

Possible chemical controls of illite/smectite composition during diagenesis

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ABSTRACT. Re-interpretation of the significance of phase assemblages present in two sequences of rocks having experienced similar burial diagenesis allows one to establish that the change of oxidation state of iron in sediments could have the effect of changing the smectite content of the mixed layer mineral. This is used to explain an almost isothermal change in the composition of a sequence while others do not show such a rapid change. An indicator of the reaction is seen in the composition of the chlorite present in the rocks which is iron-rich and alumina-poor compared to chlorites in rocks showing a slower rate of change in the smectite content of the mixed-layered mineral. In order to reveal such a relation, one must make an analysis of the clay mineral assemblage, especially in the number of phases present during the course of diagenesis.

KEYWORDS: illite, smectite, diagenesis.

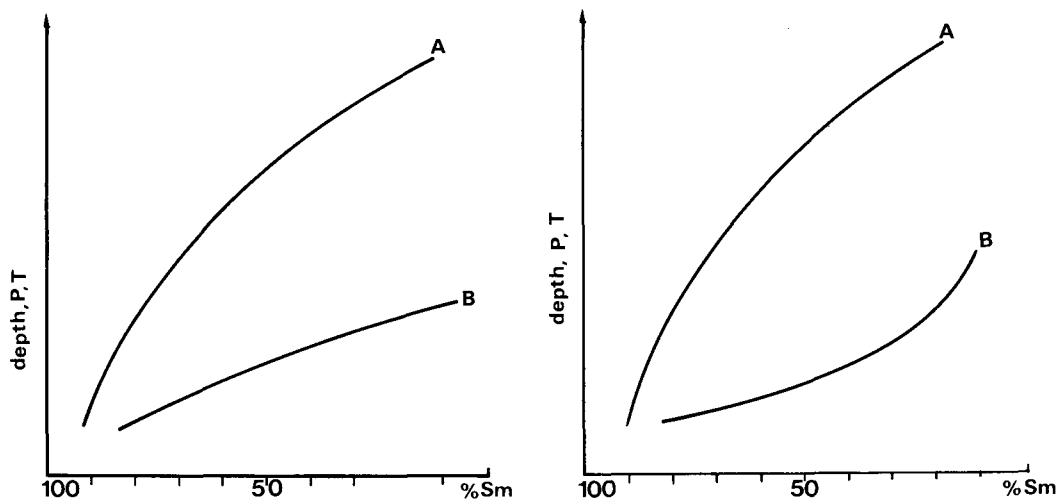
Mixed layer minerals are well known in sequences of shales and sandstone which have been affected by burial diagenesis. The overall reactions critical to the stability of these minerals and the minerals with which they are associated are also known (Hower *et al.*, 1976; Boles and Franks, 1979; Velde, 1977). Such knowledge has led to the use of clay minerals as indicators of diagenetic conditions. One of the great hopes has been to use the composition (interlayer component percentage) of the mixed-layer mineral as an indicator of palaeo-thermal conditions. In order for such a method to be valid, the evolution of the mixed layer minerals in all cases must follow the same sequence in coordinates of depth and temperature for a reasonable range of lithologic (chemical) variation. A reconnaissance of the literature concerning recent, diagenetically transformed sediments shows that the composition of mixed-layer minerals in shales, for example, is not always the same at the same present-day temperature (Lahann, 1980). This situation would seem initially to invalidate the use of clays as outlined above. However, if one can understand the reasons for the differences in the composition of the clays from one situation to another, it is possible that the increased information will lead to a greater

use of the clay minerals in an interpretation of the palaeo-conditions of the diagenetic process.

Observations

Theoretical possibilities. Initially, two basic phenomena can be invoked to explain the differences in the depth-temperature versus mixed-layer mineral composition plots which can be used to follow diagenetic change. (1) The reaction rate of the material is such that the age of the sediments becomes a significant factor in the present-day composition of the minerals. Thus at a given temperature, different compositions can be found if there is a great difference in the age of the materials. (2) Chemical controls which affect the composition of the clays. Thus the lithology or the chemical evolution of the material will give a different clay mineral composition for a given depth or temperature of diagenesis.

Fig. 1 shows the predicted configuration of the depth-composition curves in the case of an important kinetic effect. It can be seen that in comparing curve A which represents a younger series to curve B there is a significantly different compositional range for the same temperatures of burial. Here for the temperatures observed the reaction rate is comparable to the time needed to increase the temperature. The two curves have the same general shape which indicates that the same reaction mechanism is at work to produce the illite layers in the edifice of the mixed-layer mineral. In general, the change in composition of the mixed-layer illite/smectite minerals in a given sequence of buried rocks is such that a rather continuous sequence has been noted. This has led authors to surmise that the change in composition of the clay minerals is dominated by physical rather than chemical factors (see Velde, 1977). It is generally assumed that the shale mineralogy is sufficiently constant in composition to avoid any local fluctuations in the composition of the mixed-layer mineral present. If there is a chemical effect acting on the clay mineral



FIGS. 1 and 2. FIG. 1 (*left*). Illustration of the kinetic effect of reaction rate in the change of smectite content of the mixed layer mineral as it affects profiles of composition versus depth (or $P-T$). The curve A represents a younger series and B an older one. The reaction kinetics are such that at the same depth ($P-T$) the composition of the mixed layer mineral is different. FIG. 2 (*right*). Illustration of two profiles which result from solid-solution change in two different series of mixed-layer minerals (i.e. which do not have the same composition of the component layers). Differences in shapes are due to differences in reaction products.

composition, it must be expressed throughout the whole series of rocks, according to the conclusions of the preceding authors (i.e. continuous change in the composition of the clay minerals). The series of compositions as a function of temperature should be continuous as shown in fig. 2. However, in this figure we have assumed that there are two different series of mixed-layer minerals which have a different reaction mechanism. The mineralogy determined by X-ray diffraction appears to be the same, but in reality the minerals are significantly different. An example of such a mis-identification would be the illite/smectite series and the glauconite-celadonite/smectite series, which are nearly the same in their X-ray diffraction characteristics. Two different compositional series will have curves of different shape and slope.

If there is a chemical effect which is locally expressed in a series, contrary to the stated observations of the previous authors, one should see different depth-temperature curves with rapid or discontinuous compositional variation for rocks in the same geologic region. This situation is represented in fig. 3. Here one sees a sharp change in the composition of the clays, which nevertheless is continuous, but which takes place over a short temperature range. The above are the types of variation which one is likely to encounter in the diagenetic change of mixed-layer minerals in rocks of similar lithologies.

Natural profiles of mixed layer mineral composition. In considering the multiple causes which can change the composition of clays mentioned above, it is evident that the two variable observations (depth and percent smectite) cannot give enough information to solve the complex multivariable

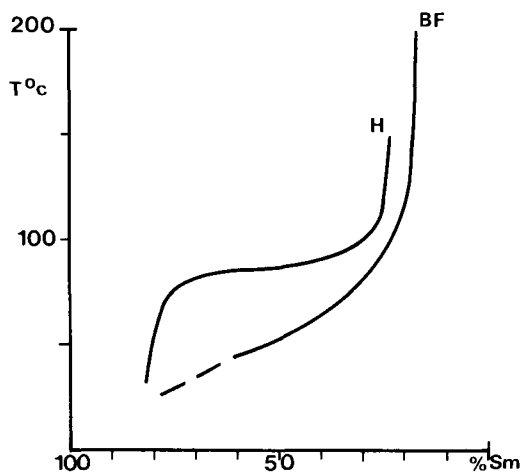


FIG. 3. Illustration of an isothermal or rapid reaction zone compared to a more normal (regular) sequence. Data are from Boles and Franks (1979) given as BF and from Hower *et al.* (1976) given as H in the figure.

system which is possible given the variables discussed above. Differences in slope and shape of depth-composition curves can be due to a combination of causes. However, the situation of a rapid change in composition, but one which is continuous, can be singled out and analyzed. In order to do this the data of Hower *et al.* (1976) and that of Boles and Franks (1979) will be examined. Both studies were made in the eastern Gulf Coast area where the geothermal gradient is similar (about 25 °C/km). Fig. 3 shows the curves presented by Boles and Franks for both studies. The two series are made up of shales of probably similar composition, where the reaction regarding the change in the smectite content of the mixed-layer mineral was considered to be the same or nearly so. When considering the compositional range of 70 to 20% smectite, it is evident that the temperature interval over which the reduction in solid solution occurs is quite different, by a factor of about three. In fact the data of Hower *et al.* (1976) show an almost isothermal change in the solid solution, occurring over less than 20 °C. The obvious reason for such a rapid rate of reaction is a change in the chemical forces acting upon the minerals present. Yet detailed chemical studies by the authors amply demonstrate similarity in composition of all of the major elements from sample to sample.

If a chemical change does occur there should be a change in the other phases present in the system. As it turns out, there is a change—the loss of kaolinite and the presence of chlorite. This shift in phase assemblage was used by Hower *et al.* (op. cit.) to explain the reduction in the smectite content of the mixed layer phase. It was proposed that kaolinite is consumed with the addition of potassium to the active clay mineral system to produce the mica component of the mixed layer mineral. Boles and Franks (op. cit.) have invoked essentially the same reaction and demonstrated it with chemical data. In the last example, the kaolinite is present at the end of the reaction series, maintaining an assemblage of chlorite-mixed-layer-kaolinite whereas kaolinite is consumed in the first series to be replaced, at least apparently, by chlorite. Thus it seems that the two series are not exactly the same in their mineralogical relations.

Discussion

If one uses the phase diagram projection proposed by Velde (1977) to represent the phase relations between the minerals cited, one can see that the chlorite and mixed-layer mineral can have a number of compositions common to the two-phase assemblage at a given pressure and temperature while the assemblage kaolinite-mixed-layer-

chlorite has only one composition of the mixed layer mineral. The representation is valid for only one set of pressure-temperature conditions. This is of course implicit in the basic analysis of phase diagrams, when the number of phases decreases the chemical variability of solid solutions increases, obeying the constraints of bulk composition.

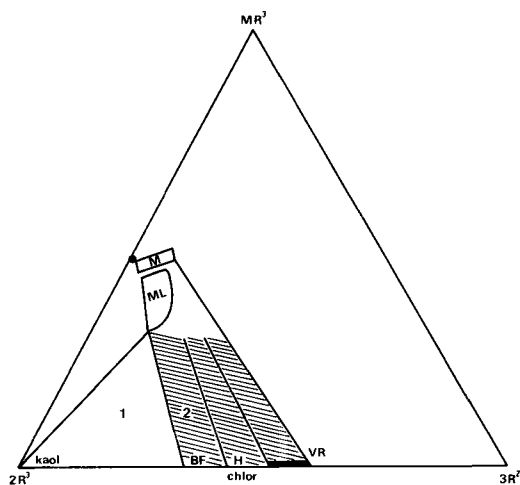


FIG. 4. Phase diagram in $MR^+ - 2R^{3+} - 3R^{2+}$ coordinates concerning the illite/smectite minerals, kaolinite, chlorite, and mica (illite) indicated as ML, kaol, chlor, M respectively. Shaded area indicates the two-phase zone where mixed layer illite/smectite and chlorite or mica-chlorite coexist. Provisional tie-lines are indicated by compositional zones for chlorite compositions using the data from fig. 5.

One might ask then, why does the bulk composition of the system change? In fig. 4 the position of the initial system with the three phases is shown by the point 1. In order to produce the two-phase assemblage chlorite-mixed-layer mineral, and thus to change the composition of this latter mineral, one must change the proportion of the divalent ion component of the system. This divalent component is either Mg or Fe^{2+} in the representation proposed. Since it is unlikely that one would find a sudden increase in the magnesium content of shales, one might look to the iron component. As has been evoked by Velde (1968) concerning the persistence of hydrous aluminosilicate phases in metamorphic rocks, the general tendency in the diagenetic-metamorphic sequence of events is to change the oxidation state of iron as temperature increases. In general, a large amount of the iron present in a sediment is in the form of iron oxide, a

phase outside of the silicate system. However, when the iron is reduced, it enters the silicates as we know of no low temperature divalent iron oxide phases. The overall effect is to shift the bulk composition of the clay to the R^{2+} side of the system where chlorite is found, and where it is possible that the tie-lines between the chlorite and mixed-layer mineral also effect a change in the composition of the mixed layer mineral. This is shown by point 2 in fig. 4.

In order to substantiate the above, one should have chemical data for minerals in a series of two-phase assemblages of mixed-layer minerals and chlorites. This is not available at the moment but one can look at chlorite compositions in several different rocks. Considering the two rock sequences from the Gulf Coast mentioned above, there are a few analyses available. The data presented by Boles and Franks (1979) for two samples are shown in fig. 5 along with data for one level in the series studied by Hower *et al.* (1976). These last analyses were made by Ahn and Peacor (in press). It can be seen, despite scatter in the data, that chlorites in the series where kaolinite is reacted out of the clay assemblage (indicated by data in table 2, p. 58, Boles and Franks, *op. cit.*), produces chlorites which are more iron-rich and more aluminous than the others where the kaolinite has disappeared abruptly through a reaction which we suppose is brought about by a reduction of the iron in the whole-rock

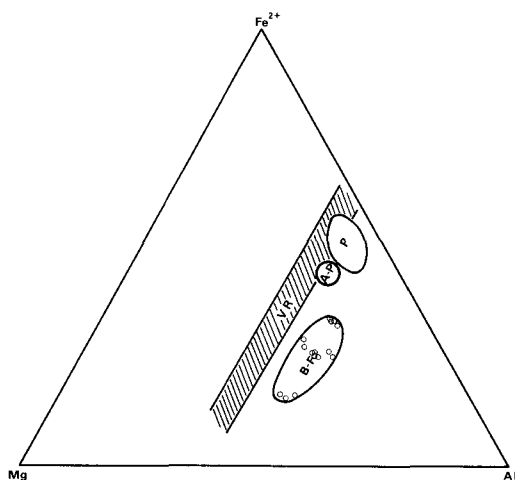


FIG. 5. Plot of chlorite compositions in Al-Mg-Fe coordinates. Data from Boles and Franks (1979) = BF; Ahn and Peacor (in press) AP concerning the sequence studied by Hower *et al.* (1976); Paradis *et al.* (1983) concerning black shale samples = P and data summarized by Velde and Rumble (1977) for mica-chlorite rocks in metamorphic zones = VR.

composition. As a comparison, we can look at the chlorite analyses from a series of rocks which formed under reducing conditions and which have aluminous bulk compositions (Paradis *et al.*, 1983). These minerals are even less aluminous and more iron-rich than the chlorite-rich diagenetic samples from the Gulf Coast. It should be noted that the common chlorite composition for the chlorite-mica or chlorite-illite assemblage is still less aluminous (Velde and Rumble, 1977). Coming back to the phase diagram in fig. 4, one sees that the more R^{2+} -rich the assemblage (lower alumina content) the higher will be the illite content for a chlorite-mixed-layer mineral assemblage. According to the sparse data available, the proposition of the phase relations in the diagenetic mineral sequence presented in fig. 4 seems to be reasonable. Provisional tie-line areas are established in fig. 4 using the data in fig. 5.

In conclusion, we can say that it seems possible that the smectite content of a mixed-layer mineral is influenced by the reduction of iron in the sedimentary rock. This gives the apparently paradoxical result that the composition of a phase is changed by varying the content of an element which is not critical to the composition of the phase. What is important is the correct phase analysis of the mineral assemblage present and an interpretation of the mineral compositions in each assemblage.

One might mention here that the rapid change in oxidation state of iron ('almost isothermal'), has been assumed but not demonstrated by bulk chemical determinations. New data would be necessary to establish this effect with certainty. It is assumed that a change in the organic chemistry of the rocks is responsible for the reduction in oxidation state of iron. Should this be the case, one would have to investigate the organic chemistry of the samples in detail in order to establish which reactions produce this effect. It is certain that there could be many, and that the proportions of silicates, oxides and organics will determine the importance of the effect. Further, the type of organic material initially present will come into prominence in the type of reactions which will occur. All this indicates that the estimation or prediction of such reactions as a function of temperature or depth is far from being a reality at the moment.

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