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TOWARDS AN ISOTOPIC MODELING OF THE ILLITIZATION PROCESS BASED ON DATA OF ILLITE-TYPE FUNDAMENTAL PARTICLES FROM MIXED-LAYER ILLITE-SMECTITE

NORBERT CLAUER*

Centre de Géochimie de la Surface (CNRS/ULP), 1 rue Blessig, 67084 Strasbourg, France

Abstract—Burial-induced and hydrothermal-related illitization in bentonites and in sandstones can be modeled on the basis of isotopic studies of fundamental particles separated from mixed-layer illite-smectite. The model envisages different reaction rates and durations relative to the varied impacts of temperature, considering that the water:rock ratio also has an influence. The different pathways for illitization are suggested on the basis of the K-Ar, Rb-Sr and $\delta^{18}O$ compositions of previously studied materials.

New information is provided on why fundamental particles separated from mixed-layer illite-smectite in shales yield K-Ar age data that are systematically greater than the ages of the fundamental particles from associated bentonites and/or sandstones, and greater than the reported stratigraphic ages. The study of pure authigenic, recent to present-day smectite from Pacific sediments shows that (1) those collected from active hydrothermal vents have $^{40}Ar/^{36}Ar$ ratios identical to that of the atmosphere, and (2) those of mud sediments have $^{40}Ar/^{36}Ar$ ratios above the atmospheric value, indicating addition of ^{40}Ar not generated *in situ* by radioactive decay. A preliminary but detailed analysis of the noble-gas (Ar, Xe, Kr) contents of authigenic smectite-rich size fractions from Pacific deep-sea red clays suggests trapping of these gases by smectite. Therefore, the results point to the fact that fundamental particles can incorporate excess ^{40}Ar into their structure when nucleating in restricted to closed systems, such as shales. This excess ^{40}Ar, which represents radiogenic ^{40}Ar released from nearby altered silicates, might be temporarily adsorbed at the surface of the rock pore spaces and is therefore available for incorporation in nucleating and growing particles.

Key Words—Burial Diagenesis, Crystal Growth, Fundamental Particles, Hydrothermal Activity Illitization, K-Ar, Mixed-layer Illite-smectite, Noble Gases, Nucleation, $\delta^{18}O$, Rb-Sr.

INTRODUCTION

It is widely acknowledged that illitization is an efficient tracer of the evolution of sedimentary basins, using various textural-mineralogical features (Hower *et al.*, 1976; Dunoyer de Segonzac, 1969; Velde, 1985; Jennings and Thompson, 1986; Šuchá *et al.*, 1993), combined organic-inorganic controls (Kübler, 1997; Clauer *et al.*, 1999), and various isotopic dating and tracing attempts (*e.g.* review by Clauer and Chaudhuri, 1995). Recent isotope studies of 'fundamental particles' in the sense of Nadeau *et al.* (1984) have provided additional potential for reconstructing the duration and mechanism of diagenesis leading to illitization of mixed-layer illite-smectite (I-S), especially in bentonites. Such isotopic studies of fundamental particles have since been applied to sandstones, but have yet to be fully understood in shales (Clauer *et al.*, 1997; Roussset and Clauer, 2003; Clauer *et al.*, 2003; Honty *et al.*, 2004).

Despite recent progress in understanding the duration and conditions of illitization in any sedimentary succession, there is still controversy about how the mechanism proceeds, depending on the immediate environment of the clay particles. Theoretical models have been proposed on the basis of either a dissolution-precipitation mechanism in porous host rocks, or a solid-state alteration process in almost impermeable host rocks (Honty *et al.*, 2004; Altaner and Ylagan, 1997). Defining reliable diagenetic isotopic ages of illitization in shales in which diagenetic clay particles are systematically mixed with detrital clay precursors remains a difficult challenge, even though radiogenic ^{40}Ar is not preferentially lost by small illite crystals, either in nature or during experimental treatments (Clauer *et al.*, 1997, and references therein). In sedimentary basins, the detrital material of shales often contains not only first-cycle coarse mica from crystalline rocks, but also burial-related diagenetic illite and I-S resulting either from continental erosion or from pedogenic weathering. Different aspects of such situations have been covered in many publications (*e.g.* Aronson and Hower, 1976; Burley and Flisch, 1989; Ehrenberg and Nadeau, 1989; Glassman *et al.*, 1989a, 1989b; Mossmann, 1991; Pevear, 1992; Clauer and Chaudhuri, 1996; Clauer *et al.*, 1999). The effect of opening interlayer sites of K-bearing clay particles of shales with alkylammonium cations was also explored, knowing that a trioctahedral

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* E-mail address of corresponding author:
nclauer@illite.u-strasbg.fr

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mica is more susceptible to K removal by such organic cations than the dioctahedral equivalent structure (references in Chaudhuri *et al.*, 1999). In doing these experiments, it was expected that one illite end-member of a given mixture (either detrital or diagenetic) is more susceptible than the other to the effects of the organic cations, which would erase its K-Ar signature in the mixture. Modeling untreated and alkylammonium-treated samples as mixtures of authigenic and detrital illites of given ages provided excellent matches between our results and simulations (Chaudhuri *et al.*, 1999).

Notwithstanding some successful studies (*e.g.* Elliott *et al.*, 1991), a definitive statement has yet to be provided about the true duration of illitization in the history of a sedimentary basin. In the modeling presented here, the results of several previous studies on diagenetic fundamental particles separated from I-S of bentonite and shale units are combined in order to constrain isotopically the different possible pathways of illitization. Such an approach has to deal with kinetic aspects of illitization, which have already been considered by many authors since 1976 (Eberl and Hower, 1976; Pytte and Reynolds, 1988; Huang *et al.*, 1993; Whitney and Velde, 1993; Elliott and Matisoff, 1996; Berger *et al.*, 1997; Eberl *et al.*, 1998; Wilkinson and Haszeldine, 2002). The problem we will have to face is that these attempts were based on theoretical or experimental approaches, and were concerned with mainly coarse clay material. Here, the attempt is different in the sense that the kinetic aspect is based on data from natural samples at the fundamental particle size, and that preliminary results have already shown that there is not a simple rule for clay nucleation and growth (Clauer *et al.*, 1997). Preliminary results from studies of the K-Ar systematics and noble-gas contents (Ar, Kr, Xe) in recent to present-day, oceanic authigenic smectite and volcanic material are also reported to explain why diagenetic K-Ar ages of fundamental particles from shales appear systematically older than the stratigraphic age of the host sedimentary rocks, making a case for excess radiogenic ^{40}Ar relative to the amount of K_2O present.

STUDIED MATERIALS AND THE FUNDAMENTAL-PARTICLE CONCEPT

Since the beginning of K-Ar isotope studies of clay minerals, many have questioned the use of this dating method because the small size of the particles potentially renders them incapable of retaining radiogenic ^{40}Ar. The grounds for this scepticism were largely created by the results of pioneering studies of glauconites which provided isotopic ages that were often younger than the stratigraphic ages (Hurley *et al.*, 1960). A common explanation given for these young ages was that Ar is readily lost due to the size of the particles. In fact, the ultimate answer to this question was provided only recently by the first K-Ar dating attempt of illite-type fundamental particles separated from I-S of bentonite units (Clauer *et al.*, 1997). This study and others on similar fundamental particles (Środoń and Clauer, 2001; Rousset and Clauer, 2003; Clauer *et al.*, 2004) have proved that (1) there is no Ar release due to the small size of the particles, as smaller fractions are sometimes older than coarser, and (2) high potentials exist for evaluating the duration of illitization while burial is progressing in a sedimentary basin. Such evaluations of the duration of illitization were attempted previously (*e.g.* Elliott *et al.*, 1991), but they have systematically emphasized the difficulty in obtaining meaningful data for clay material in the shale units, which appears not to be addressed properly by simply splitting the clay material, even into individual fundamental particles.

In summary, the aforementioned K-Ar studies of fundamental particles extracted from I-S of bentonites show that fractions consisting of such particles yield K-Ar ages strictly related to the diagenetic history, implying no occurrence of detrital contamination, as controlled by electron-microscope observation. Alternatively, the coarser fractions may yield K-Ar data biased by inherited radiogenic ^{40}Ar found to be supplied by either pyroclastic or detrital components. The thinnest fundamental particles containing no pyroclastic and/or detrital contribution yield K-Ar ages that are either similar to or older than those of the corresponding slightly thicker fundamental particles, implying that illitization processes along a crystal-growth mechanism. In other words, those of the smallest fundamental particles, which failed to grow after nucleation, are providing theoretically the oldest ages. Consequently, the K-Ar age of fundamental particles, which underwent a long-lasting continued crystal-growth process, represents an integral of varied quantities of K that were progressively incorporated into the I-S structure. The amounts of radiogenic ^{40}Ar generated by decay of ^{40}K, are consequently varied in the particles, depending on the growth rate and therefore on the size of the particles, relying strictly on the thermal history of each host-rock sample. The results of Clauer *et al.* (1997) were completed by Rb-Sr and oxygen isotopic determinations of the same fundamental particles of I-S from the same bentonites (Clauer *et al.*, 2003). If one considers the fluid chemistry remaining identical during the entire illitization process, which is only a preliminary assessment, then the δ^{18}O results suggest that illitization in the bentonites of the East-Slovak Basin could have occurred either during temperature increase or decrease, which is not what is generally assumed. On the other hand, if one considers that the temperature remained approximately the same, then the water:rock ratio had to change during crystal growth. The ^{87}Sr/^{86}Sr ratio of the Sr initially trapped in the particles or being incorporated during crystal growth, appears to be systematically above the contemporaneous sea-water value, decreasing progressively when particle size increases, suggesting an external supply of Sr into the bentonite unit with an $^{87}Sr/^{86}Sr$ ratio close to that of the seawater. This external Sr probably diffused into the bentonite unit from nearby shales, as did K. The mean K-Ar ages of the fundamental particles were also used to elaborate on the kinetic characteristics of the reaction, which are addressed below.

All previous studies of fundamental particles from I-S of shales provide K-Ar data that are systematically older than the corresponding depositional ages. These data represent measured ratios of K_2O and radiogenic ^{40}Ar amounts which do not necessarily represent geologically meaningful ages. The fact that these data are older than depositional ages points to an excess of radiogenic ^{40}Ar relative to the K amount during the conversion of detrital into authigenic illite. Gilg *et al.* (2003) even suggested, in examining altered glass-rich silicic rocks of Eastern Germany, that the expected diffusion of radiogenic ^{40}Ar from detrital illite during diagenetic alteration might have been somehow impeded in the non-permeable shales. One can then envisage that the radiogenic ^{40}Ar was released into the pore space by nearby altered detrital minerals. However, when escape was impeded, it could have adsorbed on the surfaces of the pore-wall particles, and even been partly incorporated by the authigenic illite-type fundamental particles during nucleation and growth in the pore space, as suggested by Clauer *et al.* (2004).

Most previous studies have suggested alternative explanations for the excess radiogenic ^{40}Ar in the clay fractions of shales, such as a mechanical mixing of small authigenic and large detrital particles. In this case, which has been addressed by Lerman and Clauer (2005) by modeling the Ar loss from shale-type clay material, the K-Ar data of the clay mixtures should decrease with the size of the particles to values that are close to or even younger than the stratigraphic age of the rock unit (see discussion in Clauer and Chaudhuri, 1995). Such mixtures commonly occur for larger clay particles of shales, as sample processing certainly contributes in reducing artificially the size of the different mineral components. However, in order to become an appropriate interpretation for I-S fundamental particles, K-Ar values younger than stratigraphic ages have yet to be reported for shales. Instead, the available K-Ar data of the fundamental particles, even the smallest or thinnest, are systematically far older than the stratigraphic ages of the host shales. Another explanation, based on authigenic I-S particles growing on very small detrital particles, has been offered to explain the excess radiogenic ^{40}Ar (D.R. Pevear, pers. comm.). In this case, K-Ar data which increase for fundamental particles when particle size decreases due to a relative increase in the proportion of the detrital component, have yet to be obtained. No proof of these theoretical explanations has yet been reported, so there is a need to search for another hypothesis. Included here is a study of the behavior of several noble gases (Ar, Kr, Xe) in clay particles in the context of a potential excess of radiogenic ^{40}Ar in fundamental particles of shales.

Note that the isotopic modeling developed here is based only on recent isotopic dating and tracing studies of illite-type fundamental particles defined after the concept of Nadeau *et al.* (1984). This concept implies the dissolution of smectite layers in the I-S, followed by crystallization and growth of illite layers in the same I-S (Nadeau *et al.*, 1984; Inoue *et al.* 1987; Eberl and Środoń, 1988). Such illite-type layers can be separated after infinite osmotic dispersion to become the so-called fundamental particles. Depending on the exact mechanism of illitization, solid-state transformation or dissolution/precipitation, and assuming that the particle separation was the best, one might expect different isotopic ages for fundamental particles of varied thickness.

REVIEW OF THE AVAILABLE K-Ar DATA ON FUNDAMENTAL PARTICLES

Fundamental particles extracted from deeply-buried I-S of bentonite layers from the East-Slovak Basin and of a bentonite outcrop from nearby Zempleni highlands were studied in detail. While more mineralogical, chemical and isotopic information is now available for this environment (Honty *et al.*, 2004), Clauer *et al.* (1997) discussed the geological framework, as well as the sedimentological constraints, allowing reconstruction of the burial histories of the basinal samples. According to Šuchá *et al.* (1993), illitization of progressively buried I-S started in this basin at a temperature of ~70ºC, the R0/R1 transition taking place at an expandability (= % of smectite layers in the I-S) of 35% and a temperature of 105ºC, and the R1/R >1 transition occurring at an expandability of 13% and a temperature of 155ºC. These changes are believed to have occurred during maximum paleotemperatures. Independent evidence from Środoń (1995) also indicates that illitization is controlled mainly by the maximum paleotemperature. Therefore, the duration of illitization can be estimated for each bentonite sample, depending on its burial depth and temperature, but this information is not applicable to the Zempleni highland bentonite sample, which was generated during hydrothermal activity for which the paleotemperature could not be determined.

The interpretative modeling of I-S diagenesis used here follows the approach of Pollastro (1993), Środoń (1995) and Clauer *et al.* (1997). It considers that illitization of smectite in shales and mudstones is a continuous process, which starts at ~70ºC and is completed when the rock unit enters the zone of maximum paleotemperature. In fact, the process could last longer in the bentonite units due to a slow supply of

K by diffusion from surrounding rocks (Altaner *et al.*, 1984). Thus, measurement of the illite:smectite ratio (also expressed as the percentage of smectite layers, %S) in I-S of shales relates to the maximum paleotemperature. Therefore, the K-Ar data of I-S from any bentonite sample represent an integral over the entire period of illitization (starting at 70ºC and continuing to or slightly beyond the phase of maximum paleotemperature). In this respect, three interpretations can be offered for the trend in the K-Ar data from diagenetic I-S of the studied bentonite units from the East-Slovak basin.

(l) The fact that illitization of the bentonite I-S lags behind that of the shale I-S outlines differences in expandability. It could be due to a slow K diffusion into the bentonite beds, as stated above, but it is more likely that the lag in expandability results from the occurrence of detrital particles in the I-S of the shales having the same size as the authigenic fundamental particles of the I-S. The I-S of the Cicarovce bentonite sample of the East-Slovak Basin has a bulk expandability of ~55% corresponding to a maximum paleotemperature of 110ºC, which has been maintained until the present time. Therefore, illitization apparently started 12 Ma ago, when the material entered the 70−80ºC temperature zone, and it lasted until the present time. On the other hand, the I-S of the Trhovište bentonite sample of the same basin has a bulk expandability of ~17% corresponding to a maximum paleotemperature of ~155ºC. An episode of uplift identified at ~7 Ma ago decreased the temperature and probably stopped illitization, and lasted from 14.5 to 7 Ma. The measured K-Ar data of the fundamental particles from both samples fit reasonably well within these estimates of the theoretical illitization time interval, which was determined independently on the basis of the evolution of the organic matter (Clauer *et al.*, 1997, 2003).

(2) Alternatively, an intense recrystallization could have taken place right after the maximum temperature, driven not only by the thickness of the particles but also by variations in the chemical compositions or by crystallographic defects. In this case, the amounts of either K or radiogenic ^{40}Ar could be less than expected from the theoretical process. As a consequence, expandability would not have been affected, but the K-Ar data could have decreased.

(3) A further explanation would be that the illite-type fundamental particles lost some radiogenic ^{40}Ar by diffusion independent of the particle size. In this case, the thinnest fundamental particles, which are also the smallest in the *ab* dimension (Šuchá *et al.*, 1993), should not yield younger K-Ar data than the thicker ones.

We explore here another hypothesis for the K-Ar data of the fundamental particles separated from I-S in shales, based on published oxygen and Rb-Sr isotopic data (Clauer *et al.*, 2003), and on new K-Ar results and noble gas contents of authigenic smectite extracted from recent to present-day mud-type sediments of the Pacific Ocean. The purpose is to elaborate on a preliminary isotopic model for illitization of bentonite I-S at the size of fundamental particles.

NEW DATA ON RECENT SURFICIAL AUTHIGENIC SMECTITE OF OCEANIC SEDIMENTS

Noble-gas contents were determined in pure smectite size fractions of authigenic 'deep-sea red clays' (DSRC) from the southern Pacific Ocean, in order to collect information about their behavior in small clay particles of recent surficial oceanic sediments. As the samples were taken at or just below the interface between seawater and sediment, it can be assumed that the extracted clay material was not part of an impermeable rock preventing free escape of the gases, as can be the case in a deeply buried and compacted shale. However, the pore openings in recent sediments from the Pacific Ocean are only about five times larger than that, at ~1 nm, of shales buried at ~2000 m (Horseman *et al.*, in press). Note that noble gases do not tend to behave as fluid-soluble speciations, so they may not escape readily, even in uncompacted fluid-saturated mudstones. Last but not least, the material studied here originated next to volcanic seamounts or spreading centers, so that it is authigenic. Collected far from any continental supply, it can also be considered to be essentially free of any detrital component (Hoffert *et al.*, 1978). Alternatively, as the samples occur close to sub-marine volcanic seamounts or to hydrothermal vents, volcanic material is probably contributing to the sediments.

The geological setting

Several smectite-rich size fractions were extracted from a surficial sample (uppermost 2 cm) of a core located at 11º28.6′S and 144º00.5′W in the southern Pacific Ocean, to the NNE of the Tuamotu Archipelago (Figure 1). The site of the core is characterized by a water depth of 4725 m, which is below the carbonate dissolution limit, and by bottom currents moving from West to East towards the closest continent. The core was drilled during the Transpac 1 oceanographic cruise organized by the French Centre National pour l'Exploitation des Océans (CNEXO). It is made up of an homogeneous, fine, dark brown, ~4 m thick mud unit, containing minute amounts of coarse material (>63 μm) comprising mainly palagonite in the upper part and phillipsite in the lower part of the core, both derived from volcanic material. The clay fraction of the uppermost 2 cm of the sediment, which is studied here, was examined by X-ray diffraction and transmission electron microscopy (TEM), and analyzed for its chemical composition (Clauer *et al.*, 1982). It consists almost exclusively of smectite, with differential thermal analysis curves and chemical compositions typical of nontronite, an Fe-rich smectite, occurring as rolled up sheets

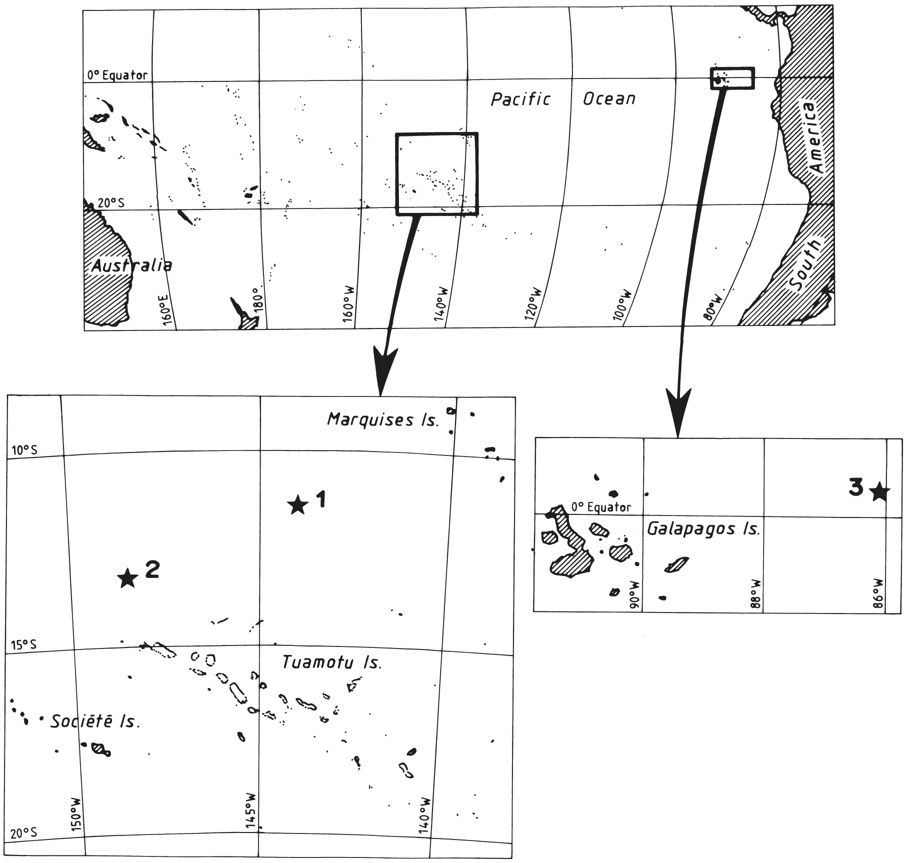

Figure 1. Locations of the sampling sites of smectite from Pacific Ocean sediments. The stars labeled 1 and 2 represent the sites of the drillings mentioned in the text.

surrounded by elongated fibers (TEM images in Clauer *et al.*, 1982). This nontronite is considered to be authigenic, derived from volcanic material of the nearby seamounts, as the bottom currents are further directed towards the continent. The lack of fossils prevented a stratigraphic age determination of the core, but the few radiolarians found in the uppermost 7 cm of the sediment are of Plio-Quaternary age (A. Schaaf, pers. comm.). The Rb-Sr isotopic age of the volcanic-derived phillipsite from the lower part of a nearby core (13°15′S, 148°30′W; Figure 1) was set at 14.7±3.3 (2σ) Ma by the isochron technique (Clauer, 1982), with an initial $^{87}Sr/^{86}Sr$ ratio of 0.70441±0.00036 (2σ) significantly below sea-water value, which confirms the volcanic origin.

Two additional clay fractions were taken near the Galapagos Spreading Center (GSC) at a sediment depth of 3 to 16 m. They belong to borehole 509B drilled during DSDP leg 70, coinciding with IPOD-DSDP leg 54 site 424 (Honnorez *et al.*, 1981). This hole is located at 1°N and 86°W in the equatorial Pacific Ocean, on the southern flank of the GSC, ~22 km from the axis (Figure 1). The drilling recovered 33.4 m of sediment before touching the basaltic basement. The upper part of the core was described as a hydrothermal mound of the GSC (Buatier *et al.*, 1989). This mound and others nearby are considered to occur in areas characterized by high heat flows above small and active vertical faults in the basement (Williams *et al.*, 1974). They contain Fe-rich clay material of smectite and celadonite types which precipitated from fluids exiting the highly permeable basement in the vent area and are ascribed to low-temperature hydrothermal activity (Honnorez *et al.*, 1983).

Analytical procedure and results

The <2 μm fractions of the Tuamotu and Galapagos core samples were separated by sedimentation in distilled water after dispersion by shaking; further size fractionation of the DSRC nontronite in smaller sizes was conducted with an ultra-centrifuge. The >2 μm fraction of the Tuamotu core, consisting mostly of volcanic matter, was also collected and analysed for comparison. The K-Ar determinations follow a procedure close to that described by Bonhomme *et al.* (1975). The samples were stored for at least 12 h at 80°C under vacuum to release all adsorbed atmospheric Ar during sample preparation and handling. Then they were fused, still under vacuum, to extract the gases which were split to keep only the inert gases for Ar analysis by mass

Table 1. K-Ar dates of smectite and glass fractions from Pacific clays.

Samples		K_2O (%)	Ar* (%)	$^{40}Ar^*$ (10^{-6} cm^3/g)	Age (Ma + 2σ)	$^{40}Ar/^{36}Ar$	$^{40}K/^{36}Ar$ (10^{-6})
Tuamotu Archipelago							
Sample 1	<0.4 μm	1.37	40.7	2.39	53 (3)	498.5	64.6
	0.4–0.8 μm	1.67	47.7	4.10	75 (4)	564.7	60.7
	0.8–2 μm	1.73	54.8	4.32	76 (4)	654.3	79.7
	>2 μm	3.45	25.0	2.05	18 (2)	393.9	91.8
Galapagos Spreading Center							
Sample 1	<2 μm	0.18	2.4	0.09	±0	307.1	2.4
Sample 2	<2 μm	0.34	1.5	0.12	±0	303.1	4.2

spectrometry. The whole procedure was systematically controlled by periodic measurement of the GLO reference and of the atmospheric $^{40}Ar/^{36}Ar$. The K_2O contents of the different fractions were determined by atomic absorption spectrometry to calculate the K-Ar data with the usual decay constants and an overall analytical uncertainty of ~±2%.

The amounts of Ar, Kr and Xe were measured at the Max-Planck Institut for Chemistry, Mainz (Germany), following a procedure described by Schultz *et al*. (1991). The samples were pre-heated at ~150ºC for 60 min, and they were degassed afterwards either at ~800ºC for 45 min, or at ~1420ºC for 60 min. The gas concentrations are accurate to better than ±5%. The blanks of all extraction lines and mass spectrometers were systematically and carefully controlled before each extraction to avoid any contribution by the equipment to the gas contents of the analysed fractions. The contaminant contributions were found to be systematically smaller than the gas concentrations by a factor of at least 100.

The results are twofold: the K-Ar data (Table 1) and the contents of the noble gases (Table 2). The very recent <2 μm smectite fractions from GSC yield K-Ar results of 0 Ma considering the analytical uncertainty, as they contain only minute amounts of detectable radiogenic ^{40}Ar highlighted by an average $^{40}Ar/^{36}Ar$ ratio of 305.1±2.0 (2σ). This value is only very slightly above 300.3±0.3 (2σ), which is the mean $^{40}Ar/^{36}Ar$ ratio calculated from several determinations during the course of the study for the control of the atmospheric Ar, and slightly above the theoretical atmospheric $^{40}Ar/^{36}Ar$ ratio of 295.5 (Nier, 1950). In the case of the Tuamotu sample, the youngest K-Ar value was found for the coarse >2 μm fraction, consisting almost exclusively of volcanic glass and from which the authigenic <2 μm nontronite of the DSRC derives. Its K-Ar value of 18±2 Ma is identical, within analytical uncertainty, to the Rb-Sr age of 14.7±3.3 Ma (2σ) obtained for phillipsite from a nearby site (Clauer, 1982). Alternatively, the small size fractions of the nontronite from deep-sea red clays yield K-Ar values ranging from 53 to 76 Ma, which is far older than the expected stratigraphic and/or volcanic formational age. This excess cannot be explained by supply of detrital material, as none has been recorded, so that the only valid explanation for such abnormal high values, relative to a Plio-Quaternary stratigraphic reference age, is incorporation by trapping or adsorption of excess of ^{40}Ar during mineral precipitation.

The Ar, Kr and Xe contents of the <2 μm GSC sample are systematically greater than the contents of the same gases in the <0.4 and the 0.4–0.8 μm fractions of the DSRC nontronite (Table 2): 1.6 times more Ar, 6.7 times more Kr and 3.4 times more Xe. The <0.4 μm fraction of the DSRC sample is also systematically enriched in noble gases relative to the coarser 0.4–0.8 μm fraction: 1.3 times more Ar, 4.6 times more Kr and 2.5 times more Xe. The older smectite from DSRC contains almost as much Ar, Kr and Xe as the younger smectite from GSC which precipitated from hydrothermal fluids of the crust. Also, the smallest particles of the authigenic deep-sea smectite contain more Ar, Kr and Xe than the coarser particles indicating

Table 2. Noble-gas contents of nontronite fractions from Pacific clays.

Samples		Ar (10^{-6} cm^3/g)	Kr (10^{-9} cm^3/g)	Xe (10^{-10} cm^3/g)
Tuamotu Archipelago				
Sample 1	<0.4 μm	5.0	2.5	4.9
	0.4–0.8 μm	4.0	0.55	2.0
Galapagos Spreading Center				
Sample 1	<2 μm	7.1	10.7	12.0

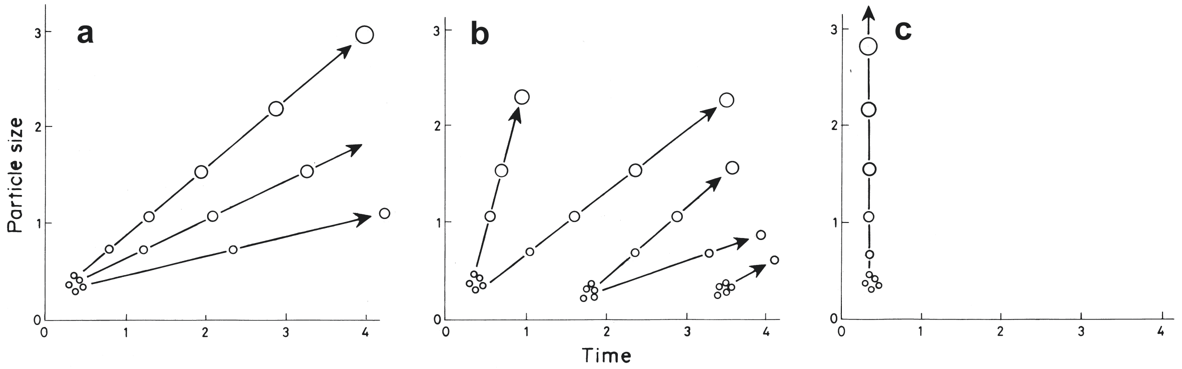

Figure 2. Theoretical sketch of particle-size growth relative to time in fundamental particles following: (a) one diagenetic nucleation; (b) several episodic diagenetic nucleations; and (c) one hydrothermal nucleation.

that the noble gases analyzed are not released from smaller particles because of size or increasing age.

The GSC nontronite also contains as much Ar as the air, and more Kr (two times) and Xe (eight times). The smallest <0.4 μm fraction of the DSRC nontronite contains less Ar than the air (two times), but more Kr (two times) and Xe (five times), whereas the coarser fraction is more depleted: four times less Ar, two times less Kr and three times more Xe. On the other hand, all the smectite fractions analyzed are significantly depleted in the same gases relative to the deep Pacific Ocean waters (Ozima and Podosek, 2002; Porcelli *et al.*, 2002), though that of the GSC and the smallest, <0.4 μm, fraction of the DSRC, are far less depleted in Kr (about eight times) than the coarser DSRC nontronite (20 times). The Ar contents are about similar for all fractions, depleted by a factor of 9 to 10. Relative to the same Pacific seawaters, the Xe contents are more scattered but less depleted for the GSC sample and the <0.4 μm DSRC fraction (six times), than for the coarser 0.4–0.8 μm DSRC fraction (nine times).

SOME HYPOTHESES FOR ILLITIZATION OF BENTONITE FUNDAMENTAL PARTICLES

Crystal growth can be represented diagrammatically so that growth of fundamental particles relates to measurable time (Figure 2). Growth depends on temperature, on chemical thermodynamic parameters and on the accessibility of the particles to the interstitial fluid. As already stated, if initial fundamental particles, which grew little or not at all, can be separated from coarser ones, they should yield the oldest K-Ar ages (Figure 2a). Alternatively, if crystal growth was not unique but periodic (episodic), separation of the smallest fundamental particles should provide K-Ar data younger than those of the associated coarser fundamental particles (Figure 2b). Also, if crystal growth relates to a short-lasting hydrothermal activity, the fundamental particles of any size should yield about the same K-Ar age (Figure 2c).

In fact, these theoretical explanations are based on the analytical evidence of I-S fundamental particles extracted from bentonite units of the East-Slovak basin and nearby Zempleni heights. They also relate to additional results from the same basin (Honty *et al.*, 2004; Honty and Clauer, unpubl. data). The smallest illite-type fundamental particles of the bentonite unit from Trhovište borehole yield K-Ar ages that are younger than those of the coarser particles: ~8 and 10.5 Ma, respectively. The K-Ar values cover part of the theoretical duration of illitization, which extended from 14.5 to 7 Ma (Figure 6 in Clauer *et al.*, 1997). The smallest fundamental particles of the bentonite unit from Cicarovce borehole yield older K-Ar ages than the coarser particles: 7.25 Ma and 3.75 Ma, respectively. This range nearly fits the mid-point of the theoretical duration of illitization, which spans from ~12 to 0 Ma. For the Zempleni sample, all size fractions provide the same K-Ar values within analytical uncertainty, from 13.5 to 15.6 Ma.

As such, the K-Ar data of the fundamental particles from bentonite I-S do not represent equally meaningful geological ages, as they integrate a long-lasting, burial-related process, which has generated particles since the beginning of illitization with little or no K contents, and with little or no radiogenic ^{40}Ar contents resulting from radioactive decay of the ^{40}K incorporated. The increase in K over time during crystal growth increased the amount of radiogenic ^{40}Ar. As already stated, the K-Ar data appear to provide information about the type and the kinetics of the crystal-growth mechanism, depending on the size of the particles. For instance, one can envisage in a diagram relating particle growth to time, that increase in size of the particles was constant or not over time, giving either a linear or a curved trajectory (Figure 3). The latter curves certainly record changes in the processing kinetic rates, which could have been either small at the beginning and greater while processing, or on the other hand, large at beginning, decreasing later, all depending on temperature variations and fluid chemistry over time. It can also be assumed that particle growth was followed by one or several additional nucleation episodes. In summary, and depending on these kinetic aspects, which are different from those

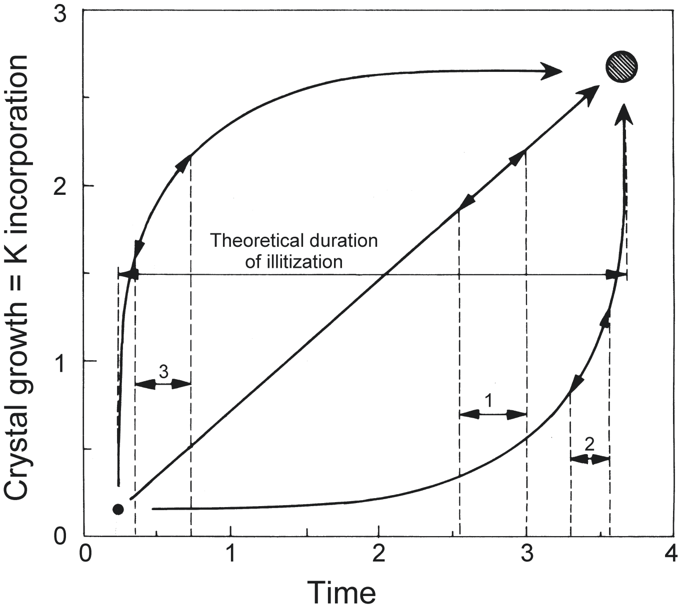

Figure 3. Theoretical sketch of crystal-growth rates relative to time. Nucleation begins in the lower left corner of the diagram with a small particle and ends in the upper right corner with a larger particle. The theoretical duration of illitization is conventionally considered to be between the beginning and the end. Three illitization rates are sketched: a uniforn one giving the straight line from lower left to upper right with zone 1 where most of the K-Ar data may plot; a process slow at the beginning and rapid at the end given by the lower exponential curve and with zone 2 where most of the K-Ar data may plot; and a process rapid at the beginning and slow at the end given by the upper exponential curve and with zone 3 where most of the K-Ar data are expected.

already available in the literature, the K-Ar data of bentonite fundamental particles may concentrate near the middle of the trajectory when the growth was about constant during the whole process, implying an almost constant temperature increase, which seems to be the case for the Cicarovce bentonite. The K-Ar data could also concentrate either at the beginning of the whole theoretical process, or towards the end, as seems to be the case for the Trhovište bentonite, suggesting varied growth rate and temperature increase (Figure 3).

While electron microscope observations allow us to follow the growth process, the $\delta^{18}O$ values of the different sizes of fundamental particles provide information about the conditions (Figure 4): a decrease in the $\delta^{18}O$ values from small to coarse particles, as for the Cicarovce fractions, suggests a temperature and/or a water:rock ratio increase, whereas an increase in the $\delta^{18}O$ values from small to coarse particles, as for the Trhovište material, suggests a temperature and/or a water:rock ratio decrease. Constant $\delta^{18}O$ values for all particles, whatever the size, suggests constant formation temperature and/or constant water:rock ratio, as is suggested by the Zempleni hydrothermal bentonite material.

DISCUSSION

Particle-growth conditions during illitization following varied theoretical pathways were addressed above by different isotopic methods. Note that the following discussion of isotopic modeling is based only on results obtained from fundamental particles.

Duration and crystallization conditions during burial-induced illitization in bentonites

One possible overall interpretation of the data collected from the two bentonite units in the East-Slovak Basin and from that of the nearby Zempleni mountains is as follows, on the basis of the available results. (1) The bentonite unit collected in the Cicarovce borehole underwent burial diagenesis lasting from ~12 Ma until the present day, at a maximum temperature of ~130ºC. Illitization seems to have occurred in a single crystal-growth process. It is more likely that the temperature rather than the water:rock ratio increased during the process. The K-Ar data obtained for the fundamental particles plot near the middle of the process, suggesting an apparent constant kinetic rate for growth. (2) The bentonite unit in the nearby Throvište borehole (~20 km away) underwent burial diagenesis lasting from ~14.5 to 7 Ma, with a maximum temperature of ~165ºC at ~11 Ma ago. Illitization seems to have included several (at least two) nucleation and growth episodes. The temperature, rather than the water:rock ratio, appears to have decreased progressively. The K-Ar data of the fundamental particles plot towards the end of illitization, suggesting a progressive increase of the kinetic growth rate. (3) The Zempleni bentonite is of hydrothermal origin, but its formational temperature is unknown. Illitization was rapid, as all

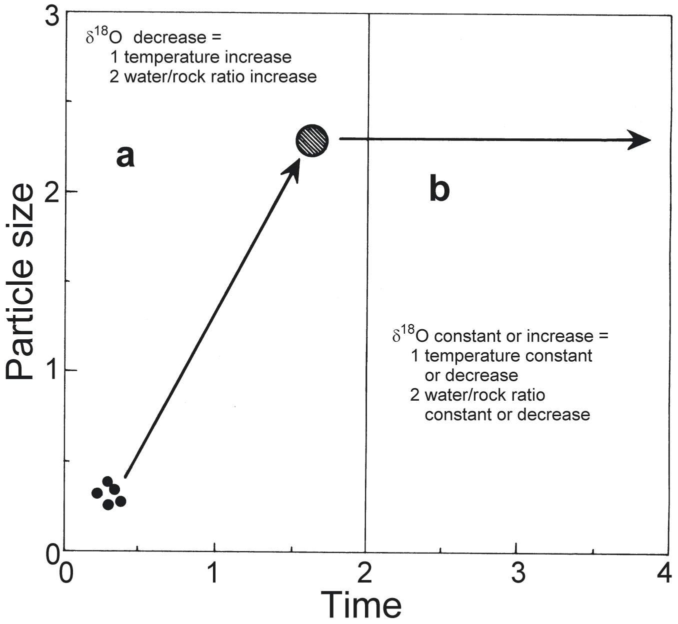

Figure 4. Theoretical sketch of the potential changes in the $\delta^{18}O$ of the fundamental particles when size changes relative to time. In part a when the $\delta^{18}O$ decreases while particle size increases, the temperature and/or the water:rock ratio increase; in part b, when the $\delta^{18}O$ increases or remains constant when the particle size stays constant, the temperature and/or the water:rock ratio are either constant or decrease.

K-Ar data are similar within analytical uncertainty, along a single nucleation-growth process. Supposedly, the water:rock ratio, rather than the temperature, increased during the process.

Ar behavior in I-S of shales during burial-induced illitization

A recent compilation of K-Ar data from I-S of various sizes in deeply buried shales of the Gulf Coast, the North Sea and the Mahakam delta in Indonesia showed that illitization proceeds very similarly in these three very different basins, at least in terms of the increase in the proportion of illite layers in the I-S and in terms of the associated K contents (Clauer and Chaudhuri, 1996). The evolution of the K-Ar data of I-S is consistent in the three basins, despite clear differences in the provenance of the detrital components, the deposition ages, the burial depths and the tectonic history. This consistency clearly highlights that the K-Ar values older than the stratigraphic age do not result simply from a random mixture of detrital and authigenic particles; there has to be a similar process occurring in the detrital/authigenic mixed clay material during the burial evolution. On the other hand, and as already stated, several isotopic studies of fundamental particles of I-S from shales also provided consistently older K-Ar data than the fundamental particles of I-S from associated bentonites. Addition of the study on fundamental particles from shales and associated sandstones buried deeply beneath the Mahakam delta in Indonesia (Clauer *et al.*, 2004), and the behavior of noble gases in modern oceanic sediments, allow us to envisage a very preliminary explanation for the consistently high K-Ar data of fundamental particles from shales.

(1) In addition to the theoretical possibility of detrital illite-type fundamental particles being sandwiched with authigenic ones in an I-S of an impermeable shale-type rock, which releases radiogenic ^{40}Ar to the pore system, it can also trap this radiogenic ^{40}Ar as well as that released from altered detrital particles, as suggested by Gilg *et al.* (2003) and Clauer *et al.* (2004). This radiogenic ^{40}Ar amounts to at least 0.45×10^{-6} cm^3 g^{-1} of fundamental material in any shale containing >1.4 wt.% of K_2O, which is less than the amount of Ar found in any of the authigenic recent to present-day oceanic nontronite. It may be added that the contents of noble gases increase systematically from coarse to fine smectite of the Tuamotu oceanic sediments, clearly favoring a trapping (adsorption or incorporation) and not a release (escape) of these gases. Despite contents eight to 12 times lower than the corresponding contents of the Pacific Ocean deep water, the recent clay particles contain at least as much noble gases as the atmosphere, if not slightly more. All these results suggest that smectite-type clays of sedimentary units behave as traps (sinks?) for noble gases, which is completely unexpected as it has been argued for decades that small clay particles probably tend to lose radiogenic ^{40}Ar, as well as the other noble gases, by extension, due to size and defects. Interestingly, smectite crystallizing in hydrothermal vents where the amounts of fluids are extremely large compared to those in sediments, yields a $^{40}Ar/^{36}Ar$ ratio very similar to that of the atmosphere. In turn, dissolution of detrital silicate particles of shales during

diagenesis, as is the case for the volcanic material in the DSRC, release radiogenic ^{40}Ar into the pore system of the host rocks. This free radiogenic ^{40}Ar is expected to adsorb on pore-wall particles, as suggested by the theoretical decomposition of ^{40}Ar diffusion in fine-grained shales (Lerman and Clauer, 2005). Whenever clay nucleation and growth proceed, the new particles may trap (by adsorption or incorporation) some of the available ^{40}Ar, because they are potentially capable of scavenging noble gases.

(2) The K-Ar systematics and the noble gas contents of authigenic smectite from Pacific DSRC support the above interpretation for the abnormally old K-Ar data of fundamental particles from I-S of shales. Indeed, even in recent to present-day mud-type sediments, radiogenic ^{40}Ar seems to remain in the pore system instead of escaping, probably because of its preferential tendency to adsorb on the mineral surfaces instead of dissolving in fluids, and also because the pore opening is very small, at the nanometre scale. Therefore, the properties of scavenging noble gases seem to be real for clay particles, but yet to be confirmed in detail. However, it must be kept in mind that detrital material, even in minute amounts, may be mechanically mixed with pure authigenic fundamental particles, and that detrital fundamental particles can be sandwiched with authigenic ones in I-S, both being possible constituents in any sample. Thus they represent a possible alternative explanation that should never be ignored in spite of the fact that sandwiching of detrital/authigenic fundamental particles is the opposite of the concept outlined above.

Two questions remain unanswered at this point and need to be addressed: (1) can it reasonably be envisaged that clay particles are capable of absorbing or incorporating noble gases when nucleating and growing? (2) Can fundamental particles of shales still be dated by isotopic means? The answer to the first question needs to take into consideration the atomic radius of the elements likely to integrate into the structure of well crystallized illite-type particles. If one considers the interlayer sites of clay material as potential locations, it appears that the radius of Ar (1.58 Å), Kr (1.69 Å) and Xe (1.90 Å) is only slightly greater (1.3 times at the most) than those of K (1.33 Å) and Rb (1.49 Å), for instance. Therefore, incorporation of noble gases into illite interlayer sites is possible without inducing major distortions in the structure and knowing that they are totally inert. The answer to the second question depends on a number of aspects, such as identification and quantification of the detrital illite-type fundamental particles that contribute to the original I-S, and the amount of excess radiogenic ^{40}Ar that the authigenic fundamental particles might have incorporated during nucleation and growth.

As the amounts of detrital fundamental particles and radiogenic ^{40}Ar incorporated by authigenic fundamental particles probably vary among samples, a preliminary step should certainly include the plotting of the data in a K-Ar isochron diagram. It would certainly be appropriate to analyze also the smallest extractable size fractions of any I-S, because they might contain similar amounts of radiogenic ^{40}Ar in the detrital and in the authigenic layers. Extraction of meaningful ages might then be assessed by drafting sub-parallel arrays in an isochron diagram. Indeed, sub-parallel alignments suggest identical or similar ages, which are only obtained when the analyzed size fractions contain an almost pure authigenic component. If such sub-parallel arrays are obtained, the varied initial ^{40}Ar/^{36}Ar ratios of the different lines, all above the atmospheric value, reflect the varied amounts of radiogenic ^{40}Ar that the fundamental particles incorporated during crystal growth from their own environment.

CONCLUSIONS

Illitization of fundamental particles separated from mixed-layer illite-smectite of bentonites, and to some extent of sandstones, has been modeled on the basis of the K-Ar systematics and δ^{18}O compositions. The model envisages different reaction rates and durations, related to varied impacts of the temperature. New hypotheses are provided for the reaction kinetics, while the water:-rock ratio also has some influence during the process, different pathways being suggested.

New information about the noble-gas contents and K-Ar systematics of authigenic smectite of recent to present-day oceanic sediments helps to understand better why, beyond a generally admitted contamination by detritals, fundamental particles of shales yield K-Ar values that are systematically older than the ages of the fundamental particles of associated bentonites or sandstones, and/or older than the stratigraphic age reference. The study of such smectite samples from Pacific sediments outlines preliminary results showing that: (1) those collected close to fluid-active hydrothermal vents yield ^{40}Ar/^{36}Ar ratios identical to that of the atmosphere; and (2) those extracted from authigenic mud sediments away from vents yield ^{40}Ar/^{36}Ar ratios significantly above the atmospheric value, indicating incorporation of ^{40}Ar neither related to detrital solid inputs mixed with the authigenic particles, nor generated by radiactive decay in the authigenic mineral structures. A preliminary control of the noble gas (Ar, Kr and Xe) contents of smectite size fractions from Pacific deep-sea red clays highlights an unexpected behavior of the smectite-type material acting as a trap for noble gases. All these new results suggest that nucleating fundamental particles might incorporate Ar into their structure and be characterized by an ^{40}Ar/^{36}Ar ratio greater than that of the atmosphere. This seems to occur when the fundamental particles grow in restricted to closed systems, such as that of shales in the pore spaces of which radiogenic ^{40}Ar released from altered silicates might be adsorbed and mixed with the atmospheric Ar already present.

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