NOTES

THE ILLITIZATION PROCESS IN DEEPLY BURIED SHALES OF THE GULF COAST AREA[1]

Key Words—Illitization process, K-Ar dating, K-feldspar alteration, Mass transfers.

The mineralogical change from smectite to illite is generally considered to be the most important diagenetic reaction in progressively buried shales. A considerable body of knowledge about this reaction has come from investigations of chemical and isotopic variations attendant with mineralogical changes in deeply buried Tertiary sediments in the Gulf Coast (Weaver and Wampler 1970, Weaver and Beck 1971, Perry and Hower 1972, Perry 1974, Aronson and Hower 1976, Hower *et al* 1976, Yeh and Savin 1977, Yeh 1980, Morton 1985, Ohr *et al* 1991). The recent article by Eberl (1993), reviewing the data of Aronson and Hower (1976), Hower *et al* (1976), Yeh and Savin (1977) and Yeh (1980) and suggesting the occurrence of three reaction zones for illite formation, has provided additional perspective on the burial induced illitization of illite/smectite mixed-layer minerals in Gulf Coast sediments. Our examination of the existing data finds the conclusions of Eberl to be less than convincing.

The change from I/S minerals to illite in the buried shales of the Gulf Coast was portrayed previously in terms of three depth-related age variations (Perry 1974, Odin 1982). Eberl (1993) described these three trends as "plateau ages," one of 55 Ma for a shallow zone of less than 2.4 km depth, one of 46 Ma for a middle zone of 2.4 to 3.6 km depth, and another of 33 Ma for a deep zone of greater than 3.6 km depth. Three separate trends have also been described in terms of changes in both the K and the Ar contents as a function of depth for the clays. We do not fully agree with Eberl's characterization and interpretation of some of the trends in K content. For example, he noted that the K contents of the illite minerals remained constant in the deepest zone. We would rather consider that K contents somewhat varied, as did the K-Ar dates. The variations being outside the limits of the experimental error and the mineralogical effect due to kaolinite as a dilutant, the K contents may be even interpreted to have decreased in some instances. We agree with Eberl's claim that the K content remains essentially constant within the upper zone. But he did not consider how the min-

eralogical composition of the clay fractions affects the K content, as the presence of K- and radiogenic ^{40}Ar-enriched illite-type minerals together with K- and radiogenic ^{40}Ar-poor kaolinite minerals obscures the true evaluation. However, we are not convinced by the interpretation that Eberl offers for this constancy of K, although he apparently felt that the K should have increased as a function of depth within this zone because of a decrease by 20% in expandability. Furthermore, Eberl recognizes some differences in the K data between that of Aronson and Hower (1976) and that of Hower *et al* (1976), and he relates them to differential removal of K resulting from different experimental procedures. We do not consider that to be the case, because the experimental studies by Thompson and Hower (1973) and Aronson and Douthitt (1986) have shown that most of the K in sheet silicates is strongly bound and cannot be considered to be loosely held in the interlayer sites allowing loss during any normal sample preparation.

In calculating an age loss as a function of depth, Eberl defines the fraction age loss as the difference between the calculated and the measured K-Ar age divided by the calculated age. In doing this for the very fine clay fraction, he assumes a constancy of 55 Ma for the K-Ar age, as indicated by the measured date for the shallow samples. This assumption is not valid for the entire section, because it implies a constant age for the source of the sediments. This assumption is unjustified if one takes into account the widely different K-Ar dates that were presented by Hurley *et al* (1963). The Gulf Coast sediments have also been reported to have some prominent stratigraphic breaks or unconformities (Perry 1974), and the Sm-Nd isotopic data of Ohr *et al* (1991) showed that the provenance for the sediments in the lower sequence is different from that in the upper sequence. The zig-zag pattern in the trend of K in the deep zone may very well reflect variations in the source of the sediments. We, therefore, do not believe that the age loss curve is meaningful.

Eberl concluded that three reaction zones occurred in connection with different formation mechanisms for the illite in Gulf Coast shales. He believes that illite formed in the shallow zone by a process of transfor-

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[1] A discussion of Eberl (1993).

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mation of I/S minerals, that the same mineral formed in the intermediate zone by a process of neoformation, and in the deep zone by a process of recrystallization in response to Ostwald ripening. We have no doubt about the existence of three plateau ages for the clay minerals of the Gulf Coast sediments, as has been suggested by Perry (1974), recognized by Odin (1982) and reiterated recently by Eberl (1993). But we do not agree with Eberl about his interpretations of three different mechanisms of illite formation with respect to the three plateau ages. As the K content, the ^{40}Ar content, and the K-Ar dates remained constant for the clays in the shallow zone, we must assume that the clays in this zone are truly detrital and that changes in the expandability of the smectitic clay within this zone are not related to burial diagenetic effects. We consider this zone to be essentially one of no reaction.

The reaction in the intermediate zone is typical for one of rapid increase in K content. Eberl used the oxygen isotope data of Yeh and Savin (1977) to support the inference he has drawn about neoformation in this zone. Yeh and Savin observed that the calculated isotopic temperatures determined from coexisting quartz and clays correspond to the measured temperatures in the intermediate zone, and Eberl used this concordance to sustain a neoformation reaction in this zone. We fail to see how such a concordance between paleo- and present-day temperatures can be related to any specific mode of mineral reaction. Furthermore, as Yeh and Savin considered their data relative to the present-day geothermal gradient, the diagenetic reaction appears to have occurred at a relatively shallower depth compared to the present depth of burial, which means that the occurrence of such a concordance is also highly questionable.

The reaction in the deep zone has been described by Eberl as one of recrystallization by Ostwald ripening. The isotopic evidence he has used in reaching this conclusion is that the ^{40}Ar has decreased with depth within this zone. This observation of Eberl is at variance with ours, as he maintains that the K is relatively constant, while we consider that the K contents varied randomly so that the trends in K with depth within the deep zone may be described as consisting either of a random scatter or of several subtrends. Similarly, ^{40}Ar contents appear to have increased, decreased, and also remained constant at different intervals within this zone. In other words, the ^{40}Ar variation is random. We do not think that a trend of ^{40}Ar decrease in the zone is as clearly evident as Eberl has presented it. Furthermore, to account for the coherency in his observations of constant K-Ar age and K content with associated decrease in ^{40}Ar, Eberl believes that a balance has occurred between radiogenic ^{40}Ar accumulation by the decay of ^{40}K and radiogenic ^{40}Ar loss by the recrystallization process. He has not shown any evidence or reason to discount the possibility that a decrease in the ^{40}Ar content with depth may be related to the loss of radiogenic ^{40}Ar by fine particles at these burial temperatures.

The oxygen isotope data are equivocal. The δ^{18}O values of the clays decrease progressively with depth, which can be best interpreted in terms of stabilization of the I/S minerals at progressively higher temperatures attendant with depth (Yeh and Savin 1977, Morton 1985). We find that the merits of the use of the available isotopic data to build a case for Ostwald ripening are highly questionable. In our opinion, the K-Ar isotopic variations within the deep zone reflect either variations in the composition of the original smectitic minerals that have been illitized, or more probably several discrete episodes within a limited time period of illitization. A high degree of uncertainty is often associated with the determination of different clay sized fractions in a shale, making this criterion a questionable piece of evidence for Ostwald ripening. Eberl's use of the chemical data is not also very convincing, as the SiO_2 and the Al_2O_3 variations, even if significant, are continuous throughout the sequence, suggesting, as do the oxygen isotope data, a case for a continuous evolution. The changes in the trends for these elements with depth do not correspond with those of the K-Ar dates.

In view of the existing K-Ar dates, we believe that the reaction involving illitization in the Gulf Coast shales consists principally in a transformation process with variable rates, occurring below a 2.4 km-thick upper zone where no significant change is detectable. This process, which could be replaced in the deeper zone by a dissolution-precipitation reaction, is mainly monitored by the uptake of K and the release of radiogenic ^{40}Ar from clay particles. Depending on the relative behavior of the detrital and authigenic K-bearing minerals, the K-Ar dates increase, decrease, or remain about constant. How this illitic reaction develops still remains a major problem in the study of clays in deeply buried sediments.

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Erratum

Equation 5 appearing in Warren, C. J., M. J. Dudas, and S. A. Abboud. 1992. Effect of acidification on the chemical composition and layer charge of smectite from calcareous till. *Clays & Clay Miner.* **40**: 731–739 for the calculation of the total amount of expandable 2:1 clay assigned to each charge range is incorrect. Equation 5 (on page 733) should appear as:

$$p = -8669.1 + 16672(d) - 10727(d)^2 + 2320.3(d)^3 \qquad R^2 = 0.9994$$

for d-spacings (d) in the range of 1.36 to 1.77 nm.