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MODELED SHALE AND SANDSTONE BURIAL DIAGENESIS BASED ON THE K-AR SYSTEMATICS OF ILLITE-TYPE FUNDAMENTAL PARTICLES

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Abstract—The clay fraction of the sedimentary succession beneath the Mahakam Delta (eastern Kalimantan, Indonesia) consists mainly of mixed-layer illite-smectite, with minor amounts of kaolinite and/or dickite, discrete detrital illite and chlorite. On the near-shore anticline, evolution of this mixed-layer material is characterized by a decrease in expandability with depth. The mechanism of conversion of smectite to illite layers depends on the lithology of the host rocks: it evolves along a solid-state transformation in the shales and a dissolution-precipitation in the sandstones.

Illite fundamental particles from two sandstones buried at ~4000 m in the Tambora field next to the Handil field on the same near-shore anticline yield a mean K-Ar age of 15.7±1.6 Ma (2σ), which is younger than the stratigraphic age but still slightly biased by minute amounts of discrete detrital illite. Recalculated after modeling, which takes into account the occurrence of the discrete detrital illite, this K-Ar age becomes 14.4±0.7 Ma. The K-Ar values of the fundamental particles from associated buried shales are significantly older, which can be explained by a mixture of (1) a precursor material similar to that presently deposited in the delta of the Mahakam River, and (2) authigenic fundamental particles incorporating Ar with a $^{40}Ar/^{36}Ar$ ratio above atmospheric value during nucleation and growth on the same detrital precursor.

Application of the modeling to the burial evolution of <0.4 μm particles from both the shales and the sandstones of the basin points to a contribution of detrital micaceous material in both lithologies, (1) in the sandstones as a detrital component dissolving progressively and mixed mechanically with the authigenic fundamental particles, and (2) in the shales as a detrital precursor progressively releasing radiogenic ^{40}Ar by burial alteration, and at the same time acting as a support for the fundamental particles for the growth of authigenic fundamental particles that were found to incorporate Ar characterized by an excess of ^{40}Ar.

Key Words—Burial Diagenesis, Clay Fraction, Fundamental Particles, Illite-smectite, Mahakam Delta, Indonesia.

INTRODUCTION

Clay materials from associated shales and sandstones were progressively buried in the Handil oil field of the near-shore anticline of the Mahakam Delta Basin located in eastern Kalimantan (Indonesia). A previous study by Clauer *et al*. (1999) showed that these clay fractions consist mainly of mixed-layer illite-smectite (I-S) with subordinate amounts of kaolinite and/or dickite, discrete detrital illite and chlorite. The I-S from the near-shore anticline was characterized by a downward decrease in expandability. The process of conversion of smectite layers into illite layers in the I-S appeared to be lithology-dependent, along a transformation process in a restricted system within the shales, and along a dissolution-precipitation process in an open system within the sandstones. Understanding of this lithology-dependent process was further improved by oxygen-isotope studies of the downward-changing I-S. However, the K-Ar systematics of the <0.2 μm clay fractions of the sandstones and associated shales buried at 4200 m, provided dates that are older than the 18 Ma stratigraphic (depositional) age of the host rocks, documenting the presence of detrital illite, as in many previous studies (see discussion and references in Clauer and Chaudhuri, 1995).

Alternatively, recent K-Ar dating attempts on illite-type fundamental particles separated from I-S of bentonites (Clauer *et al*., 1997; Srodon and Clauer, 2001; Środoń *et al*., 2002; Clauer *et al*., 2003a) highlighted a major potential for increased understanding of clay diagenesis by isotopic dating and tracing. Building on this approach, we separated fundamental particles from I-S of two deeply buried sandstones and two shales in close stratigraphic association, from the Tambora oil field located near that of Handil in the same anticline. The term ‘fundamental particles’ is used here after the Nadeau *et al*. (1984) proposal. It designates the thinnest particles that are technically separable from I-S of any rock. These particles can now be analyzed in detail for their mineralogical, geochemical and isotopic characteristics because separation is possible on the

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basis of an infinite dispersion of the single I-S particles (Clauer *et al*., 1997). It should be mentioned here that Morton (1985) studied such small particles of Oligocene shales from the Frio Formation in the Gulf Coast by Rb-Sr and oxygen-isotope determinations. He suggested that the evolution of the I-S material was punctuated early by changing pore-water chemistry, and that its isotopic characteristics were "frozen in" 23.6 Ma ago, remaining unaltered since, despite further burial over seven to eight thousand feet.

The present study was undertaken to make a preliminary evaluation of the contribution of a mineralogical and K-Ar isotopic analysis of fundamental particles from I-S of two deeply-buried sandstones and two nearby shales to a better understanding of the illitization process induced by progressive burial of the extensively studied sedimentary sequence beneath the Mahakam Delta (Clauer *et al*., 1997 and references therein). At this point, it is appropriate to mention that (1) because there was no more core material available from previous boreholes, we had to take samples from boreholes located near those studied previously, and (2) preparation and separation of fundamental particles from I-S is still difficult enough to prevent processing tens of such separations, even if quite unique, before preliminary, well-focused studies provide worthy conclusions. It is therefore logical that the present study only represents a preliminary attempt, and that consequently it suffers from a limited number of results leading to possible 'over-interpretations'. It was not meant to solve all analytical and scientific aspects, but to add new information to a scientific debate. To the best of our knowledge, this study contains (1) the first K-Ar dating attempt of fundamental particles separated from I-S of diagenetic sandstones, as well as (2) the first theoretical approach based on appropriate analytical results considering a possible occurrence of excess radiogenic ^{40}Ar trapped by nucleating fundamental particles in shale-type restricted-pore environments. The theoretical approach required detailed deliberation, as the expected result is contrary to current beliefs. This explains the special care taken in the discussion. As a basis for the study carried out here, we recalled most of the basic information on the clay material from previous studies. Details of the structural evolution of the sedimentary basin, petrofabric data of the rocks, characteristics of the fluid inclusions in the minerals, and vitrinite reflectance data of the organic matter are available in Clauer *et al*. (1999).

GEOLOGICAL SETTING AND PREVIOUS RESULTS

The active delta of the Mahakam River integrates an area of ~5000 km^2 in the Makassar Strait, between the islands of Kalimantan and Sulawesi (Figure 1). A biostratigraphic zonation details the 8 km thick sedimentary sequence beneath the delta (Allen *et al*., 1979), which underwent a smooth tectonic overprint. This tectonic overprint developed sub-parallel, NNE–SSW-oriented anticlines during the middle-to-upper Miocene (Figure 1; Magnier and Sansu, 1975). This tectonic activity also lifted the sedimentary succession by 1000 m, ~4.5–5 Ma ago (Bessereau, 1983).

In the Handil field, which is located on the same near-shore anticline as the Tambora field, the clay fraction in the cored rocks consists mainly of I-S which becomes progressively more illitic downwards, in both the shales and sandstones (Clauer *et al*., 1999). Mathematical decomposition of the X-ray diffraction (XRD) peaks allowed identification of three orders of stratification for these minerals. Random ordering of illite and smectite layers was observed down to ~1100 m. Between 800 and 1100 m depth, the amount of illite layers in the I-S increases abruptly from 35 to 60%, and the I-S acquired some short-distance order (Figure 2). Short-distance ordering was reported for the air-dried I-S between 1100 and 3000 m. The amount of illite layers remained constant between 1100 and 2400 m, increasing to 90% at ~3000 m, just before acquiring long-distance order. Between 3000 and 3950 m, long-distance order was found, slightly below the top of the overpressured zone characterized by relatively higher temperatures and pressures. In fact, no difference in the XRD patterns could be detected between the <2 μm fractions extracted from shales and those extracted from associated sandstones throughout the entire sedimentary succession studied.

Distinct morphologies of the I-S particles were observed by transmission electron microscopy (TEM), depending on the rock type. At shallow depths (210–340 m), all particles from both the shales and sandstones appear as odd flakes with irregular edges. With increasing depth, more and more laths are visible in the separates of the sandstones, even becoming dominant in the deeper part of the section. They are generally long and fine with euhedral terminations. In contrast, the I-S particles of the deeply-buried shales remain dominated by aggregates of flakes and veil-type particles. This morphological diversity suggests that the diagenetic process was different in the shales and in the sandstones, even though XRD characteristics are similar for the <2 μm fractions of both facies.

The K-Ar dates of the <0.4 μm fractions from sandstones decrease from 80.1±5.0 to 21.6±2.0 Ma with increasing depth, whereas those from shales decrease from 79.9±3.8 to 49.7±2.1 Ma. It looks like the K-Ar system of the clay fractions from both the sandstones and shales evolves in a similar fashion down to ~2000 m, and that beneath that depth the K-Ar dates of the sandy clay material continued to decrease while that of the shaley clay material remained unaffected (Figure 3). Interestingly enough, the <0.4 μm clay fractions of the uppermost sandstones and shales buried

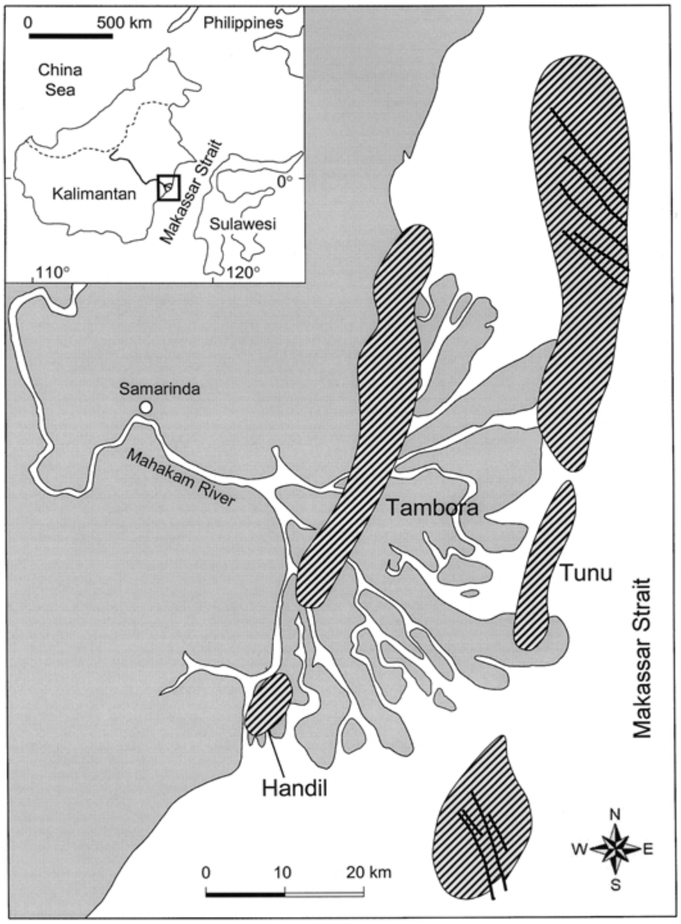

Figure 1. Location of the Mahakam delta and extension of the drainage basin shown by the dashed line in the upper left sketch. The enlargement outlines the two near-shore anticline axes with the extension and names of the oil fields (from Clauer *et al.*, 1999).

to <500 m yield approximately the same K-Ar dates of ~80 Ma. These nearly identical K-Ar dates for fractions from different lithologies suggest that the original detrital micaceous material of the rocks from the upper zone was fairly homogeneous in its K-Ar systematics.

SAMPLE DESCRIPTION AND ANALYTICAL PROCEDURE

Two sandstone and two shale core samples were collected from the sedimentary succession of Tambora oil field which is located on the same near off-shore anticline as the Handil oil field studied previously (Clauer *et al.*, 1999). The four rock samples are considered to be strictly equivalent to the corresponding lithologies at similar depths in the Handil field from which no more cores are available. They were taken at depths between 3717 and 4151 m.

The four samples were first disaggregated by a gentle freeze-thaw technique. After disaggregation, the samples were dispersed in distilled water and the <2 µm fractions separated by sedimentation. The <0.2 µm fractions were first processed following Jackson's (1975) method (acetate buffer, H_2O_2, dithionite, washing and dialysis), then ultra-centrifuged and diluted to a concentration of 1 g/40 L, in order to ensure an infinite osmotic swelling (Środoń *et al.*, 1992). Afterwards, they were further separated into three subfractions (<0.02, 0.02−0.05 and 0.05−0.2 µm) using a continuous-flow ultra-centrifuge. The finest fractions were ultimately collected by flocculating the suspensions with NaCl and then removing the excess electrolyte by centrifugation and dialysis. The different size fractions were X-rayed as random powders in order to determine the mineral composition and as oriented slides after glycol solvation in order to identify the clay minerals. The expandability of the I-S was determined using the techniques of Środoń (1980, 1981, 1984). The ratio of the peak intensities of I-S at ~5.4 Å and of I-S plus discrete illite at ~3.35 Å was used to measure the amount of I-S in the total illitic fraction of each sample (Table 1).

The K-Ar determinations were made using a method close to that of Bonhomme *et al.* (1975). Prior to Ar extraction, the samples were heated at 80ºC under

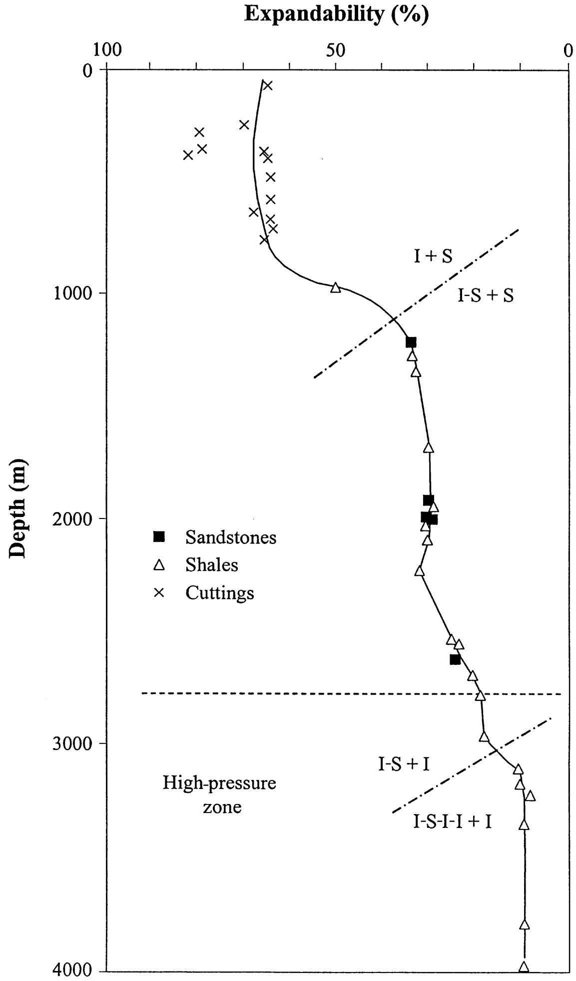

Figure 2. Evolution of the clay expandability (<2 μm) down through the sedimentary sequence.

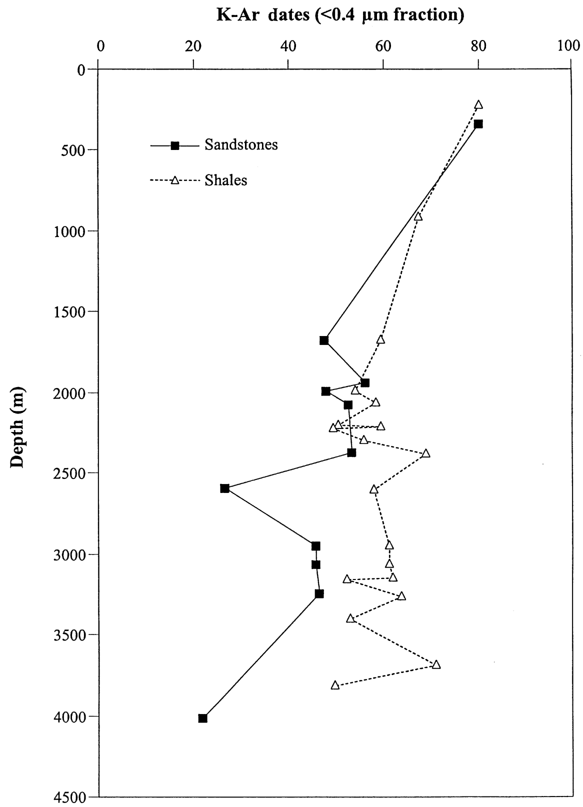

Figure 3. Evolution of the K-Ar dates of I-S (<0.4 μm) down the sedimentary sequence.

vacuum to remove atmospheric Ar adsorbed during sample preparation. The K was measured by flame spectrophotometry with an accuracy better than 1.5%. The analytical precision was periodically controlled by measuring the standard mineral GLO which averaged

Table 1. Results of the mineralogy determined by XRD of the I-S size fractions from the sandstones and shales.

Samples	Kaol (7.16 Å)	I-S (5.4 Å)	I (5.0 Å)	I+I-S (3.4 Å)	I-S/I+I-S
1: sandstone – 3716.75 m (Sd1)					
<0.02 μm	14 (18%)	18 (51%)	11 (31%)	62	0.29
0.05–0.2 μm	38 (40%)	13 (32%)	11 (28%)	56	0.23
2: shale – 3827.25 m (Sh1)					
0.05–0.2 μm	110 (52%)	18 (18%)	28 (30%)	103	0.17
3: sandstone – 3840.25 m (Sd2)					
<0.02 μm	6 (9%)	20 (59%)	11 (32%)	64	0.31
0.05–0.2 μm	29 (24%)	24 (45%)	17 (31%)	91	0.26
4: shale – 4151.25 m (Sh2)					
<0.02 μm	57 (43%)	20 (28%)	22 (29%)	75	0.27
0.02–0.05 μm	27 (51%)	7 (23%)	8 (26%)	26	0.27

Kaol, I-S and I stand for kaolinite, mixed-layer illite-smectite and illite, respectively. The peak highs of each measured fraction were measured at 7.16, 5.4 and 5.0 Å, respectively; they were recalculated in % in brackets. The amounts of illite + illite-smectite were determined at 3.4 Å The I-S/I+I-S ratios in the last column result from dividing peak highs. Not enough powder was available for the missing size fractions.

24.59±0.09 (2σ) × 10^{-6} cm^3/g STP of radiogenic ^{40}Ar for eight independent measurements, and the atmospheric $^{40}Ar/^{36}Ar$ ratio of the analytical blank of the whole equipment which averaged 292.3±2.5 (2σ). The recommended value for the standard is 24.85±0.24 × 10^{-6} cm^3/g, whereas that of the atmospheric $^{40}Ar/^{36}Ar$ ratio is 295.5. Because the values obtained were internally consistent and close to the theoretical values, no corrections were applied to the isotopic determinations. The K-Ar dates were calculated with the usual decay constants (Steiger and Jäger, 1977) and have an overall analytical precision of better than 2%.

ANALYTICAL RESULTS

Eight of the 12 size fractions extracted provided enough material to perform XRD work (Table 1). The XRD patterns of oriented specimens, recorded after glycol solvation, are presented (Figure 4) with the identification of the different peaks and the amount of smectite layers (% S) in I-S, measured from the reflection near 33°2θ (Środoń, 1984). All size fractions contain I-S and kaolinite. Discrete illite can also be traced in all fractions with a reflection or a shoulder at 5.0 Å (17.5°2θ). Chlorite is present in all size fractions of the deepest shale sample at 4151 m.

All I-S of the R1 type represent about 30% of the illite-type material (I-S/I+I-S in Table 1). They contain close to 28–37% smectite layers (Figure 4). In fact, most of the I-S contain 28–30% S, except the two analyzed fractions of the shallower (Sd1) sandstone, which are enriched in smectite layers (35–37% S). The kaolinite content varies significantly, generally increasing in the coarser fractions. Its relative abundance was

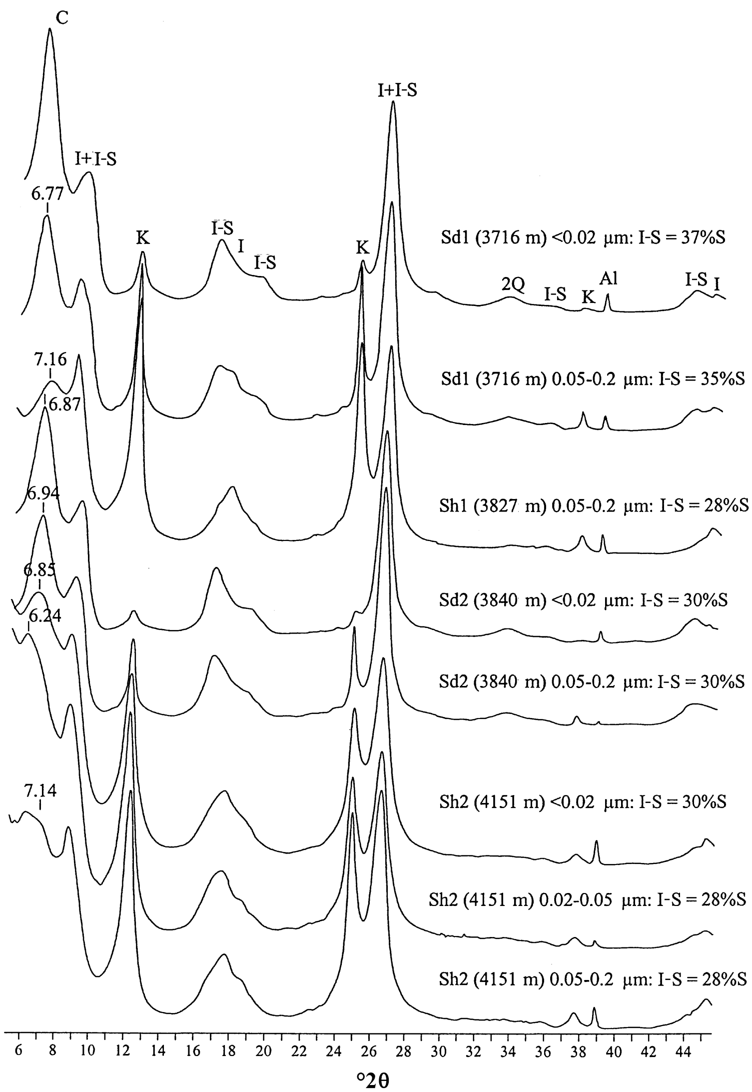

Figure 4. XRD patterns of oriented specimens of different size fractions after glycol solvation.

approximated from XRD peak intensities by calculating in percent the 001 kaolinite intensity relative to the sum of the 001 of the kaolinite plus the 003 peak of illite plus I-S. The fact that the I-S amounts are fairly constant with similar %S means that the differences in the K-Ar data reported are definitely not related to mineralogical variations of the K-carrying, illite-type material.

The two <0.02 μm fractions extracted from sandstones yield K-Ar dates of 14.1±0.5 and 17.3±0.5 Ma, whereas the dates of the coarser fractions increase significantly, up to 74.5±2.1 Ma. The K-Ar dates of the two <0.02 μm fractions extracted from shales are older than the corresponding fractions from sandstones, but close again at 39.8±2.9 and 43.0±1.4 Ma. The ages from coarser fractions from shales are also relatively larger, up to 65.0±2.8 Ma (Table 2); they are close to the K-Ar values of the same size fractions from sandstones. The smallest, <0.02 μm, clay particles from two sandstones give a mean K-Ar value of 15.7±1.6 Ma, which is less than the stratigraphic age of the rocks at this depth. All other K-Ar dates are greater than the stratigraphic age, clearly reflecting the occurrence of detrital components.

By plotting the results in an isochron ($^{40}Ar/^{36}Ar$ *vs.* $^{40}K/^{36}Ar$) diagram, most of the data points plot in the left part of the diagram (Figure 5a). Only two, those of the finest <0.02 μm fractions of the two sandstones, plot to the right. These data points are not randomly scattered, but fit three arrays: (1) the four coarsest 0.05−0.2 μm fractions from both the shales and sandstones plot along a line with the steepest slope and the lowest initial $^{40}Ar/^{36}Ar$, slightly less than 250; (2) the data points for the three available intermediate 0.02−0.05 μm fractions from two shales and one sandstone fit a line with a smaller slope and a higher initial $^{40}Ar/^{36}Ar$ ratio of ~270; (3) the two smallest <0.02 μm fractions of the two shales fit a line with, again, a smaller slope and a larger initial $^{40}Ar/^{36}Ar$ value, close to that of the atmospheric $^{40}Ar/^{36}Ar$ ratio (295.5). The two smallest <0.02 μm fractions of the two sandstones, plot to the right of the diagram.

DISCUSSION

During burial diagenesis, the evolution of clay minerals follows complex pathways governed by a series of interrelated physical and chemical factors, including the origin of the mineral precursors, the porosity and permeability of the host rocks, as well as the chemical characteristics of the pore fluids, the temperature, and the duration of the reactions (*e.g.* discussions in Clauer and Chaudhuri, 1995). Each of these parameters has very specific effects on the geochemical and/or isotopic systematics of clay particles, as it has been shown, for instance, that the Rb-Sr and K-Ar systematics of the same clay material may behave differently in the same conditions (*e.g.* Clauer *et al.*, 1982, 2003b). To understand better the evolution of clay minerals in the deeply buried sedimentary rocks of the Mahakam Delta Basin, previous discussions focused more specifically on the potential influence of the host-rock lithology on the K-Ar systematics of the I-S (*e.g.* Clauer *et al.*, 1999). The purpose here is to provide new considerations to improve this evolutionary construction, on the basis of complementary mineralogical and isotopic information from fundamental particles.

Age of the fundamental particles

In a first approximation, one might agree that (1) the true diagenetic age of the authigenic fundamental particles from I-S is ~14 Ma or slightly younger, and (2) the true original age of the detrital illite is at ~80 Ma, seen from K-Ar determinations of the <0.4 m fractions from both sandstones and shales collected in the upper section of the sedimentary sequence (Clauer *et al.*, 1999). All K-Ar dates of the size fractions studied here result from mixtures of these authigenic I-S and detrital illite (even if almost undetectable in the finest fractions from sandstones) on the basis of the XRD determinations. The occurrence of kaolinite and chlorite can be

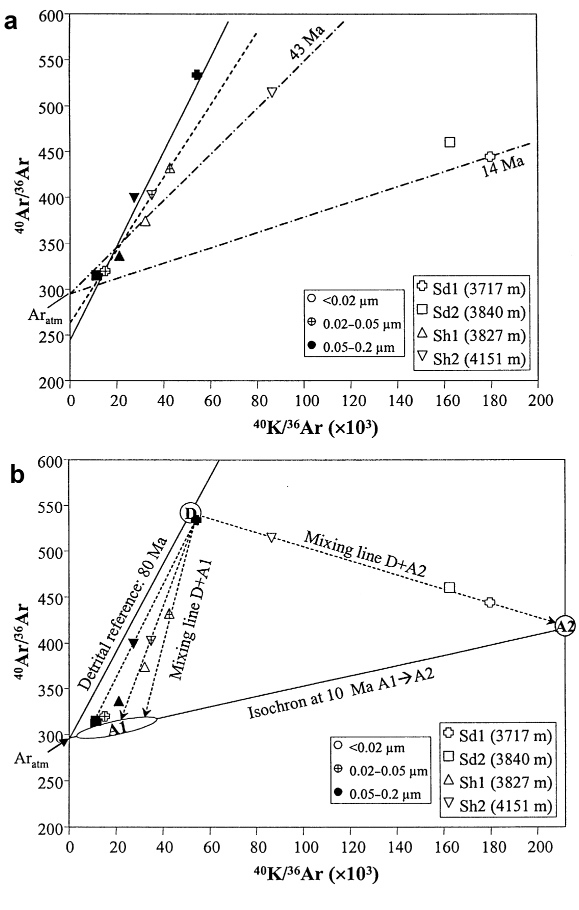

Figure 5. (a) K-Ar isochron diagram for the different size fractions of the sandstones and the shales from deeper parts of Tambora field. (b) A theoretical sketch of the results.

ignored as they do not interfere with the K-Ar results, containing insignificant amounts of K, if any. The data points from such mixtures should plot on a straight line joining 100% diagenetic I-S of 14 Ma age to 100% detrital illite of 80 Ma age (in a diagram relating %I-S in I+I-S to the K-Ar results). This is clearly not the case, as the data points fit more or less a trend joining two end-members containing only ~30% I-S at ~14 Ma and still 20% I-S at ~80 Ma (Figure 6). Indeed, the K-Ar data relate to the I-S/I+I-S ratio, as they roughly decrease when the ratio increases, but the relationship cannot be explained by a simple mechanical mixture of 14 Ma I-S and 80 Ma illite. On the other hand, if it is clear that the mixtures result from the separation and purification procedure, it cannot be argued that they result from a genetic relationship among the discrete detrital illite and the authigenic I-S particles, especially in the shales.

The finest, <0.02 µm, fractions of both the Sd1 and Sd2 sandstones contain an extremely small amount of discrete illite, XRD detectable, with tiny 10 and 5 Å reflections (Figure 4). They provide similar K-Ar dates averaging 15.7±1.6 Ma. The occurrence of discrete illite, even in minute amounts, is determining as it needs to consider that both K-Ar dates are slightly biased, the true diagenetic age being smaller. Also, on the basis of the Clauer *et al.* (1999) study, the <0.4 µm I-S from the upper portion of the nearby Handil field already contains ~30% illite layers before illitization started, which means in turn that a third of the illite layers of <0.4 µm in buried I-S might be of detrital origin. Therefore, even pure I-S in buried sandstones might still yield a noticeable detrital signature, meaning that the fundamental particles separated from these I-S could have resulted from intergrowth of detrital and diagenetic illite layers.

The use of isochron diagrams $^{40}Ar/^{36}Ar$ *vs.* $^{40}K/^{36}Ar$ is not common in K-Ar isotopic studies, because most investigators assume quite systematically that the Ar initially incorporated in the minerals while nucleating and growing, is of atmospheric isotope composition. Such an assumption is reasonable for high-temperature minerals enriched in K and being old, as a precise estimate of the $^{40}Ar/^{36}Ar$ ratio of the Ar initially trapped

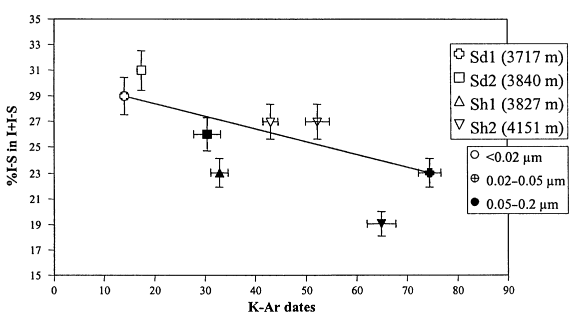

Figure 6. K-Ar dates as a function of the ratios among mixed-layer I-S and illite from samples of the Tambora field.

in the mineral structures is almost impossible. This assumption is also correct for low-temperature domains as long as mixtures of two generations of minerals do not introduce artefacts in the diagram draft as discussed by Clauer and Chaudhuri (1995). This means in turn that such graphic representations might be very helpful, especially when one suspects that the initial Ar in any of a mineral or size fraction might have a $^{40}Ar/^{36}Ar$ ratio different from that of the atmospheric one. In the present case, the XRD results showed that all fundamental particles contain detrital illite layers, and that the I-S content is fairly constant among the samples with constant amounts of smectite layers. The scatter of data points presented in Figure 5a as a series of three lines in the left part and two data points on the right side can therefore be explained by variations in the content of discrete illite. The left-side arrays characterizing the coarser size fractions, with the steepest slopes and initial $^{40}Ar/^{36}Ar$ ratios significantly below the atmospheric ratio are, in this respect, clear mixtures of two generations of illite-type minerals (Harper, 1970; *e.g.* discussion in Clauer and Chaudhuri, 1995). When moving to the right side of the diagram, the fundamental particles obviously contain fewer detrital illite layers, while containing more K_2O, without significantly more illite-enriched I-S (Table 1).

In addition, the two arrays consisting of the coarsest (0.05−0.2 µm) and intermediate (0.02−0.05 µm) size fractions cannot be considered as isochrons, because they yield initial $^{40}Ar/^{36}Ar$ ratios significantly below the atmospheric value of 295.5, which is unrealistic (Figure 5a). The occurrence of distinct arrays supports the hypothesis of mixtures consisting of one type of authigenic clay material, and either (1) varied types of detrital material, which were not identified before (Clauer *et al*., 1999), or (2) one type of detrital material at different evolutionary stages depending on the size of the particles; the smallest is the most altered with increased losses of K_2O and radiogenic ^{40}Ar as suggested by Clauer and Chaudhuri (1999). In this case, the area of the data points is necessarily bound by a detrital reference line set at 80 Ma, and an authigenic reference line set arbitrarily at 10 Ma, both lines intersecting the $^{40}Ar/^{36}Ar$ abscissa at the atmospheric value of 295.5.

Usually, the detrital material of sediments yields narrow ranges, especially if of the same mineralogical type, here the area D (Figure 5b), whereas the authigenic material ranges widely on the initial horizontal 'iso-chron', mainly depending on the state of evolution of the material. In the case of I-S, or fundamental particles, it mainly depends on the amounts of K_2O in the particles, between A1 and A2 (Figure 5b): the higher the K_2O contents, the closer to A2. Any A1+A2 mixture will fit the authigenic reference at 10 Ma, and any addition of detrital D material will move the corresponding data points on any of the dashed lines (Figure 5b). If, alternatively, the detrital material is mixed with A1 authigenic I-S, the data points will plot on the D–A1 mixing line. As a consequence, the results obtained here plot in a triangle limited by: (1) the detrital reference line at 80 Ma, which is the K-Ar age of the detrital material of nearby Handil field (Clauer *et al*., 1999); (2) an authigenic reference set hypothetically at 10 Ma, as it has to have a slope lower than the line drafted through the finest fraction of sandstone Sd1; and (3) a mixing line joining the detrital end-member D and the authigenic end-member A2, which still contains minute amounts of illite (Figure 5b). In any case, dashed mixing lines can be drafted from D to an enlarged A1 area, which might correspond to mixtures of both. It might be added that this interpretation of the data scatter into mixing lines also explains initial $^{40}Ar/^{36}Ar$ values of the mixing lines that are less than the atmospheric ratio, as can be seen in Figure 5a.

Modeling the burial-related evolution of the K-Ar systematics of fundamental particles

Several potential mechanisms based on reasonable and controlled assumptions can be conceptualized in an attempt to model the K-Ar isotopic systematics of fundamental particles from I-S during burial that matches the contents of radiogenic ^{40}Ar and of K_2O measured in the smallest and thinnest particles of the four deeply buried rocks. In the sandstones studied here, the <0.02 μm size fractions were assumed to have resulted from nucleation of a smectite crystallizing next to the detrital clay material, which underwent progressive illitization by K supply, as shown by Šuchá *et al*. (1993) for bentonite I-S with a progressive decrease of expandability relative to depth and temperature increase. This hypothesis, which is supported by TEM observations of coarser fractions of buried sandstones from the nearby Handil field, needs the system to be open (Furlan *et al*., 1996), with two stages of K incorporation, between 800 and 1200 m depth and between 2800 and 3000 m, to match the S-shaped XRD curve of the illitization process (Figure 7 of Clauer *et al*., 1999, reproduced here as Figure 2).

Several preliminary aspects needed to be set for the model. For instance, the newly formed I-S was assumed to nucleate next to clay material similar to that presently found at shallow depths and yielding a K-Ar date of 80 Ma (Clauer *et al*., 1999), and some of the illite layers presently in the I-S of the sandstones buried to 4000 m were considered to be still of detrital origin. In other words, the K_2O and radiogenic ^{40}Ar contents of the detrital clay material still present in the fundamental particles of the deeply buried sandstones were taken at 0.34% K_2O and 0.90×10^{-6} cm^3/g radiogenic ^{40}Ar, respectively, to match the results already published for the detrital clay component of the uppermost part of the Handil sequence (Clauer *et al*., 1999). These amounts also needed to provide a K-Ar value of 80.3 Ma identical to that of the present-day detrital clay material deposited in the uppermost sedimentary succession, when the 'K-Ar clock' of the newly formed fundamental particles started after sedimentation. The chosen increase in the amounts of K_2O and radiogenic ^{40}Ar relative to depth also needed to fit the measured amounts of K_2O and radiogenic ^{40}Ar of the two finest size fractions of the deeply-buried sandstones, allowing the authigenic I-S to accumulate enough radiogenic ^{40}Ar for a K-Ar value of ~14 Ma. The accumulation period being relatively short, it was needed to allow accumulation of a significant amount of K_2O. The increase of the K_2O content was assumed to be ~2.1% per my from 0.34 to 4.6% between 800 and 1200 m and from 4.6 to 6.2% between 2800 and 3200 m, which is reasonable relative to the evolution of the expandability of the I-S (Figure 2). The progressive increase of K_2O from 0.34 to 6.2% (plotted as open squares in Figure 7a), fits the average content of the measured separates of fundamental particles from two sandstones buried at 3717 and 3840 m, when corrected for kaolinite contribution. The progressively increasing K_2O in the fundamental particles decayed into radiogenic ^{40}Ar (plotted as filled squares in Figure 7a). Next to this progressive accumulation of radiogenic ^{40}Ar, radiogenic ^{40}Ar was assumed to be released from progressively altered detrital illite particles present since deposition (plotted as open triangles in Figure 7a). This release was calculated along a logarithmic law relative to depth similar to that used by Clauer *et al*. (2003). Finally, the total calculated radiogenic ^{40}Ar (from authigenic and detrital particles) matches the amounts of radiogenic ^{40}Ar determined in the smallest fundamental particles of the two deeply buried sandstones (Figure 7a), as the calculated K-Ar age of the fundamental particles from I-S of the sandstones comes out to be 13.9 Ma. The suggested evolutionary model appears to be reliable in taking into account: (1) the occurrence of detrital illite since illitization started; and (2) the progressive alteration of this detrital illite relative to depth (Clauer *et al*., 1999; Clauer and Chaudhuri, 2001).

The next step in the elaboration of a burial-related model for the K-Ar systematics was modeling the K-Ar data of fundamental particles from I-S of the deeply buried shales, as the results are quite different from those of the same particles in the sandstones (Table 2). The following assumptions were made: (1) the pure authigenic illite-type fundamental particles were considered to yield the same K-Ar age of ~14 Ma as that of the I-S in the sandstones, and (2) the amounts of K_2O and radiogenic ^{40}Ar from detrital illite mixed with the authigenic fundamental particles since the beginning of the diagenesis, were the same as for the sandstones, to allow enough radiogenic ^{40}Ar to accumulate in the authigenic component for an appropriate final K-Ar value of ~14 Ma. The starting amounts were taken at 0.34% K_2O and 0.90×10^{-6} cm^3/g of radiogenic ^{40}Ar.

The increase from 0.34% K_2O in the upper 800 m to 5.70% in the deepest part is drafted in Figure 7b (plotted as open squares). As for the calculation of the sandstone fundamental particles, the detrital material was considered to lose some radiogenic ^{40}Ar relative to depth, along the same logarithmic law as above (plotted as open triangles in Figure 7b). The combination of accumulation and release of radiogenic ^{40}Ar, together with increase in K_2O, does not match the analytical results (plotted as open crosses along the full line in Figure 7b). In other words, not enough radiogenic ^{40}Ar was produced on the basis of the classical decay calculation.

As the K_2O content cannot be increased on the basis of the analytical results, we needed to identify a process that could have added radiogenic ^{40}Ar to that produced by the natural decay of the K_2O present in the

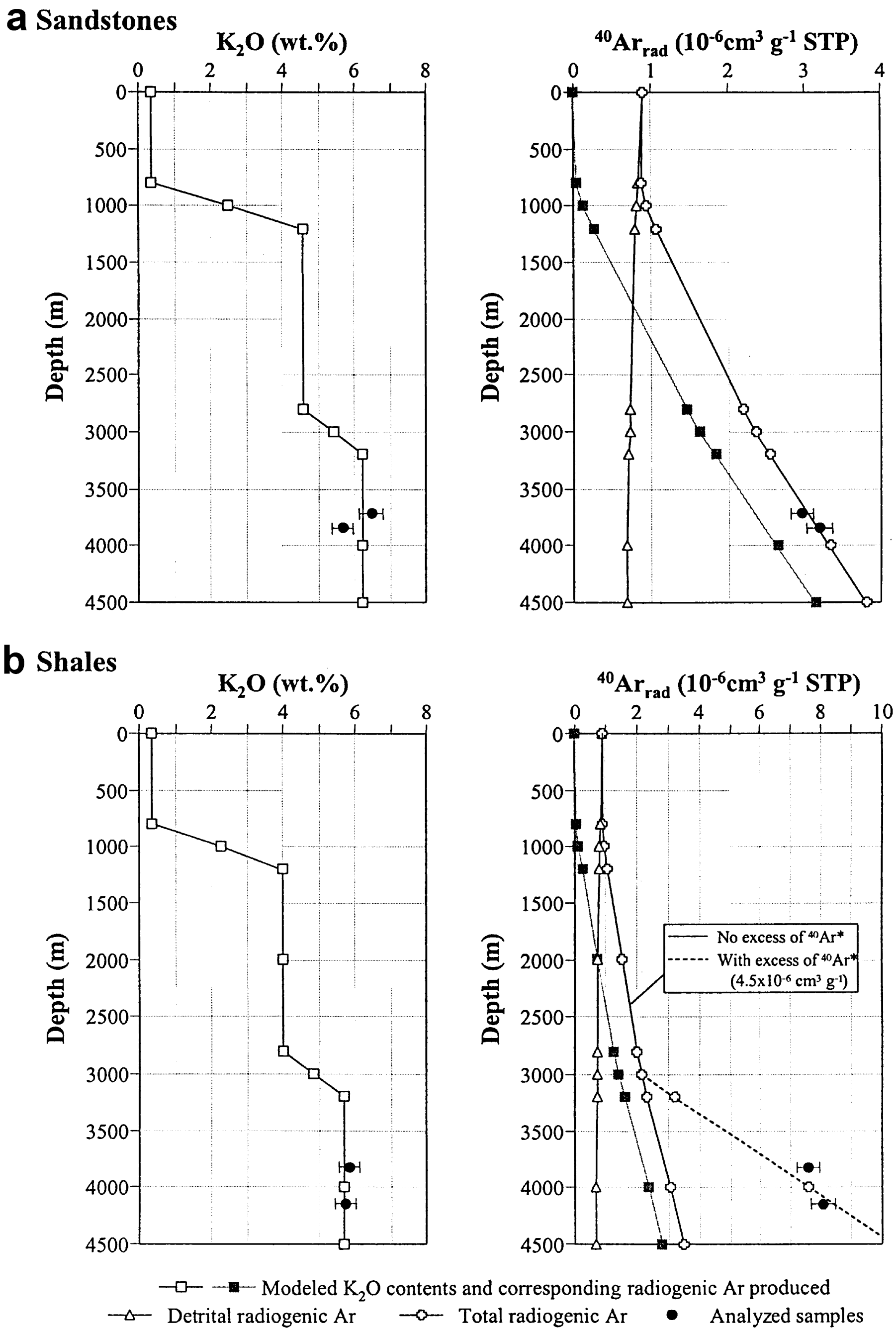

Figure 7. Evolution models for K_2O and radiogenic ^{40}Ar of fundamental particles from sandstones (a) and from shales (b); explanations in the text.

fundamental particles, in order to fit the analytical results. Based on the Šuchá *et al*. (1993) study, illitization starts at ~70ºC which means we cannot consider a start in the Handil and Tambora fields until a depth >3000 m. In other words, the possibility of increasing the duration of the process by starting the accumulation of radiogenic ${}^{40}Ar$ earlier than assumed previously, which would increase its amount in the fundamental particles of the lower succession with the same amount of K_2O, appears unreasonable. This hypothesis remains unrealistic, even in considering a higher paleotemperature before the slight uplift of the sedimentary sequence during the tectonic structuration of the near-shore Mahakam anticline, which occurred 4.5–5 Ma ago. The only remaining explanation that can be offered, to the best of our knowledge, is that the fundamental particles could have grown in a pore environment characterized by a slight excess of radiogenic ${}^{40}Ar$. This potential excess of radiogenic ${}^{40}Ar$ might have induced a ${}^{40}Ar/{}^{36}Ar$ ratio of gas-type Ar in the shale pore system greater than that of the atmospheric value, not resulting from addition of a detrital mineral phase to the authigenic one**.** This hypothesis appears reasonable for the following reasons: (1) such an excess of pore radiogenic ${}^{40}Ar$ might be expected in an overall overpressured zone, as no escape of fluids is, by definition, expected in such an environment; and (2) excess radiogenic ${}^{40}Ar$ has already been determined in basinal gases (Zartman *et al*., 1961; Clauer, unpublished data). In assuming that incorporation of radiogenic ${}^{40}Ar$ by nucleating illite layers started at a depth of ~3000 m, which is the upper limit of the overpressured zone described in the near-shore anticline, an accumulation of 4.5×10^{-6} cm^3 of radiogenic ${}^{40}Ar$ per gram of fundamental material is needed in the pore system over 1000 m, between 3000 and 4000 m (plotted as open crosses along the dashed line in Figure 7b). A rough mass calculation shows that such an excess of radiogenic ${}^{40}Ar$ can be produced in any shale-type rock containing >1.4 wt.% K_2O, which is quite low, and therefore quite common.

In summary, the fact that addition of ${}^{40}Ar$ in nucleating illite layers of I-S might occur in deeply buried sedimentary rocks acting as closed or restricted systems such as shales, to explain the K-Ar results of fundamental particles highlights a new perspective interpreting the behavior of Ar in sedimentary rocks, and consequently the reliability and meaning of K-Ar dating of mineral splits of such rocks. It is still difficult to speculate beyond this statement as more information is needed to check if abnormally high ${}^{40}Ar/{}^{36}Ar$ ratios of gas Ar occur during illite nucleation and growth, especially in quite impermeable rocks.

Modeling the evolution of the K-Ar systematics of detrital/authigenic clay mixtures from sandstones and shales during burial

The downward evolution of the K-Ar dates of the <0.4 μm fractions in the sandstones and shales of Handil field (Clauer *et al*., 1999), were examined as a preliminary test of the model envisaged above, combining 'detrital' illite altering next to 'authigenic' fundamental particles during progressive burial. In this case, the behavior of the K-Ar systematics of the studied fractions results from (1) a progressive increase of K and radiogenic ${}^{40}Ar$ contents in the nucleating and growing authigenic illite layers, and (2) a progressive decrease of K and radiogenic ${}^{40}Ar$ contents in the detrital particles altering down the sequence. The overall result of this combined behavior is different in the <0.4 μm fractions

Table 2. K-Ar results of the illite fundamental particles from I-S of the sandstones and shales.

Samples	K_2O (%)	Ar* (%)	${}^{40}Ar^*$ ($10^{-6}cm^3/g$)	${}^{40}Ar/{}^{36}Ar$ (10^{-3})	${}^{40}K/{}^{36}Ar$ (Ma±2σ)	Age (Ma)
1: sandstone – 3716.75 m (Sd1)						
<0.02 μm	5.31	33.4	2.43	444	179.4	14.1 (0.5)
0.02–0.05 μm	3.15	7.8	3.00	320	14.5	29.3 (1.0)
0.05–0.2 μm	4.72	44.7	11.57	534	53.7	74.5 (2.1)
2: shale – 3827.25 m (Sh1)						
<0.02 μm	3.09	20.7	4.00	373	33.0	39.8 (2.9)
0.02–0.05 μm	3.37	31.2	5.73	430	43.6	52.0 (1.8)
0.05–0.2 μm	2.26	12.0	2.41	336	20.8	32.8 (1.6)
3: sandstone – 3840.25 m (Sd2)						
<0.02 μm	5.17	36.7	2.90	460	162.1	17.3 (0.5)
0.05–0.2 μm	2.86	6.1	2.83	315	10.8	30.4 (2.5)
4: shale – 4151.25 m (Sh2)						
<0.02 μm	3.27	42.5	4.59	514	86.1	43.0 (1.4)
0.02–0.05 μm	2.63	26.6	4.50	402	34.6	52.3 (2.2)
0.05–0.2 μm	2.14	26.2	4.57	400	27.2	65.0 (2.8)

from sandstones and from shales in the deeper part of the sequence (Figure 3). In the upper part, between 180 and ~1600 m depth, the K-Ar results of the <0.4 μm fractions from both lithologies are quite similar: they decrease by about the same rate, which might mean that among the different parameters potentially affecting the K-Ar data of the size fractions, either the increase of the K content, or the decrease of the radiogenic ^{40}Ar content was dominant. As the temperature in this part of the sequence was between 20 and 55ºC, the release of radiogenic ^{40}Ar from detrital components might be the leading process, because illitization with K_2O incorporation into the particles did not really start in the depth range.

From 1600 m depth, the K-Ar systematics of the <0.4 μm fractions from both lithologies evolve along different paths. The K-Ar dates from sandstones continue to decrease, implying a dominant K supply, despite accumulation of radiogenic ^{40}Ar in the authigenic mineral phases due to radioactive decay, which was, in addition, implemented by a release of radiogenic ^{40}Ar from a detrital component continuing to alter and even to dissolve while temperature increases. The case of the K-Ar systematics in the <0.4 μm fractions from shales is notably different: the K-Ar values remain fairly constant between 1600 and 3800 m, at values from 49.2±2.6 Ma to 70.9±2.3 Ma. Such similar values cannot result from a steady-state behavior, as recently reported by Lerman and Clauer (submitted). Indeed, such a steady state would require much more time than allowed by the stratigraphic age. Also, the K-Ar values should not be as scattered as found in the case of a steady-state behavior.

The nearly constant values obtained in the <0.4 μm fractions from shales of the Mahakam Delta sequence between 1600 and 3800 m, which have also been reported for similar size fractions from shales of a Mesozoic hydrocarbon reservoir in the North Sea by Glasman *et al*. (1989), need a rigorous compensation among (1) increase in the K and radiogenic ^{40}Ar contents from progressively buried authigenic fundamental particles, and (2) decrease in the K and radiogenic ^{40}Ar contents from progressively buried, and consequently altered and even dissolved, detrital particles, to keep the K-Ar values similar. These combined increases and decreases need to remain almost balanced as the scatter is narrow over a depth of ~2200 m. Such a balanced behavior among authigenic and detrital clay-type material appears to be very difficult to explain, unless the K and radiogenic ^{40}Ar contents released from detrital components were directly, and almost completely, incorporated into the newly formed authigenic fundamental particles.

Such behavior is not expected to occur in an open system like a sandstone pore environment in which fluid migration is easy, inducing potential supply or removal of K and escape of radiogenic ^{40}Ar. Alternatively, it could be a reasonable explanation for the observed K-Ar results of <0.4 μm fractions from shales generally behaving as a closed/restricted pore system. In fact, if all K and radiogenic ^{40}Ar were completely incorporated into the new mineral phases, the K-Ar data should increase slightly downwards, monitored by the accumulation of radiogenic ^{40}Ar produced from ^{40}K by radioactive decay. This slight increase is not seen, so some radiogenic ^{40}Ar must escape from the shales, depending on the individual rock properties. In turn, such varied escape of radiogenic ^{40}Ar could explain why the K-Ar data of the <0.4 μm fractions are slightly scattered. Another fact which favors incorporation of Ar having an initial ^{40}Ar/^{36}Ar ratio above atmospheric value by nucleating fundamental particles, are (1) preliminary determinations of noble gases (Ar, Xe, Kr) that are trapped into and not expelled from recent oceanic smectite-type particles (Clauer, unpublished data), as well as (2) preliminary K-Ar data of an aqueous-pyrolyzed shale not showing any release of radiogenic ^{40}Ar after having been heated at 365ºC for 72 h (Clauer, unpublished data). Finally, it should be noted that observation of K-Ar values of fine-clay fractions from shales becoming constant down through a sedimentary basin might also provide important information about the depth at which the shale sequence becomes impermeable, even to Ar escape.

CONCLUSIONS

The illite-type fundamental particles of mixed-layer I-S from two closely sampled sandstones buried at ~4000 m in the Tambora field, which is close to the Handil field on the near-shore anticline of the Mahakam Basin, consist mainly of authigenic particles with minute amounts of discrete detrital illite. The <0.02 μm fraction from buried sandstones still seems to contain minute amounts of a more or less altered detrital illite which is either mixed or intergrown with the authigenic illite layers of the mixed layer. The mean K-Ar value of two fractions is 15.7±1.6 (2σ) with an initial atmospheric ^{40}Ar/^{36}Ar ratio. Modeling of the burial-related increase of K_2O and radiogenic ^{40}Ar in the authigenic fundamental particles and the associated release of the radiogenic ^{40}Ar from detrital illite allows calculation of the crystallization age of the authigenic illite layers from I-S at 14.4±0.7 Ma with an initial ^{40}Ar/^{36}Ar of 307.4±12.1, which is slightly above the atmospheric ratio. The two results are within analytical uncertainty, but the second is based on a reasonable evolutionary model.

The K-Ar dates of the fundamental particles from mixed-layer I-S of the associated deeply buried shales are significantly larger than the mean value obtained for those of the sandstones, confirming the difficulties in interpreting the behavior of Ar in such quite impermeable rocks during illitization along a solid-state transformation process of detrital precursors. The K-Ar dates identical to those of the same particles of the sandstones are only obtained by assuming nucleation and growth on precursor illite-type particles similar to those presently deposited in the mud of the Mahakam river delta, which were progressively altered during burial, in a pore environment characterized by the presence of a gaseous Ar yielding a slight excess of radiogenic ^{40}Ar relative to atmospheric Ar.

Use of the model to explain the burial evolution of <0.4 µm particles from both the shales and sandstones of the basin points to a contribution of detrital micaceous material in both lithologies. It also clearly suggests that this contribution of detrital material evolves differently in the shales and in the sandstones. The detrital contaminant is mixed mechanically with the authigenic fundamental particles in the sandstones and it disappears progressively, probably by dissolution, whereas it acts as a precursor interfering in two ways with the fundamental particles in the shales: as a core on which the authigenic fundamental particles grew, which also altered progressively, releasing K_2O and radiogenic ^{40}Ar. In other words, these newly formed fundamental particles seem to have incorporated Ar characterized by an excess of ^{40}Ar released by the nearby progressively altering K-bearing detrital components.

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