

# Illite K–Ar dating and crystal growth processes in diagenetic environments: a critical review

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## ABSTRACT

K–Ar dating of illitic minerals is commonly used in studies of diagenetic series applied to oil prospecting. In spite of a great number of specialized papers, some problems remain unresolved. These are mostly due to a misunderstanding of the argon accumulation process during illitization. Criteria for identifying detrital–authigenic mineral mixtures, crystal ripening, fast precipitation or continuous nucleation–growth processes are discussed using K–Ar data available in the literature. Using different parameters, such as  $\Delta_{\text{age}}$  ( $\text{age}_{\text{K–Ar}} - \text{age}_{\text{strati}}$ ),  $\Delta_{\text{cryst}}$  ( $\text{diagenetic age}_{\text{K–Ar}} - \text{age}_{\text{strati}}$ ) or  $\Delta_{\text{frac}}$  ( $\text{age}_{\text{K–Ar fraction}} -$

$\text{age}_{\text{K–Ar finest}}$ ), it is shown that the K–Ar age significance depends on the illite nucleation–growth processes. A ‘diagenetic age’ is obtained when these processes are rapid (the K<sub>2</sub>O accumulation period is shorter than  $2\sigma$ ). If lower than this value, the K–Ar ratio depends on the proportions of new and old particles, respectively, which are controlled by the relative rates of nucleation, crystal growth and ripening.

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## Introduction

Illite contains potassium, which is a part of its definition. This potassium can be used to obtain an age, or period of existence of potassium in an illite crystal. The estimation of time is obtained through the identification and measurement of radioactive decay and decay products. A radiometric age is obtained by determining the amount of potassium in a mineral and the amount of radio-decay argon (see the review by Clauer and Chaudhuri, 1995). However, this is not as easy as it sounds for the following reasons:

- 1 mixing with other K-bearing phases such as detrital mica or K-feldspar (contamination effect),
- 2 Ar loss or capture during crystallization,
- 3 duration of K accumulation (growth stage) in the illitic phases, i.e. illite and illite–smectite mixed layer particles (I/S MLM) compared with the dating experimental error ( $2\sigma$ ).

The contamination effect due to authigenic–detrital phase mixing has been discussed in numerous papers (Pevear, 1992; Srodon, 1999; Ylagan *et al.*, 2000; Srodon *et al.*, 2002).

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Whatever the mixing law used by the different authors, detrital and authigenic phases are considered to have a fixed K–Ar age. This assumption is acceptable only if, first, the source of the detrital K-bearing phases is the same in all the studied samples and, second, if the authigenic phases have a given age. This latter point is debatable because it refers to the duration of K accumulation compared with the experimental dating error ( $2\sigma$ ). In other words the crystal growth processes of illite and I/S MLM phases should be taken into account before any interpretation of K–Ar ratio in terms of geological dating.

How can one study the effect of the growth processes related to illitization in diagenetic environments on K–Ar dating? Analysing the shapes of crystal size distributions, Eberl *et al.* (1998) showed that they are controlled by three different mechanisms: nucleation + growth, surface-controlled growth and supply-controlled ripening. However, in spite of this recent progress, a theoretical approach remains unclear because the growth processes are still not fully understood (see Srodon *et al.*, 2002). Indeed, the size of illite particles is difficult to measure in three dimensions. However, some published K–Ar data concerning different size fractions of clay samples can be used to estimate the effect of crystal growth. The present contribution aims to examine how argon is accumulated or lost during

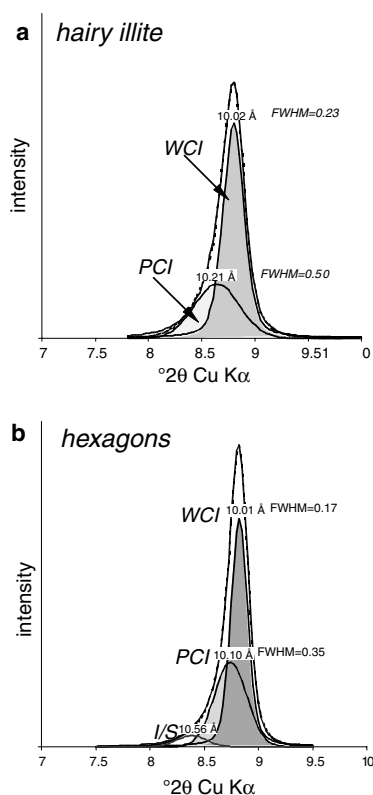
the illitization process in diagenetic environments using selected published data.

## Diagenetic illite: what do we know?

### What is illite and how does it form in diagenetic environments?

Illite is commonly identified in diagenetic sediments using X-ray diffraction (XRD) by a peak near 10 Å whose width at half maximum intensity (FWHM) is higher than that of micas (Meunier and Velde, 2004). The shape of the peak is asymmetrical and biased towards small angles. According to Lanson (1997), mathematical decomposition procedures may be used to analyse the peak shape and intensity. It has been shown that the ‘illite’ 10-Å peak results from the contribution of three different particle populations: I/S, PCI and WCI. (Fig. 1). The relative intensity of the WCI peak increases with depth in diagenetic series. Thus, the 10-Å peak becomes sharper and the Kübler index decreases (Kübler and Jaboyedoff, 2000). Illite is considered to be pure when the I/S MLM contribution becomes negligible compared with the PCI and WCI peaks.

Consequently, even if no expandable layers are detected in XRD patterns, any K–Ar dating of illite in sediments is based on an average composition of a composite population of particles



**Fig. 1** Example of decomposition of XRD patterns of the illitic phases in the Proterozoic sandstones of the Athabasca basin (Canada). (a) Illite was formed by direct precipitation from potassium-rich solutions. (b) The illitic phases have been matured by diagenetic processes.

having different size, shape and thickness. This average crystalline state changes with depth as a result of different processes (Altaner and Ylagan, 1997). It is important to identify the process at work in order to understand how potassium becomes incorporated during the change of crystalline state. In most of the diagenetic series described thus far, illite forms via two different mechanisms: direct precipitation from potassium-enriched solutions, leading to the 'illitization' of kaolin precursor minerals in sandstones, or the progressive illitization of smectite-rich precursor minerals in mudstones.

The minerals of the kaolin group have been described as precursors of illite in deeply buried sandstones (see, among others, Bjorlykke *et al.*, 1986; Erhenberg and Nadeau, 1989; Bjorlykke & Aagaard, 1992; Lanson *et al.*,

1996; Berger *et al.*, 1997). The size and shape of crystals depends on temperature (Lanson *et al.*, 1996) rather than on chemical constraints (Small *et al.*, 1992). The morphological evolution from hairy habit through lath-shaped to isometric or hexagonal plates occurs simultaneously with an increase in 'crystallinity'. In such a case, crystallinity depends on the relative proportions of PCI and WCI as indicated by XRD decomposition (Fig. 1a,b).

The illitization of smectite-rich sediments in diagenetic conditions was shown to be controlled by two concomitant mineral reactions: the increase of illite content of I/S MLM and the nucleation and growth of pure illite particles. These two reactions result from the dissolution of unstable particles and the growth of the stable ones. Concomitantly with an illite content increase of I/S MLMs up to 95%, the shape and size of the particles change: small-sized lath-shaped smectite-rich I/S particles transform progressively into large-sized more isotropic particles. Thus, illitization proceeds through crystal growth.

#### How do illite crystals grow in diagenetic environments?

Because illitization is an addition of illite layers on I/S MLMs, these particles always have a small fraction of smectite present (less than 5%). By contrast, the illite crystallites appear to have no smectite present regardless of their size. This pure illite is normally well crystallized (WCI) and has a crystal shape reasonably close to hexagonal. Observations carried out on several diagenetic series (Eberl and Srodon, 1988; Inoue *et al.*, 1988; Eberl *et al.*, 1990; Lanson and Champion, 1991; Varajao and Meunier, 1995) show that, whatever the depth, the size distribution in normalized coordinates is a log-normal curve whose parameters  $\alpha$  (mean of the logarithm of the crystal dimension) and  $\beta^2$  (variance of the logarithm of the crystal dimension) remain constant. This implies that a steady state has been reached and suggests that, even if the very restrictive conditions for Ostwald ripening are not satisfied (see Baronnet, 1991), the driving force for crystal growth during the illitization process is related to the minimization of surface free energy.

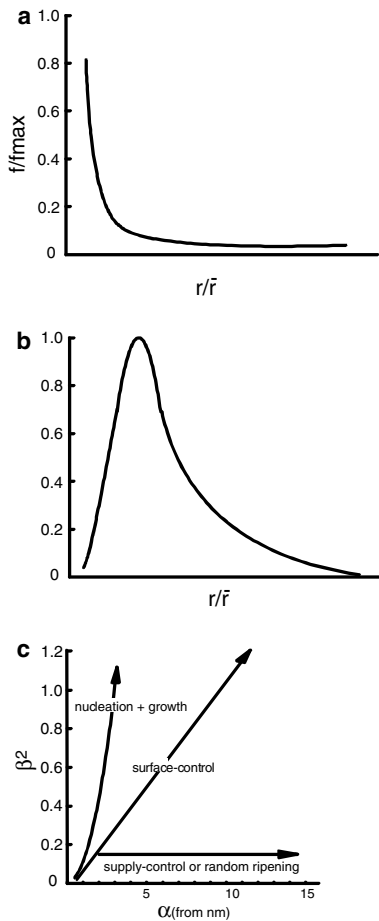
Summarizing, the increasing illite content of I/S MLM up to 95% is related to crystal growth controlled by a ripening process while pure illite particles nucleate and grow concomitantly (Wilkinson and Haszeldine, 2002). Significant progresses has been made since these first analyses with regard to the distribution of particle size in diagenetic sediments. Indeed, the distribution of particle size changes according to the relative importance of nucleation on the one hand and of ripening on the other. Eberl *et al.* (1998, 2002) showed that the distribution function is asymptotic or log-normal if nucleation or ripening dominate, respectively (Fig. 2a,b). Three general trends have been discriminated in an  $\alpha$ - $\beta^2$  plot (Fig. 2c).

We must keep in mind that K–Ar dating of diagenetic illite aims to provide absolute ages in the complex geological history of sedimentary basins. These ages are useful data in oil prospecting for example. Unfortunately, illite is frequently mixed with detrital micas whose age is much older. Thus, the above theory, which was successfully applied to hydrothermal systems (Eberl *et al.*, 2002), cannot be directly used for illite age calculation because of this contamination effect. Besides, K–Ar dating is obtained from amounts of argon and potassium not from crystal growth models. Consequently, the qualitative models presented below are based on K/Ar mass-balance and do not give documented information on the actual growth processes.

#### The K–Ar apparent age of authigenic–detrital mineral mixtures

##### Evidence of mixtures of detrital and authigenic illitic phases

Clay fractions isolated from samples of diagenetic rocks are most often heterogeneous. They are at times composed partially of detrital minerals that are older than the sedimentary bed and of more recent authigenic minerals. The K–Ar age of the clay fraction depends on the different proportions of detrital and authigenic minerals. This has been shown by Pevear (1992) for Albian–Aptian and Turonian shales from Arkansas, USA. K–Ar dating has been performed on



**Fig. 2** Theoretical analyses of the particle size distribution from Eberl *et al.* (1998). (a) Nucleation–growth process. (b) Ostwald ripening process. (c) The three types of particle size distribution plotted in an  $\alpha$ – $\beta^2$  diagram.  $r$ : measured size;  $\bar{r}$ : mean size;  $f$ : measured frequency;  $f_{\max}$ : maximum frequency;  $\alpha$ : mean of the logarithm of the crystal dimension;  $\beta^2$ : variance of the logarithm of the crystal dimension.

several size fractions of the shales (2.0–0.2  $\mu\text{m}$ ; 0.2–0.02  $\mu\text{m}$ ; < 0.02  $\mu\text{m}$ ). The detrital illite fraction has been measured by XRD using the calculation code NEWMOD (Reynolds, 1985). The results (Fig. 3) show that both series of analyses can be represented by two straight lines (simple linear regression) that converge at 0% detrital illite at about the same age: 30 Ma. This age corresponds to that of purely neogenetic illites extracted from bentonites intercalated in the Albo-Turonian series. It is considered to be the ‘diagenetic age’, as opposed

to 354 and 126 Ma, which are detrital ages. Moreover, Pevear concluded that the detrital input has changed between the Albian–Aptian and the Turonian because of major tectonic movements during this period.

According to Pevear (1992), the detrital–authigenic K–Ar age mixing function is linear. This mixing law has been discussed in several subsequent papers: Srodon (1999) claimed that the mixing function gives highly curved lines if the end-member compositions contain different percentage  $\text{K}_2\text{O}$  values. By contrast, Ylagan *et al.* (2000) considered that the curvature may be greatly reduced if the smectite content is corrected and the ionic substitutions of  $\text{K}^+$  by  $\text{Na}^+$  or  $\text{NH}_4^+$  are taken into account.

Whatever the model used, the results of age determinations of radiodecay products are uncertain because they are based on several oversimplifying assumptions, the most important of which is that once an illite- or potassium-bearing crystal is formed, it remains present. In a closed chemical system, progression in the smectite to illite conversion is accomplished through the dissolution of a high portion of mixed layered minerals (potassium bearing) and formation of new illite layers on other crystal surfaces. Illite layers in I/S MLM series cannot be simply reduced to an illite component that will provide a given K–Ar age subsequent to its

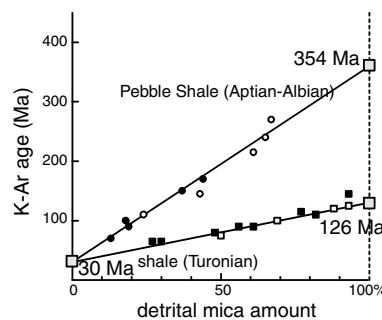
formation. Illite precipitates on I/S MLMs and on illite crystallites over long periods of time in pelitic diagenetic environments. Such a system is not static but dynamic. Measuring the quantity of authigenic illite is difficult for two reasons: the possible presence of older detrital ‘illite’ (most often micas) and the presence of discrete illite particles accompanying I/S MLMs in the authigenic fraction, which are constantly forming from older material.

The dynamic process of illite formation in shales is then largely governed by recrystallization of older minerals (Jaboyedoff and Cosca, 1999). The smectite to illite reaction forms more illite at the expense of older illite/smectite minerals. In recrystallizing, radiogenic argon is lost from the old crystals and any accreted potassium then essentially lacks an age history. As diagenesis progresses, the recrystallization reaction (smectite to illite transformation) liberates radioactive argon as potassium is displaced from an old phase to the surface of a growing mineral. The samples become younger in apparent age as the reaction progresses from smectite to illite (see data in Aronson and Hower, 1976). Thus, the accumulation of radiogenic argon cannot be correlated with the bulk  $\text{K}_2\text{O}$  contents of I/S MLM from 0 to 100% illite to derive a diagenetic age of formation.

**Identification of the crystal growth effect in the presence of detrital inheritance**

*Mixing effect:  $\Delta_{age}$*

Most often diagenetic shales are mixtures of detrital and authigenic phases, the former usually being concentrated in the coarse fractions are older than the age of deposition. The authigenic phases are concentrated in the finest fractions and are younger. Pevear (1992) showed that determining a ‘diagenetic’ age is made possible using the linear relationships between percentage detrital illite and K–Ar ages measured from different clay fractions. Taking the depositional age (mean stratigraphic age: 100 Ma and 90 Ma for Albian–Aptian pebble and Turonian shales, respectively) as the reference, a new parameter may be calculated for Pevear’s data:  $\Delta_{age} =$

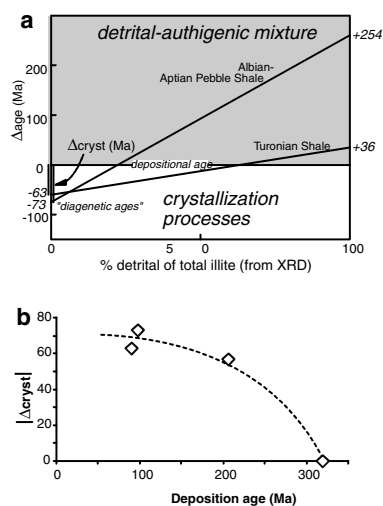


**Fig. 3** K–Ar dating of samples of diagenetic shales from two series and composed of a mixture of detrital illite and newly formed illite whose proportions have been determined by XRD (from Pevear, 1992). Points, circles, black squares and white squares correspond to different size fractions. The two straight lines have been obtained by linear regression.

$\text{age}_{\text{K–Ar}} - \text{age}_{\text{strati}}$ . The variation of this parameter vs. the percentage detrital of total illite as determined by NEWMOD computation of XRD patterns shows that the K–Ar age for each clay fraction is controlled by the mixture effect and the neogenesis process (Fig. 4a). The age difference between the depositional stage and the neogenetic clay fractions ( $\Delta_{\text{cryst}}$ ) depends on the burial and thermal history. Consequently, in case of no detrital contribution, the mixing line must not cross the reference line (depositional age). Mixtures of authigenic phases must respect the following condition:  $\Delta_{\text{age}} < 0$ .

#### Neogenetic age: $\Delta_{\text{cryst}}$

$\Delta_{\text{cryst}}$  is the ‘diagenetic’ age minus the depositional age, and is always negative. The question is how does  $\Delta_{\text{cryst}}$  vary for shale in sedimentary basins of different ages? Using available data (Table 1), it seems that the absolute value of  $\Delta_{\text{cryst}}$  decreases with increasing depositional age (Fig. 4b). The decrease in  $|\Delta_{\text{cryst}}|$  means that the period of time during which the authigenic illitic minerals are formed is of the same order of magnitude as the experimental error. In addition to



**Fig. 4** K–Ar age measurement for diagenetic rocks. (a) The linear relationship between apparent K–Ar ages and percentage illite measured from different clay fractions.  $\Delta_{\text{age}} = \text{age}_{\text{K–Ar}} - \text{age}_{\text{strati}}$ ;  $\Delta_{\text{cryst}} = \text{age}_{\text{diag}} - \text{age}_{\text{depos}}$ . (b) Variation of  $\Delta_{\text{cryst}}$  (diagenetic age – depositional age) for shales vs. depositional ages.

**Table 1** Values of  $\Delta_{\text{cryst}}$  (diagenetic age – depositional age) for shales of different depositional age.

Depositional age (Ma)	Calculated diagenetic age (Ma)	$\Delta_{\text{cryst}}$ (Ma)	$\sigma$ (Ma)	References
100	27	–73	±1–2%	Pevear (1992)
90	27	–63	±1–2%	Pevear (1992)
205	148	–57	±3–4	Velde and Renac (1996)
320	318–320	0	–	Hofmann <i>et al.</i> (1974)

the age error ( $1\sigma$ ), other error sources have to be taken into account, such as that relative to the percentage illite measurement.

#### Ages of size fractions: $\Delta_{\text{frac}}$

The  $\Delta_{\text{cryst}}$  parameter calculation is based on the definition of the ‘diagenetic age’, which is obtained from extrapolation to 0% of the linear relationship between K–Ar age and percentage detrital illite. Theoretically, as it is considered to be an end-member in the detrital–authigenic system, this gives the age of the diagenetic illite component. This is classically admitted in the Illite Age Analysis procedure recommended by Pevear (1992). However, this ‘illite age’ is questionable because diagenetic illite is not a homogeneous phase but is itself a mixture of several particle populations, which have been identified by XRD decomposition as I/S, PCI and WCI, or by TEM observations as fine or large, lath-shaped or isometric (Lanson and Champion, 1991, among others). Published K–Ar data refer frequently to particle size fractions. Using those that describe only the authigenic phases and not mixtures with detrital micas ( $\Delta_{\text{age}} < 0$ ), it is possible to relate the K–Ar ages of the different size fractions to crystallization processes. Indeed, the question is to determine how the radiogenic potassium is accumulated in the authigenic phases through the nucleation and crystal growth processes. In spite of recent progress (Eberl *et al.*, 1998; Srodon *et al.*, 2002), from a theoretical point of view this problem is too complicated to be easily solved using a crystal growth model based on a simple layer addition because the mass balance between the growing and dissolving phases is not calculable in the referenced data used here. However, this

difficulty could be overcome using a simple parameter that compares the K–Ar ages of any size fraction to that of the finest fraction:  $\Delta_{\text{frac}} = \text{K–Ar}_{\text{fraction}} - \text{K–Ar}_{\text{finest}}$ . If  $\Delta_{\text{frac}}$  is negative, the coarsest fractions are the youngest; if positive, the finest fractions are the youngest; if equal to zero, the finest and coarsest fractions have the same K–Ar age.

#### Patterns of K–Ar accumulation during illite growth processes

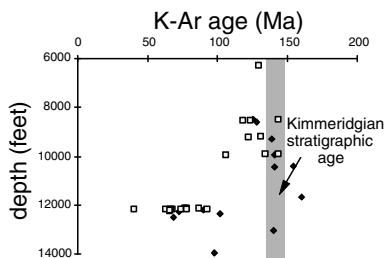
##### Long-lived diagenetic processes: ripening process dominant (shales and clayey sandstones)

Burley and Flisch (1989) have shown that the I/S MLM of the mudstones and sandstones of the Kimmeridgian have increasing illite contents (hence increasing  $\text{K}_2\text{O}$  contents) with burial depth. In these rocks, the diagenetic reactions occur in closed or nearly closed chemical systems. The K–Ar age of these minerals becomes younger as depth increases (Table 2, Fig. 5). This is the apparent paradox in dating clays in diagenetic environments: the older the bed of the buried sediment, the younger the illites and I/S MLM they contain (Aronson and Hower, 1976; Morton, 1985; Glassmann *et al.*, 1989; Mossman *et al.*, 1992; Renac, 1994; Rikenbach *et al.*, 1998).

This paradox does have a solution: the continuous rejuvenation of authigenic minerals, even if a part of the new material, stems from the dissolution of detrital minerals. The question then is how does illitization of I/S MLMs proceed in diagenetic environments? Obviously, the answer is not simply illite layer growth or accumulation on I/S MLM particles considered as the unique process at work in diagenetic environments. Because the systems are generally of

**Table 2** K–Ar age of clays extracted from shales and sandstones (see Fig. 5) of the Piper and Tartan formations, Outer Moray Firth (Burley and Flisch, 1989).

Mudrocks Depth (feet)	K–Ar age (Ma) ± 1σ	Sandstones Depth (feet)	K–Ar age (Ma) ± 1σ
8482	125.3 ± 1.5	8506	143.8 ± 1.6
8608	128.5 ± 1.5	8515	118.2 ± 1.3
9285	139.1 ± 1.6	8536	123.5 ± 1.4
9948	140.8 ± 1.6	9189	131.1 ± 1.5
10391	154.2 ± 1.7	9210	122.3 ± 1.4
10444	141.2 ± 1.9	6260	129.2 ± 1.5
11671	160.7 ± 1.8	9897	134.4 ± 1.8
12195	89.9 ± 1.4	9899	143.4 ± 1.8
12286	72.6 ± 0.8	9933	105.8 ± 1.6
12355	102.2 ± 1.1	12120	86.8 ± 1.1
12490	68.5 ± 0.8	12139	76.8 ± 0.8
13039	140.6 ± 1.6	12170	73.5 ± 0.8
13980	97.7 ± 1.2	12236	65.9 ± 0.9
		12139	77.7 ± 0.8
		12166	62.9 ± 0.7
		12180	40.6 ± 0.6
		12152	92.7 ± 1.4
		12160	77.8 ± 0.9
		12169	67.7 ± 0.8
		12179	66.4 ± 0.8
		12189	66.0 ± 0.7

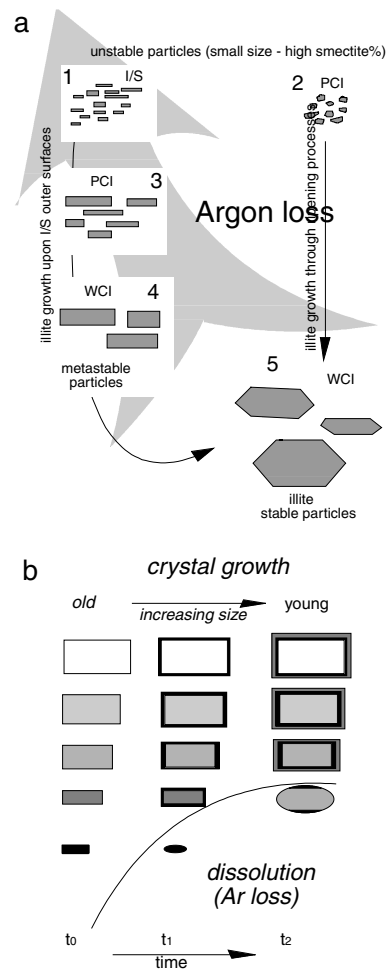


**Fig. 5** Variation in the K–Ar age of clays extracted from shales (squares) and sandstones (lozenges) of the Piper and Tartan formations, Outer Moray Firth (Burley and Flisch, 1989). The shaded area represents the stratigraphic age of this formation (Kimmeridgian).

approximately the same mass and chemical composition throughout their diagenetic history (approaching closed chemical systems at a macroscopic scale), the increasing illite content of crystallites in a sample (not total illite content nor total potassium content) is related to a maturation process in which unstable particles dissolve and more stable particles grow (see section on illite crystal growth in diagenetic environments above).

Whatever the ripening process at work, maturation through crystal

growth is undoubtedly acting in shale diagenesis. For example, the proportion of lath-shaped particles (L/S MLMs) was seen to decrease with depth in samples from a given sedimentary basin, whereas the population of poorly crystallized illite (PCI) and then well-crystallized isometric illite (WCI) particles increases (Lanson and Champion, 1991; Varajao and Meunier, 1995). The clay particles formed under given burial conditions at an instant *t* become too unstable to subsist when burial progresses or when temperature and time (*T* × *t*) increases, for various reasons: inappropriate composition (smectite percentage too high), crystal habit (outer surface/volume ratio too high) or crystal structure (polytype transition). Therefore, the smallest particles of L/S or illite are constantly dissolved; the matter thus released contributes to the growth of particles of greater size, which have also a greater illite content (Fig. 6a). At each dissolution–crystallization stage, the potassium released in solution is fixed in the crystal lattice of the growing particles but the radiogenic argon associated with this potassium escapes from all fixation and can migrate out of the reaction zone. The apparent change in the K–Ar age depends on the ratio between



**Fig. 6** Rejuvenation of the potassium stock by a ripening process. (a) The growth of L/S MLM or illite particles and the increase in the illite content depend on a dissolution process of the unstable particles, elements of which are used for the growth of illite layers. PCI: poorly crystallized illite; WCI well-crystallized illite. (b) Qualitative model for the rejuvenation effect of a ripening process (no nucleation): the K–Ar age decreases with increasing particle size.

the mass of the growing and dissolving minerals, respectively, i.e. the ratio between losses and accumulation of argon:

- 1 for losses higher than accumulation, the K–Ar age decreases with increasing size (Fig. 6b);
- 2 for losses compensated by accumulation, the apparent K–Ar age remains constant during crystal growth;

3 for losses smaller than accumulation, the K–Ar age increases with increasing size.

### Short-lived systems: nucleation dominant (illitization of kaolinite or dickite in sandstones)

Whatever the type (Fig. 2c), ripening is active over long periods of time in diagenetic series. As they are greater than the dating experimental error ( $2\sigma$ ), the K–Ar ratios do not give a geological age but only an integrated measure of the K-accumulation period. Consequently, as the rate of dissolution and crystal growth increase with temperature, the greater the burial depth, the more recent this integrated age. Thus the K–Ar ratio gives a geological (diagenetic) age if the K accumulation period of time in illitic phases is shorter than  $2\sigma$ . At present, we do not know how much time is needed for an illite particle to be formed. The question is then: is it possible to identify the particles that have experienced a sufficiently high crystallization rate to give a geological age?

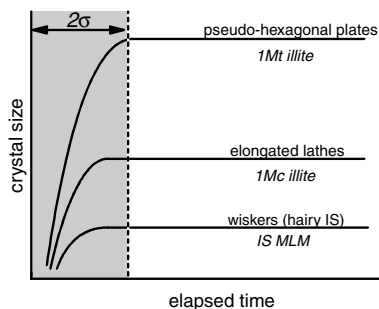
Crystal habits depend on the growth rates. It is known that whiskers (hairy illite) are formed in short periods of time whereas perfect platy hexagonal crystals grow slowly. Wilkinson and Haszeldine (2002) showed that the growth of fibrous illite is limited by the kinetics of nucleation in abnormal conditions, such as high pore fluid supersaturation, high pore fluid velocities, high temperature or presence of a catalyst. The rapid growth is favoured by these abnormal conditions and produces elongated fibrous crystals.

Most of the illitization events in porous sandstones are related to 'hydrothermal-like' episodes. This is particularly the case for the lower Permian Rotliegend sandstones, in which illite crystals grow either on kaolinite–dickite or quartz overgrowth surfaces. Whatever the shape from hairy (whiskers) to isometric pseudo-hexagonal crystals, illite was shown to be formed during the intense fracturing period of the Kimmerian tectonics at 155 Ma (Lanson *et al.*, 1996). The illitization of kaolinite or dickite requires highly oversaturated solutions with respect to illite. Thus the K-feldspars cannot be the source

of  $K^+$  ions. Such fluids were assumed to come from laterally adjacent Zechstein evaporite formations in the vicinity of faults. Because of their highly oversaturated state, the fluids trigger the nucleation and growth of I/S MLMs or illite crystals during periods of time shorter than  $2\sigma$ . They can be considered as instantaneous phenomena (hydrothermal-like) compared with the progressive illitization of shales. In the Rotliegend sandstones, the mean age is about 155 Ma whatever the composition (from 20 to 5% smectite or illite for I/S MLMs) or crystal habit (whiskers, laths, pseudo-hexagonal plates). Composition and crystal habits are dependent on local temperature conditions and degree of fluid oversaturation degree. The growth process for I/S MLM or illite crystals, which determines the argon accumulation period, is similar to that of quartz grains in metamorphic aureoles (Joesten, 1983). It is shorter than  $2\sigma$  (Fig. 7).

### Intermediate systems: instantaneous formation and continuous growth of illite

The sandstones of the upper Brent and upper Skagerrak formations in the northern Viking graben (North Sea area) have been extensively studied. They contain abundant pore-filling illite with almost no I/S MLM, although the adjacent shales do contain I/S. Matthews *et al.* (1994) showed that the average layer charge and  $K^+$  content increase with depth from 0.69 to 0.80  $K^+$  per  $O_{10}(OH)_2$



**Fig. 7** Theoretical representation of the closure of the K–Ar system for three illite types forming in the Rotliegend sandstones (modified from Joesten, 1983).

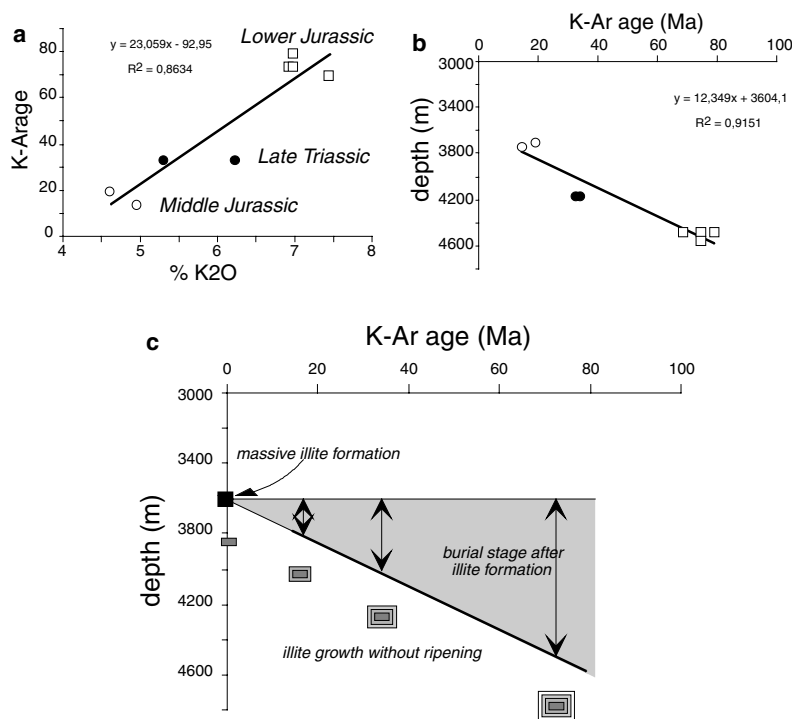
whatever the depositional age of the hosting formation. Illitic phases in the Lower Jurassic sandstones are K-richer than that of the Late Triassic sandstones. Here, the K–Ar age increases with  $K_2O$  contents (Fig. 8a) and with increasing depth (Fig. 8b).

This indicates that there is no or very little rejuvenation of the  $K_2O$  stock in the system. Consequently, ages increase with depth. The increasing  $K_2O$  content with depth implies a continuous growth of illite layers on illite particles during burial (Fig. 8c). Matthews *et al.* (1994) deduced that the formation of illitic clays from various precursors (kaolinite and dickite) in this particular area of the North Sea was rapid, but the age increase with depth shows that growth induced by increasing burial conditions was slow.

The example of the upper Brent and upper Skagerrak formations shows that, in some cases, illite forming in porous sandstones experiences a more complicated thermal history than that recorded by a simple precipitation during hydrothermal-like events. Two steps may be distinguished during its crystallization period of time: (1) a rapid nucleation and growth process ( $< 2\sigma$ ), which is temperature- and chemically controlled; (2) the slow growth ( $> 2\sigma$ ) of illite layers on I/S or illite particles, the rate of which depends on the rate of temperature increase during burial. Theoretically, the K–Ar dating obtained from clay samples may change according to the relative importance of these two steps:

- 1 if the former predominates, all I/S MLM or illite particles will have the same K–Ar age as shown by Lanson *et al.* (1996);
- 2 if the second predominates, the age will increase with depth, i.e. with temperature. The slope of the line in Fig. 8(c) depends on the rate of  $K_2O$  accumulation during the illite growth period.

This seems to be the case of illite forming in the Brent sandstones from the Heather field, North Sea (Glassmann *et al.*, 1989). Illite and quartz overgrowth post-date kaolinite cementation. K–Ar ages (Table 3) vary in much of the Palaeogene (55–27 Ma). The coarser fractions are 5–10 Ma 'older' than the finest fractions



**Fig. 8** Increasing K–Ar ages with depth in the Rotliengende sandstones (data from Matthews *et al.*, 1994). (a) Plot of K–Ar ages vs. K<sub>2</sub>O content (per Si<sub>4</sub>O<sub>10</sub>). (b) Variation of K–Ar ages with depth. (c) A qualitative model for continuous crystal growth explaining the K<sub>2</sub>O and K–Ar age variations with depth.

**Table 3** K–Ar illitic phase dating from two or three size fractions of clay samples from the Brent sandstones, Heather field, North Sea (data from Glassmann *et al.*, 1989).

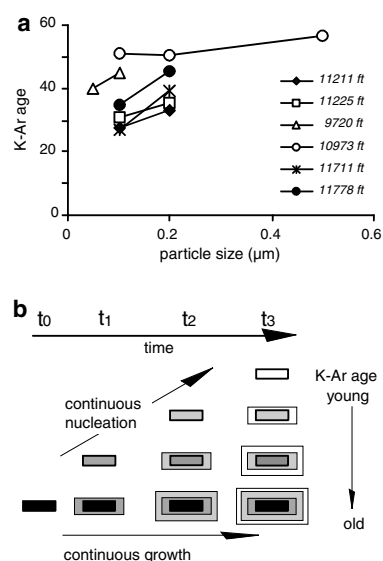
Depth (feet)	Size (µm)	%K	K–Ar age (Ma) ± 1σ
11211	< 0.1	5303	27.7 ± 0.6
	0.2–0.1	6273	33.3 ± 0.8
11225	< 0.1	4405	31.1 ± 0.7
	0.2–0.1	6281	35.3 ± 0.8
9720	< 0.05	3126	39.9 ± 1.0
	< 0.1	4163	44.9 ± 1.0
10973	< 0.1	5485	50.9 ± 1.2
	0.2–0.1	6196	50.3 ± 1.1
	0.5–0.2	6545	56.9 ± 1.3
11711	< 0.1	4756	26.8 ± 0.7
	0.2–0.1	6208	39.3 ± 0.8
11778	< 0.1	4866	34.8 ± 0.8
	0.2–0.1	6032	45.7 ± 1.1

(Fig. 9a). Glassmann *et al.* (1989) suggested that, contamination being negligible, this age difference must be related to the length of growth history experienced by illitic particles. The fact that the finest fractions are the youngest suggests a continuously active nucleation during the sandstone burial stage. The coarser fractions grow on

old cores and are always older than the finest ones (Fig. 9b).

### Diagenesis of bentonites

K–Ar data of illitized bentonites from different depositional ages (Moe *et al.*, 1996; Srodon *et al.*, 2002) are given in Table 4. It appears that the coarser



**Fig. 9** Effects of a continuous nucleation–growth process on the fraction size vs. K–Ar age relation. (a) K–Ar age variation between fine and coarse fractions from clay minerals sampled at different depths from Glassmann *et al.* (1989). (b) Schematic representation of a nucleation–growth process continuously active during diagenesis.

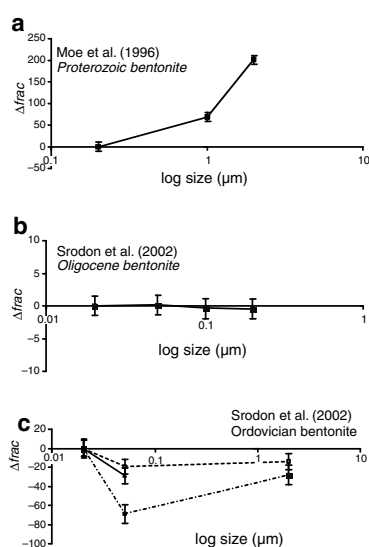
fractions may have the same age for recent (Oligocene) or older deposits (Ordovician–Proterozoic). The three trends are shown in a  $\Delta_{frac}$  vs. log size plot (Fig. 10). What do these trends indicate? Three possible pathways can be envisaged:

- 1 same ages for coarse and fine particles: this is made possible when nucleation and crystal growth are sufficiently rapid to produce a fine-to coarse-grained particle population in a period shorter than the dating experimental error ( $< 2\sigma$ );
- 2 coarser particles younger than the finer particles: this results typically from a ripening process (random ripening according to Eberl *et al.*, 1998) in which the finest particles are the oldest ones and are continuously dissolved, whereas the coarser particles grow continuously;
- 3 coarser particles older than finer particles: this implies concomitant nucleation and crystal growth. Thus, the internal core of the coarser particles is the oldest fraction.

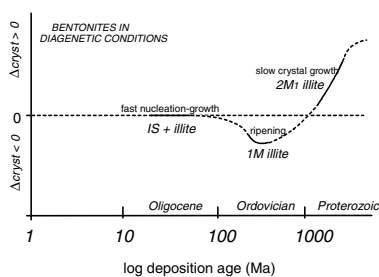
The illitization of bentonite is a diffusion-controlled process (Velde

**Table 4** Variation of the  $\Delta_{\text{frac}}$  parameter ( $\Delta_{\text{frac}} = K\text{-Ar}_{\text{fraction}} - K\text{-Ar}_{\text{finest}}$ ) with time in diagenetic bentonites (data from Srodon *et al.*, 2002).

Size	K–Ar age (Ma)	$\Delta_{\text{frac}}$ (Ma)	$2\sigma$
Oligocene bentonites (Srodon <i>et al.</i> , 2002)			
< 0.02	17.9	0	1.1
0.02–0.05	18	0.1	1.7
0.05–0.1	17.5	–0.4	1.6
0.1–0.2	17.4	–0.5	1.2
< 0.02	18.6	0	2
0.02–0.05	19.5	1.1	2.5
0.05–0.2	20.1	1.5	2.6
Ordovician bentonites (Srodon <i>et al.</i> , 2002)			
< 0.02	363	0	10
0.02–0.05	294	–69	8
0.05–2	335	–28	9
< 0.02	360	0	9
0.02–0.05	341	–19	9
0.05–2	346	–14	9
< 0.02	382	0	10
0.02–0.05	353	–29	9
Proterozoic bentonites (Moe <i>et al.</i> , 1996)			
< 0.2	606	0	8
0.2–1	675	69	9
1–2	807	201	11

**Fig. 10** Variation of the  $\Delta_{\text{frac}}$  parameter (K–Ar age difference between a given size fraction and the finest fraction) vs. the fraction size in bentonite deposits of different depositional age. (a) Proterozoic (Moe *et al.*, 1996). (b) Oligocene (Srodon *et al.*, 2002). (c) Ordovician (Srodon *et al.*, 2002).

and Brusewitz, 1982; Altaner *et al.*, 1984). This factor could vary with time. However, even if we ignore the thermal history experienced by the Oligocene, Ordovician or Proterozoic bentonite deposits during their burial

**Fig. 11** Hypothetical steps in the illitization process of bentonites in diagenetic conditions according to the variation of  $\Delta_{\text{cryst}}$  with time.

stage, their respective K–Ar trends could be considered as steps in a continuous crystallization process. Indeed, the first step, which is a fast nucleation and crystal growth process, is the early diagenetic step during which smectite is transformed into illite + I/S MLM (Oligocene). Then, for longer periods of time, the K–Ar ages of the different size fractions are controlled by a ripening process leading to the formation of 1M illite. At least, for Proterozoic deposits, the dominating process is a slow crystal growth forming large, ‘perfect’ 2M<sub>1</sub> crystals (Fig. 11). All three processes, i.e. smectite illitization, ripening and crystal growth, may coexist at a given time but one is dominant and controls the apparent K–Ar ages.

## Conclusion

We have seen that K–Ar age is not simply a result of nucleation and growth of illite layers on I/S MLMs. In some cases the largest particles are younger than the finest particles, whereas the reverse occurs in other cases. This means that illite crystal growth should be considered in more detail before interpreting K–Ar analyses in terms of radiometric age. The model proposed by Srodon *et al.* (2002) may be successfully applied for geological series in which the size distribution of illitic particles results from continuous nucleation and growth in an open system (bentonites). It is inappropriate to use the model for particle distributions created by a maturation process. It is also inappropriate for systems in which quick precipitation occurs, giving the same radiometric age to all particles whatever their size. What is the significance of a ‘diagenetic age’? Srodon *et al.* (2002) have clearly shown that the diagenetic age depends closely on the thermal history experienced by the sediments, the thermal history being a function of the burial rate and the local value of the geothermal gradient. We must also consider that it depends on the way in which illite grows during illitization.

Illite growth processes depend largely on two factors: (1) the chemical system characteristics – open (high degree of oversaturation triggering nucleation and growth of illite on kaolin precursors), and closed (low degree of oversaturation favouring growth rather than nucleation); (2) the duration of crystallization. The example of the diagenesis of bentonite deposits shows that in more or less equivalent physicochemical conditions, crystal habit and polytype will change over time. Consequently, the argon accumulation mechanism also changes when particles grow and there is a change of crystal habit from hairy to lath and from lath to platy hexagonal.

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