 4 percent V.M.). The upper limit of the anchizone is the lower limit of the existence of liquid hydrocarbons. Kaolinite and mixed-layer illite-montmorillonite are presumed not to be present in anchizone sediments; however, the compiled data indicate that kaolinite, commonly along with pyrophyllite, is present in the underclays associated with the anthracite coals of the northeastern United States, along with pyrophyllite, illite, and chlorite. Mixed-layer paragonite-muscovite has been reported in some Alpine anchizone deposits (Hoefs and Frey, 1976). The temperature range is estimated to be from 200° to 350°C. Paragonite is a common component of anchizone and higher grade pelitic and marly rocks of the Alps (Frey, 1974). Earlier Frey and Niggli (1971) considered that the upper anchizone boundary (7.5 crystallinity index) coincided with coals containing 35 to 19 percent V.M. (compared with Kisch's boundary at 8 percent V.M.). The lower boundary is similar to that proposed by Kisch. Quinn and Glass (1958) found anthracite and low-rank meta-anthracite of the Narragansett basin, Rhode Island, associated with rocks of the muscovite-chlorite subfacies of the greenschist facies, and a higher-rank meta-anthracite with rocks of the biotite-chlorite subfacies.

Albrecht and Ourisson (1969) studied a well penetrating the Cretaceous Douala shales of the Cameroun and established that extra stable heavy saturated hydrocarbons were most abundant in the depth range of 1300 to 2200 m. Present day well temperature over this interval increase from 60° to 105°C. My interpretation of Dunoyer de Segonzac (1970) x-ray data indicates that through this interval the proportion of illite layers in the montmorillonite increases from approximately 10 percent to 70 percent. The illite layers increase to approximately 90 percent at a bottom hole depth of 418.5 m and temperature of 155°C.

Pusey (1973 b) established a correlation between ESR-kerogen data and the "first-collapse" of montmorillonite in the Cretaceous of South Texas. Oil is produced above the "first collapse" of montmorillonite (120°C) but gives way to dry gas below the "first collapse".

Foscolos and Kodama (1974) and Foscolos et al. (1976) have studied the clay minerals and organic material in a series of Lower Cretaceous shales from northeastern British Columbia and have established diagenetic relations. They found that the amount of 2M illite, its crystallinity index, and its sharpness ratio increases with depth. The proportion of illite layers in mixed-layer illite-montmorillonite increases from approximately 50 percent to 85 percent with depth (maximum depth 3078 m). In the <0.08 μm fraction, K_2O increases with depth; $SiO_2 + Fe_2O_3 + MgO/Al_2O_3$ and C.E.C. decrease.

Vitrinite reflectance values show considerable variation in the shales where diagenetic reactions have been minor, but increase systematically as mineral diagenesis increases. The interval of maximum yield of extract and hydrocarbons (mg/g organic C) coincides with the interval where the proportion of illite in the mixed-layer illite-montmorillonite increases from 25 percent to 75 percent. The relation, particularly the upper boundary, is not good. In part, this is because the assumption is made that the starting material contained a fully expanded montmorillonite. The data suggest that the original (detrital) expanded clay contained approximately 50 percent illite layers, rather than fully expanded montmorillonite.

In Figure 18, I have plotted the vitrinite reflectance values vs. the percent illite layers in the mixed-layer clay for the Lower Cretaceous shales and for the literature data as interpreted by Foscolos et al. (1976). Also included are temperature ranges for the various vitrinite reflectance values. Temperature data are from Demaison (1974). On the upper boundary of the graph are plotted the paleotemperatures calculated by Foscolos and Kodama (1974) for the Lower Cretaceous shales, assuming a geothermal gradient of 3.6°C/100 m. The literature data are reasonable, but some of the vitrinite reflectance values for the Lower Cretaceous shales are higher than those observed in other areas.

Gill et al. (1977) studied the clays in the sediments associated with coals in the South Wales coalfield and established a relation between coal rank and mineral diagenesis-metamorphism. They describe a diagenetic zone for terrigenous rocks in which the illites have a sharpness ratio (S.R.) of 2.0-3.0; the carbonate rocks in this zone have a S.R. of 2.1 to 2.5 and the mixed-layer clays 35 to 40 percent expanded layers. The fixed carbon values range from 65 to 80 percent. In the metadiagenetic zone (late stage diagenesis), the respective S.R. values are 3.0 to 4.0 and 2.5 to 3.2 and the mixed-layer clays in the carbonate rocks contain 20 to 35 percent expanded layers. Fixed carbon values range from 80 to 90 percent. In the anchizone, anthracites with fixed carbon greater than 90 percent, the S.R. values are 4.0 to 6.0 for terrigenous rocks and 3.2 to 4.0 for carbonates. The carbonates contain mixed-layer clays with 0 to 20 percent expanded layers plus new vermicular kaolinite and dickite. The terrigenous rocks contain allevardite and pyrophyllite.

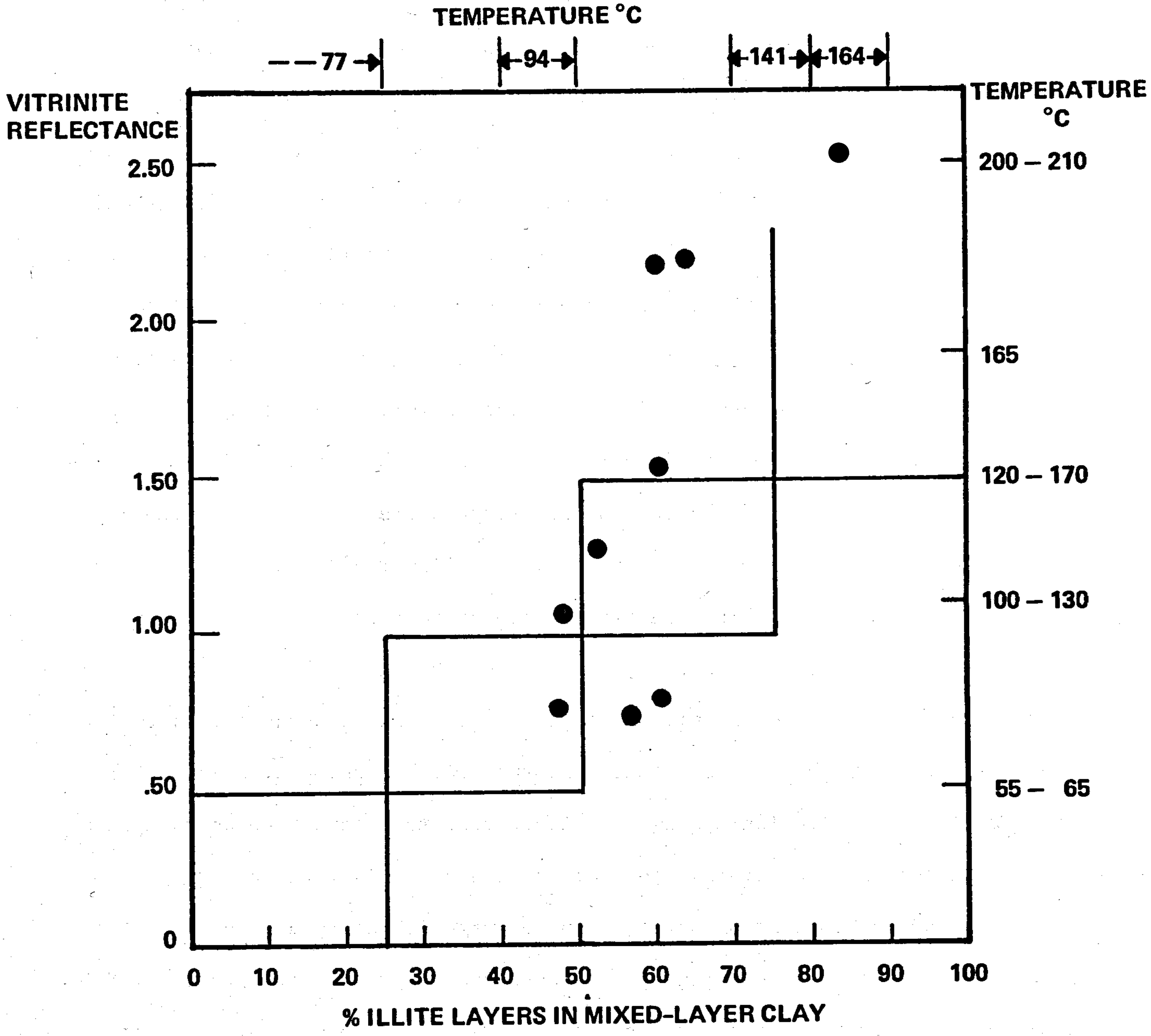


Figure 18. Relation of percent illite layers in mixed-layer illite-montmorillonite to vitrinite reflectance and temperature. Dots and temperature values at top of graph are based on data from Foscolos, et al. (1976). Squares outline range of values from literature. Temperature scale on right axis is based on data from Demaison (1974) and relates to V.R. values.

Van de Kamp (1977) attempted to relate LOM values to clay mineral changes. He states that the montmorillonite zone occurs in the interval LOM 0 to 7; mixed-layer illite-montmorillonite, LOM 7 to 9-10; illite zone, LOM 9-10 to 14; greenschist facies, LOM greater than 14. These associations are incompatible with other data. A more realistic relation would be: montmorillonite, LOM 0 to 9-10; mixed-layer illite-montmorillonite, LOM 9-10 to 18-20; illite, LOM 16+. An LOM value of 20 is considered to be equivalent to 2 percent V.M. (meta-anthracite) and the greenschist facies; however, the data does not support this. Hood et al. (1975) report that the organic matter in the Carboniferous shales from the Shell Rumberger 5 (Oklahoma) should have an LOM value of 20 at approximately 7500 m, which should be in the greenschist facies. My x-ray analysis of a shale core from 7318 m (Total Depth) from the same well showed that it is composed of illite and chlorite (dioctahedral) and 25 percent mixed-layer illite-montmorillonite. The sharpness ratio is 2.9, the crystallinity index 10.0, and the bottom hole temperature approximately 220°C.

The deeper samples in this particular well illustrated some of the problems involved in establishing the diagenetic-metamorphic grade of rocks with a high content of sheet silicate minerals. The LOM and vitrinite reflectance values indicate that the organic matter in the shales has been altered to the level of the greenschist facies (meta-anthracite); but the clay suite, sharpness ratio, and crystallinity index indicate that the clays have been exposed only to diagenetic conditions. The temperature value is intermediate, but fits the clay interpretation better than the organic interpretation. It has been assumed that the beginning of the anchizone (crystallinity 7.5, S.R. 2.3-4.0) and the formation of anthracite coincide with the loss of mixed-layer illite-montmorillonite and the formation of pure illite. In many instances, if not all, this is not correct. Expanded layers persist in "illites" to much higher temperatures and crystallinity and sharpness ratio values than those selected to define the upper boundary of the anchizone. That time is not a significant factor in the illitization of montmorillonite is illustrated by the presence of mixed-layer illite-montmorillonite, with 20 to 30 percent expanded layers, and even discrete montmorillonite in Precambrian rocks 1.7 to 2 B.Y. old.

In detail the LOM scale and the other organic scales do not correlate well with the changes in the clay minerals. The organic material is significantly affected by time as well as temperature, whereas the clay minerals are much more responsive to temperature than time. However, clay minerals alterations involve a number of kinetic barriers and progressive changes are often not linearly related to temperature. Eberl et al. (1978) has shown experimentally that the presence of interlayer ions such as Na and Ca inhibits the conversion of smectite and illite. Smectites may react relatively rapidly to increases in temperature, but when alteration has proceeded to the stage where the chemistry is not "right" (K greater than Ca + Mg + Na) no further changes occur, with time, until there is a major increase in temperature. Original composition is also a factor. Montmorillonites with high Fe + Mg/Al ratios require higher temperatures to undergo illitization than those with low ratios (Boles and Franks, 1979).

It is going to be very difficult to relate clay mineral and organic diagenetic reactions. Present suggestions are only locally applicable. As clay mineral reactions are not as time dependent as organic material reactions, they should be more indicative of paleotemperatures than organic material.

Jackson (1977) established a relation between the crystallinity and S.R. of illite and the ratio of aliphatic to condensed-aromatic components as a function of time. He concluded that the breadth of the illite peak and degree of humification of polar organic matter vary in a complex and apparently systematic way through geologic time. He suggests that the original structure and composition of the organic matter influenced postdepositional changes in the crystallographic properties of sedimentary clay minerals. The data are too few to be convincing. Further, it seems likely that the pattern is due to variations in the depth of burial (temperature) rather than any organic control of illite diagenesis.

Carbonates

Curtis (1978) has reviewed the data on carbonate cementation during diagenesis. He points out that the activities of chemical species in solution will be controlled by the composition and amounts of the solids present rather than the other way round. It is unlikely that Eh and pH control the precipitation of diagenetic minerals.

He suggests that the diagenetic carbonate cements in mudstones tend to replace pore water. Therefore, the cement/elastic component volume ratios should be indicative of the depth of burial. This is true only if cementation goes to completion at a given depth. Carbon isotope data demonstrate that the source of the carbonate often lies in organic matter degradation reactions. Carbonate types vary with burial depth and Curtis relates them to the established organic diagenetic zones and temperatures. Calcite and pyrite precipitate in the shallow bacterial sulphate reduction zone. Ferroan calcite, ferroan dolomite, or siderite precipitate in the zones of bacterial fermentation and decarboxylation. The rate of bicarbonate generation and iron reduction increases with depth and temperature until the reactant materials become exhausted. The temperature at the base of the lower zone is given as 75°C above surface temperature. In the deeper zones where liquid hydrocarbons and methane are generated, carbonate formation is not strongly influenced by bicarbonate derived from organic matter; instead the main processes are dissolution, re-precipitation, or replacement reactions involving unstable primary carbonates and early diagenetic carbonates. In these higher temperature zones any carbonate mineral may form.

Zeolites

Zeolites will be discussed briefly. Most of the information comes from a comprehensive review by Kisch (1974).

A study of the Tertiary coals of Japan by Shimoyama and Iijima (1976) showed that clinoptilolite and mordenite (largely in tuffs) occur with lignite and subbituminous coals. The base of this zone occurs at approximately 85-90°C. The bituminous coals belong exclusively to the analcime zone. In the upper half of the analcime zone, alkali clinoptilolite is replaced by heulandite and locally by calcium clinoptilolite. In the lower half, laumontite substitutes for heulandite, for calcium clinoptilolite and, in place, for mordenite. In New South Wales, analcime is associated with coals having a carbon content below about 85 percent (high volatile bituminous) and laumontite with coals having a higher carbon content (Kisch, 1966 a).

In a number of areas kaolinite, montmorillonite, and mixed-layer illite-montmorillonite are found in laumontite-bearing sequences. The evidence from the associated coal rank indicates that the laumontite zone correlates with lower grades of metamorphism than the anchizone (Figure 17). Limited data suggest that the beginning of the prehnite-pumpellyite facies corresponds to a slightly lower coal rank (15 percent V.M.) than the beginning of the anchizone (8 percent V.M.). The coals associated with anchizone glaucophanelawsonite-schist facies are largely anthracites and low-rank meta-anthracites. The coals associated with glaucophanitic greenschist facies are presumably meta-anthracites.

Zen and Thompson (1974) have suggested slightly different coal rank-zeolite associations. The main difference is the extension of the laumontite zone into the anchizone.

THERMODYNAMIC INVESTIGATIONS

The primary purpose of this paper is to evaluate the chemical and mineralogic changes that have been determined by a study of natural rock; however, for the sake of completeness, experimental and theoretical phase equilibrium studies will be discussed briefly. Some of the more pertinent experimental data have been discussed earlier in this paper.

The stability relation of minerals in the $K_2O - Na_2O - SiO_2 - Al_2O_3 - H_2O$ system are relatively well known at elevated temperatures. In most instances these stability relations are established by heating glasses of various composition under hydrothermal conditions. The phases produced are primarily a function of the composition of the initial solid complex. The reactions occur in a closed system. Because the amount of water relative to solid is small, the chemical composition of the water will change until it equilibrates with the solid. Under low pressure-temperature conditions, laboratory investigations are hampered by the sluggish kinetics of mineral equilibrium and by the persistence of metastable phases. Phase relations are established using thermodynamic calculations, extrapolation of hydrothermal data, and the knowledge of natural mineral assemblages.

Garrels and Christ (1965), Hess (1966), and others have described the procedure for making equilibrium calculations. It is assumed that the chemical reactions occur in water and that the minerals are in equilibrium with the water. Thus, it is necessary to know the composition of the aqueous solution as well as the composition of the mineral reactants and products. Al is relatively insoluble and is assumed to be an inert component.

The stable mineral assemblage for a given set of physical and chemical conditions is that with the lowest free energy under those conditions. An equation is written for an equilibrium reaction between two minerals conserving Al in the solids. For a given pressure and temperature, these reactions are defined by equilibrium constants. The equilibrium constant (K) is equal to the product of the activities of the products raised to the power of their numerical coefficients divided by the product of the activities of the reactants raised to the power of their numerical coefficients. The log of the equilibrium constant is taken, and the activities are arranged into terms of log Na^+/H^+, log K^+/H^+, etc. and log SiO_2. These units are used to characterize the aqueous environment in the system and are used to describe the phase equilibria.

A typical example is the K- mica - kaolinite reaction.

$$2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O = 3H_4Al_2Si_2O_9 + 2K^+$$

$$\log K = \log \frac{K^{+2}}{H^{+2}}$$

It is then necessary to relate the free-energy changes of the reactions to their equilibrium constants and to define the free-energy content of the various types of substances. It is necessary to obtain the free energy of the reaction to form one mole of the substances in their standard states from the stable elements under standard conditions. The standard free-energy change of a reaction is the sum of the free energies of formation of the products in their standard states, minus the free energies of formation of the reactants in their standard states

$$\Delta F^\circ_r = \Sigma\Delta F^\circ_f \text{ products} - \Sigma\Delta F^\circ_f \text{ reactants.}$$

The standard free-energy of reaction is related to the equilibrium constant by

$$\Delta F^\circ_r = -RT \ln K.$$

Equilibrium is obtained only when the free-energy of a reaction is zero. If the ΔF_r° is negative, the products are stable relative to the reactants; if ΔF_r° is positive, the reactants are stable.

The amount of silica in solution is primarily limited by amorphous silica saturation. At 25°C the solubility of amorphous silica ranges from 100 to 160 ppm at $pH < 9$. Solubility increases to approximately 800 ppm at 200°C.

The accuracy of the calculated stability relations depends on the accuracy of the thermodynamic data used and in knowing the composition of the phases involved. Many of the values for the standard free energies of formation of compounds, dissolved species, and elements at various temperatures are subject to large uncertainties. This limits the reliability of the predicted phase relations. Tardy and Garrels (1974) have developed a method of estimating the standard free energies of formation of layer silicates. It is based on the assumption that the oxides and hydroxide components of these silicates have fixed Gibbs energies of formation within the silicates. All of these calculations are based on assumed chemical compositions of the mineral phases. Because the chemical composition of most clay minerals varies over a wide range, no single diagram can accurately represent the phase relations.

Figures 19 and 20 are examples of a collection of activity diagrams calculated by Helgeson et al. (1969). Though the aqueous phase is not shown, it is a coexisting phase in all stability fields and is saturated with the minerals shown in the diagrams. The diagrams are based on a standard state of unit activity of the solids and unit activity of the aqueous species in a hypothetical one molar liquid solution at one atmosphere and the temperature of interest. Increasing pressure has only a slight effect on equilibrium constants at temperatures below 300°C.

The thermodynamic calculations do not take into account the kinetic factors. Some reactions in silicates are rapid but many are sluggish and occur

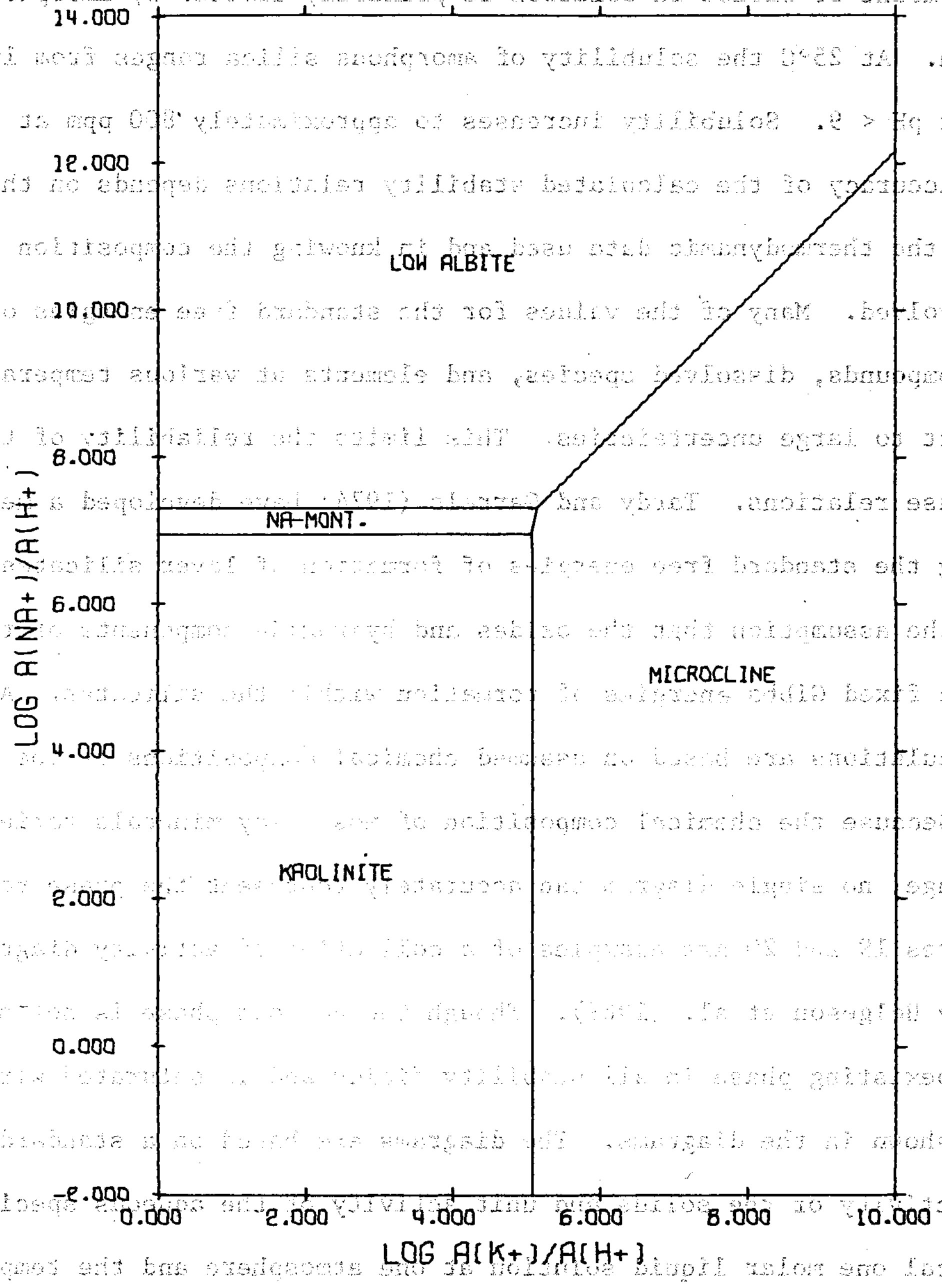


Figure 19. The system $HCl-H_2O-Al_2O_3-K_2O-Na_2O-SiO_2$ at 60^0C; log $a_{H_4SiO_4}$ = -3.52 = quartz saturation. After Helgeson et al. (1969).

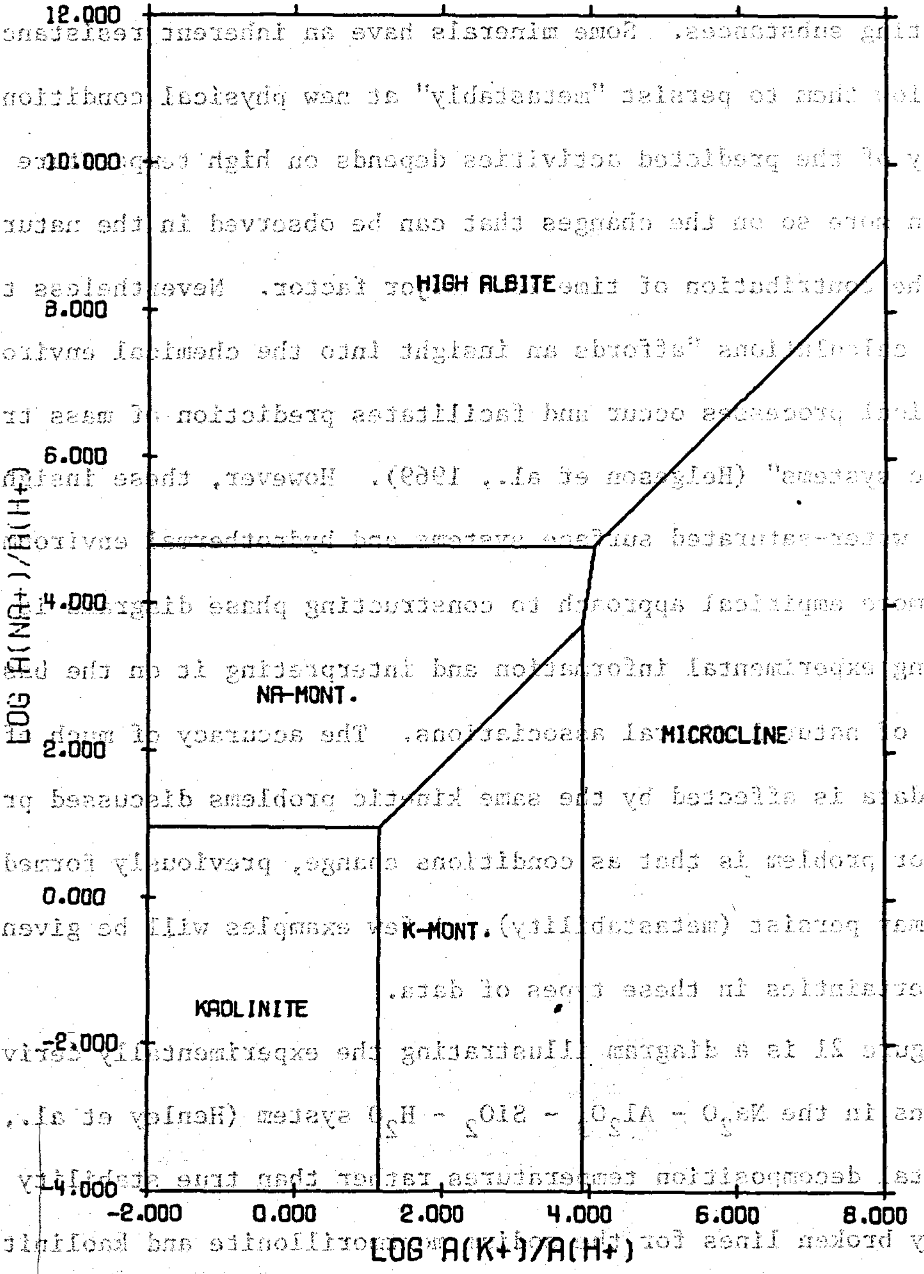


Figure 20. The system $HCl-H_2O-Al_2O_3-K_2O-Na_2O-SiO_2$ at 300°C; log $a_{H_4SiO_4}$ = -1.94 = quartz saturation. After Helgeson et al. (1969).

over long periods of time. Factors affecting the rates of reaction of materials include their structural state, textural character, and the influence of nonreacting substances. Some minerals have an inherent resistance to change that allow them to persist "metastably" at new physical conditions. Thus, the validity of the predicted activities depends on high temperature experiments and even more so on the changes that can be observed in the natural system where the contribution of time is a major factor. Nevertheless the thermodynamic calculations "affords an insight into the chemical environment in which geochemical processes occur and facilitates prediction of mass transfer in geologic systems" (Helgeson et al., 1969). However, these insights apply best to water-saturated surface systems and hydrothermal environments.

A more empirical approach to constructing phase diagrams is based on obtaining experimental information and interpreting it on the basis of observations of natural mineral associations. The accuracy of much of the experimental data is affected by the same kinetic problems discussed previously. The major problem is that as conditions change, previously formed crystalline phases may persist (metastability). A few examples will be given to show the uncertainties in these types of data.

Figure 21 is a diagram illustrating the experimentally derived stability relations in the Na_2O - Al_2O_3 - SiO_2 - H_2O system (Henley et al., 1961). Experimental decomposition temperatures rather than true stability limits are shown by broken lines for the sodium montmorillonite and kaolinite. The decomposition product of the montmorillonite obtained in the experimental work is a mixed-layer sodium montmorillonite-mica. Mixtures of paragonite and mixed-layer phase show a slow conversion to mica, and results are generally inconclusive. However, they conclude that paragonite is probably the thermodynamically stable phase over much or all the field of formation of the mixed-layer material.

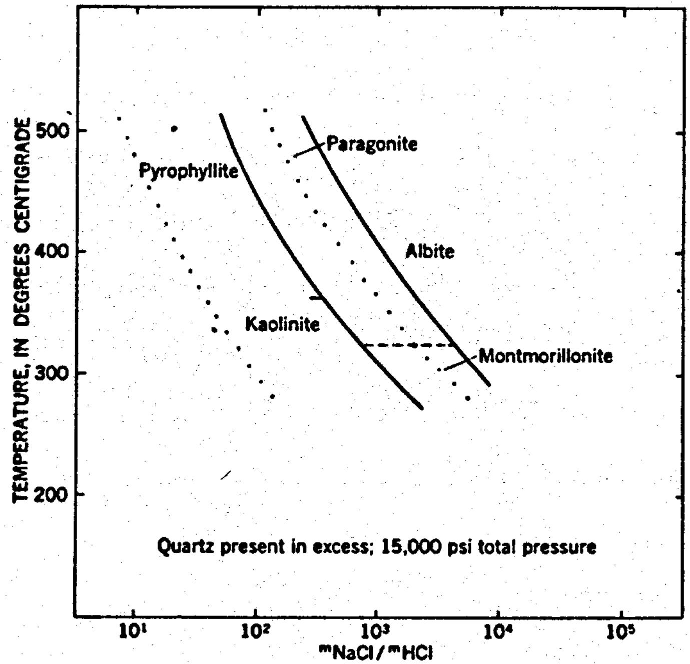


Figure 21. Some stability relations in the system Na_2O-Al_2O_3-SiO_2-H_2O as a function of temperature and the m NaCl/m HCl ratio. Corresponding relations in the terms of m KCl/m HCl are indicated by dotted lines for the system K_2O-Al_2O_3-SiO_2-H_2O. The field of K-mica is between the dotted curves, with K-feldspar at higher values of KCl/HCl and pyrophyllite and kaolinite at lower values. After Hemley et al. (1961).

Velde (1977) has reviewed much of the experimental data and, using his knowledge of natural associations, constructed a number of phase diagrams. One of these diagrams for the experimental system muscovite-pyrophyllite is shown in Figure 22. Though Fe and Mg are not present he considers that the solid solution in muscovite is indicative of an Al-rich illite. Farther from the muscovite end member, a mixed-layer phase is formed consisting of Al-illite and montmorillonite. The mixed-layer phase is shown to be stable to 400°C; however, Eberl and Hower (1977), based on hydrothermal kinetic experiments, concluded that this is likely an unstable phase and is reacting towards forming illite. They also noted that Velde has pyrophyllite appearing as a reaction product at about 300°C, whereas under the same conditions they did not find it in runs below 345°C. Velde admits a certain element of personal bias is involved in the interpretation.

Eberl et al. (1978) established that the hydrothermal stability of dioctahedral smectite can be increased by saturation with interlayer cations of hydration energy greater than K. They noted that it is not clear whether smectite stability at elevated temperatures is an equilibrium or a kinetic phenomemon.

Figure 23 is Velde's summary of the experimental results of the effects of pressure and temperature on the minerals present between muscovite and a chlorite composition. The temperature scale is more likely to be established from a study of the natural system than from experimental data or thermodynamic calculations. At the lowest temperatures, disordered interlayer minerals are present. With increasing temperature the proportion of expanded layers decrease and the layers become more ordered. Because most shales contain several clay minerals, the phase relations they reflect are those towards the center of the diagram.

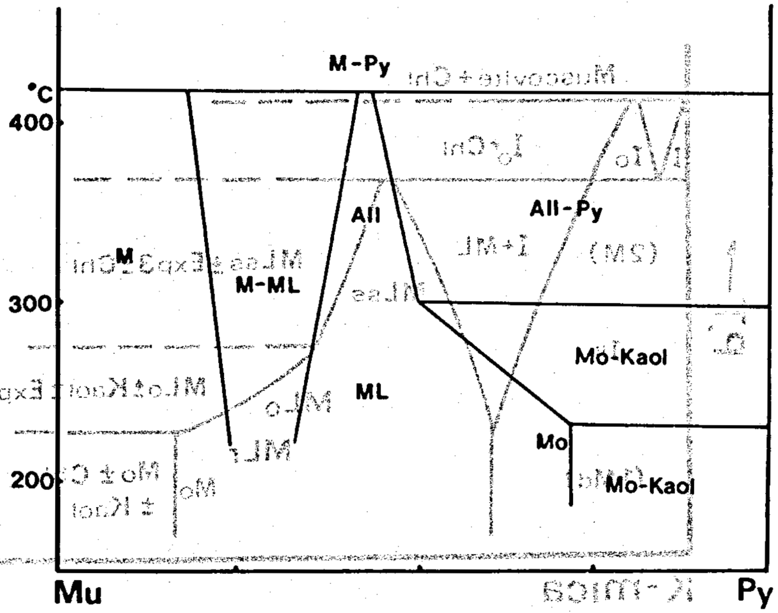


Figure 22. Phases found between the compositions muscovite (Mu)--pyrophyllite (Py) at 2Kb pressure (after Velde, 1969). M = mica (tending to an illite-like phase); ML = random mixed layered phase; All = allevardite-like phase; Mo = fully expandable phase; Kaol = kaolinite; Q = quartz; Py = pyrophyllite. After Velde (1977).

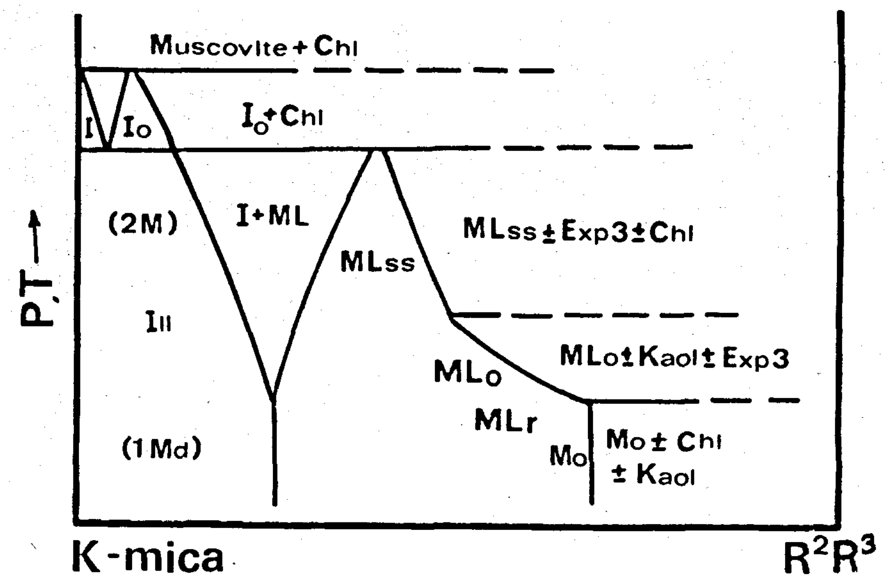


Figure 23. Possible general phase relations for illite and associated phyllosilicates as a function of varying P-T conditions. Ill = illite, either predominantly 1Md or 2M in polymorph; I = illite, 2M mica; I_o = 4 layer ordered mixed layered phase; ML_{ss} = mixed layered 3 or 2 layer ordering giving a superstructure reflection; ML_o = mixed layered, ordered structure with no superstructure; ML_r = mixed layered non-ordered; M_o = fully expandable montmorillonite; Chl = chlorite; Kaol = kaolinite; Exp = expanding chlorite and/or corrensite. After Velde, 1977.

The illite field decreases in width with increasing temperature. This indicates that the illite has become more Al-rich (more muscovite-like). Velde suggests that in the natural system a similar trend is indicated by an increase in the sharpness ratio and decrease in the crystallinity index with increasing depth of burial.

At low temperatures, compositions with a high $R^{2+}R^{3+}$ content montmorillonite coexist with chlorite and kaolinite. At higher temperatures, Velde believes that the stable phases are a regular mixed-layer illite-montmorillonite and chlorite-montmorillonite, plus chlorite.

Velde points out that P_{H_2O} will play a role in determining the mineral assemblage in a rock. Permeable sandstones would be likely to have $P_{H_2O} < P_{lithostatic}$ whereas impermeable shales should normally have $P_{H_2O} = P_{lithostatic}$. Sandstones should behave as system open to certain mobile components. The shales would normally be closed to externally controlled chemical potentials of elements in the fluid phase.

This brief review of theoretically and experimentally determined phase relations illustrates some of the limitations and uncertainties of the techniques. The kinetic problems are such that the information can only suggest the nature of the phase changes to be expected with changing pressure-temperature. At present, equilibrium phase relations in shales can best be established by studying the natural system.

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