Isotope dating and tracing of clay minerals from low-temperature environments

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Introduction

Clay minerals represent one of the most common mineral phase at the surface and in the shallow-crustal subsurface of the Earth. Interestingly enough, they were widely used by mankind since High Antiquity, and therefore were studied in many scientific ways, from geology, to biology, to pharmacology, and also to medicine. In Earth sciences, they were investigated with varied success, together with other minerals of similar structure, as stratigraphic markers, tectonic and hydrothermal indicators, palaeo-hydrologic tracers, palaeo-climatic records, …. Because of all these potentials, they are prime regulators for a large variety of chemical processes at the surface and in the subsurface of the Earth. The wide interest in these minerals has a common basic need of knowing when and how they form in the various surficial and sub-surficial environments of the Earth, and how they respond to physical and chemical changes in the formation environment.

Isotope dating and tracing studies of all kinds of clay minerals from very different environments, including continental soils and weathering profiles, continental and marine deposits, buried sediments, hydrothermal and metamorphic altered sediments, have shed light on the questionings about when and how clay minerals form or alter. The present review will focus mainly on isotope dating and tracing aspects of clay minerals from diagenetic to slightly metamorphosed sediments that underwent burial or were subjected to thermal events after deposition. The fundamentals of clay mineralogy, which represents the basic step in any isotope study, will not be detailed, as they are available in excellent review books (e.g., Moore and Reynolds, 1989), but a rapid presentation of the major clay groups will be given. Some principles of isotope geochemistry, that need to be remembered when studying clay material, will also be recalled briefly as well as a short overview on some technical aspects, as successful studies often depend on their strict application (Clauer et al., 1992a). The body of the review will consist first in test studies reinforcing the reliability of the application of the isotopic methods on clays, and in an up-graded presentation of the recently published studies representing improving steps in the understanding of clay crystallization and alteration processes in diagenetic to slightly-metamorphic sediments.

A rapid review on clay mineralogy

Clay minerals are mica-type sheet silicates of nanometer size. They are characterized either by a piling up of tetrahedral (T) and octahedral (O) layers for the group of the kaolins (Figure 1), or a piling up of tetrahedral (T), octahedral (O) and again tetrahedral (T) layers for most of the clay groups : smectite, illite, mixed-layers (Figure 1). Two groups of clay minerals outline a structure that is characterized by channels instead of layers: palygorskite and sepiolite.

In the TOT clay minerals, different varieties exist depending on their interlayer organization and the hosted cations or molecules: H_2O, Ca, Na = smectites; K = illite; Fe_2O_3 or MgO = chlorite), on the type of octahedral cation (illite = Al, glauconite = Fe), or on the mutual organization of the octahedral and tetrahedral layers (2M or 1M illite polytypes; cis- or trans-vacant illite structures). Further information is available in Brindley and Brown (1980).
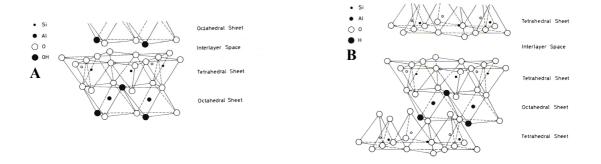
FIGURE 1. *A: Crystal structure of a 1:1 type clay mineral. B: Crystal structure of a 2:1 type clay mineral.*

Some principles of isotope geochemistry

It might be recalled at this point that the pioneering isotopic studies of clay material, with "stratigraphic" applications on glauconite types are from the mid'50s (Cormier, 1956; Wasserburg et al., 1956). Since, many isotopic studies of clay material were published based on the Rb-Sr, K-Ar, $^{39}Ar/^{40}Ar$, Sm-Nd, δD, and $\delta^{18}O$ methods, while applications of the Pb-Pb, K-Ca, and B methods were explored more recently. The basic principles of these methods can be found in varied publications, a very thorough review being available in Faure and Mensing (2005).

It is interesting to remember that among about 1700 nuclei available on Earth and in the atmosphere, only 260 are stable. Those containing the same number of protons and neutrons are the most stable, and the others decay spontaneously along one or several steps. The unstable nuclei are called radioactive isotopes and their spontaneous transformation is radioactivity. The decay is accompanied by emissions of particles (α, β, γ), positrons and heat. In "Isotope Geology", we are only interested in spontaneous fission of nuclei from naturally occurring isotopes that have half-lives in the range of the age of the Earth.

The decay rate of a nucleus of radioactive species is proportional to the number of its atoms (N) present at a given moment (t), expressed by:

$$-dN/dt = \lambda N$$

in which λ is the decay constant. By integrating, this equation gives:

$$t = 1/\lambda \ln(1 + D/N)$$

in which t is the time in millions of years, and D the number of daughter isotopes formed at t. Applicable to any isotopic method, this equation allows calculation of meaningful geologic ages, provided it has met some strict requirements. For instance, the selected rock or mineral had to behave as a closed system since formation, without loss and/or gain of both the radioactive (= parent), and the radiogenic (= daughter) isotope. Also, the amounts of the two isotopes need to be determined with best analytical accuracy and the decay constants to be known precisely. The amount of the daughter isotopes present at the formation of the mineral or the rock (at t= 0) needs also to be known precisely, in order to determine best the amount of "produced" daughter isotope during t.

In the case of light stable isotopes, such as oxygen and deuterium, fractionation may essentially result from biological activity, changes in temperature and/or water/rock ratio during clay genesis.

Specific separation and characterization techniques

Due to their specific size and occurrence in sediments and slightly-metamorphosed sediments, clay minerals need specific separation and characterization methods that are often determining in the successful application of isotope geochemistry.

Crushing vs. freezing/thawing

Crushing rocks can create artificial clay-sized framework minerals that occur normally larger in the rocks. To avoid dealing with clay fractions "contaminated" by minerals that might have a different history and different isotope characteristics, such as quartz, feldspars, micas, which can significantly bias the isotopic record of the clay minerals, it is suggested to use a more gentle disagregation method: for instance, freezing and thawing (Liewig et al., 1987). Rock pieces are placed into a bottle filled with deionized water and are subjected to repetitive feezing-thawing cycles until being reduced to sand or mud.

Size fractionation

It is agreed for decades that the clay material of sediments is concentrated in the size fraction <2 μm. It is also known for long that this "size fraction" is not a "mineral fraction", as it may contain other minerals, depending for instance on the crushing technique. To improve the purity of the clay fraction of a rock, it is suggested to perform separation in the <0.1 μm size, for instance by ultra-centrifugation. In some cases, as will be shown later, special separation can reach the <0.01 μm size.

Leaching experiments

It has been proved in many circumstances that separation and purification of clay particles may be improved by the use of chemical reagents that are not damaging the isotopic systems (Clauer et al., 1993). For instance, HCl or HAc are often used when clay particles are mixed with carbonate grains.

Characterization/Identification

The basic characterization of clay minerals includes X-ray diffraction (XRD), but a powerful complementary tool, especially for identification of clay authigenesis in the rocks is electron microscopy, either by transmission (TEM) or by scanning (SEM). Illustration is given on Figure 2, with the pore system of a sandstone containing hairy illite either filling a pore (top centre) or growing on long "pellicles" (centre in the large pore space). This two "types" of illite either formed during one event, during varied P, T, X conditions, which can be traced by $\delta^{18}O$, or during two different events (recorded by isotopic dating). Such an example is discussed later.

Some important basic aspects in isotope geochemistry applied to clay minerals

Three basic aspects need to be considered systematically when applying radioactive isotope geochemistry to clay material: (1) the effect of potential continental weathering on samples collected on an outcrop, (2) the temperature at which the collected rock could have been subjected during its history, as this temperature will determine the age of either the formation of the studied mineral, or its recrystallization; these two processes occurring at different periods, and (3) the potential occurrence of detrital framework minerals that could have been crushed to the size of the separated clay particles, as already discussed, but also of detrital clay particles that can naturally occur with authigenic, which is biasing the results.
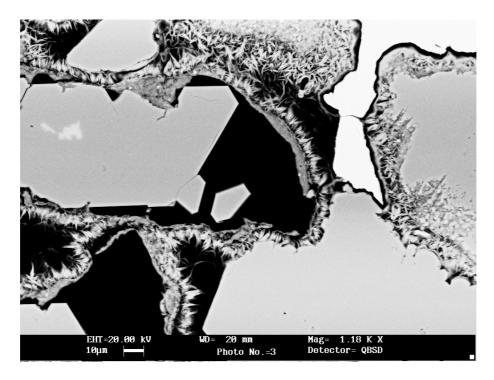
FIGURE 2. *Scanning photograph of a sandstone consisting in quartz grains (grey), siderite (white) and large pore spaces (in black) filled with authigenic illite-type clay material (Courtesy of ARAMCO).*

In summary, the interpretation of the isotopic age of any separated clay fraction, and consequently the reliability of the isotopic method applied, depend therefore on the "cleanness" of the selected rocks and the analyzed clay fractions, and on the knowledge of the thermal history and of the authigenic vs. detrital composition of the separated clay fraction.

Meteoric weathering

Continental weathering induces varied releases of isotopes out of the particles, with a systematic decrease of their «apparent ages». Furthermore, some isotopes are more mobile than others: for instance the Rb-Sr system of a given clay-mineral type appears more affected than the K-Ar system, which is more affected than the Sm-Nd system.

Temperature effect

Any temperature increase induces releases of isotopes, mainly the light and the radiogenic isotopes. The present-day temperature recorded in different drillings of the Glarus Alps progressively decreases the original Rb-Sr and K-Ar apparent age of illite, with a complete release of the radiogenic ^{87}Sr and ^{40}Ar produced by decay at 260 $\pm$ 30°C (Hunziker et al., 1986). The loss of ^{40}Ar from clay minerals in Lower Jurassic shales of southeastern France intruded by a basaltic dike is highest near the dike, as may be expected, but none is detectable beyond 2 m from dike (Techer et al., 2006; Figure 3). The K-Ar age of the dike intrusion is about 3 Ma, while the apparent age of the <2 μm clay material is about 250 Ma more than 2 m away from dike, which is older than the stratigraphic age of the shale, due to initial detrital clay material. The estimated temperature caused by the intrusion was at least about 260–300ºC, as the release of the accumulated radiogenic ^{40}Ar completely diffused. At 2 m away from dike, the host rocks were probably never heated to more than 50 ± 10ºC.
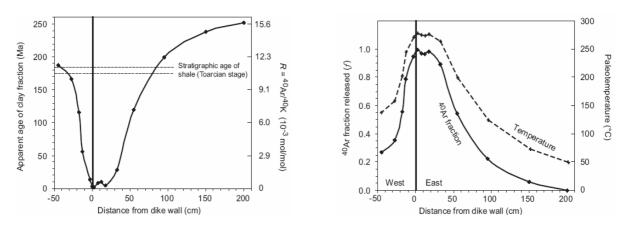
FIGURE 3. *Apparent K-Ar ages, released ^{40}Ar of clay material from shales hosting a basalt dike, and paleotemperatures (after Techer et al., 2006).*

Detrital contamination

Contamination of authigenic clay particles by detritals is a recurrent problem depending on the studied particle size (coarser fractions generally yield higher detrital contamination), on the separation techniques (extensive crushing potentially increases detrital contamination), on the rock lithologies (low-permeable shales contain often more detrital clay material than porous sandstones), and on the history of the rock sequence (increased degree of recystallization reduces the content of detrital records).

The clay material of metapelites and metatufs from northern Germany underwent various thermal impacts (Reuter, 1987). The so-called anchimetamorphic (T < 150°C) and epimetamorphic (T > 150°C) illite from metatuffs yield the same K-Ar age whatever the particle size (Figure 4). In the epimetamorphic metapelite, only <1 μm illite yields the same K-Ar age as all of those from metatufs, while a progressive increase of the detritals reflects in the increasing apparent ages. This is even more the case in the anchimetamorphic metapelite where the <0.4 μm authigenic illite is still mixed with detritals: the K-Ar data higher than those of the epimetamorphic illite.
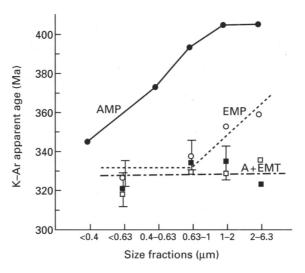

FIGURE 4. *Inclined and bench-type age spectra of clay-type size fractions of so-called anchi (AMP) and epimetamorphic (EMP) metapelites and a flat age spectrum for the same size fractions of a so-called associated anchi (AMT) and epimetamorphic (EMT) metatuffs from Rheinische Sciefergebirge (after Reuter 1987).*

Reliability tests

Stratigraphic dating of glauconite

The ultimate test for reliable application of clay isotope dating is either dating clay material that is of sedimentary origin, such as glauconites, which can be well constrained by stratigraphic means, or to compare isotopic ages of clay minerals to those of contemporaneous ore minerals (Laverret et al., submitted). Glauconite is the Fe-Mg rich equivalent of Al-rich illite, resulting often from a smectite to glauconite transition similar to the smectite-to-illite trend. For purpose of clarity, the smectite-glauconite mixed-layers are called "glauconies" (the singular is "glaucony") by many, while the pure K-rich end-member is called "glauconite".
Among several studies of stratigraphic application (e.g. Odin and Hunziker, 1982), Rousset et al. (2004) compared the Rb-Sr and K-Ar isotopic ages of Albian glauconites from southeastern France. The K-Ar (Figure 5A) and Rb-Sr (Figure 5B) data of the same fractions are identical at 97.3 ± 0.4 and 97.9 ± 3.5 Ma, respectively. Beyond the results, the initial values of the two isochrons represent strong arguments in favor of a stratigraphic interpretation: an atmospheric $^{40}Ar/^{36}Ar$ and the Albian marine $^{87}Sr/^{86}Sr$ ratio, meaning a precipitation in a marine environment containing atmospheric Ar.

Besides the necessity for the minerals to act as isotopic closed-systems since crystallization, another important aspect is the initial isotopic homogenization among the same mineral type. If initial isotopic homogenization occurs easily in most volcanic and plutonic materials, it is not the case for sedimentary minerals (Odin and Matter, 1981). On the basis of varied isotopic Rb-Sr, K-Ar, $^{143}Nd/^{144}Nd$ and $\delta^{18}O$ data determined on a transition from detritalsmectite to glauconite pellets in present-day sediments from offshore West Africa, it was shown that glauconitization is a two-step process (Clauer et al., 1992b) starting in coprolites that form an appropriate microenvironment in which smectite from surrounding mud evolves into Fe-bearing smectites to glauconies. Afterwards, progressive incorporation of K tends to the glauconite end-member. The Sr, Nd and oxygen isotope data all show the same two distinct steps. Only glauconite containing 6 to 6.5% K_2O appears to attain isotope equilibrium, so that only glauconites with such K_2O contents should be used for stratigraphic dating.

In fact, several questioned the chemical homogeneity of glauconite, even when considered pure (Smith et al., 1993; Clauer et al., 2005), raising in turn the fact that the results may sometimes fall off the stratigraphic reference values. It might also be kept in mind that glauconite of a sedimentary sequence, which is buried to temperatures beyond 70-80°C, may be affected by preferential release of radiogenic isotopes that induces a decrease in the measured age.

Dating of the oldest clay minerals on Earth

In the Barberton Greenstone Belt in NE South Africa, the Swaziland Supergroup rests on an Archean basement intruded by plutons all over, with ages at 3105-3107 Ga, obtained by
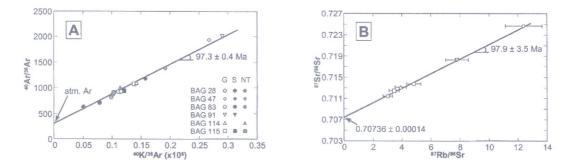

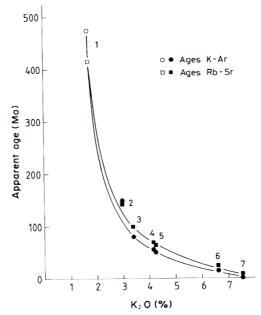FIGURE 5. *K-Ar and Rb-Sr data of Albian glauconites from southeastern France (from Rousset et al., 2004)*

FIGURE 6. *K-Ar and Rb-Sr data of a smectite to glauconite transition from present-day sediments from off-shore West Africa (after Clauer et al., 1992b)*

varied methods (Toulkeridis et al., 1994). The studied clay material belongs to the Figure 6 Tree Group that overlies the Moodie Group, on top of the Archean basement.

The results show that the Sm-Nd method is the most appropriate for the search of old ages : 3102 ± 64 Ma. This is due to the fact that the REEs are not very mobile, especially in subsurface environments. The age is almost identical to the ages of the intruding plutons, which monitored the epithermal recrystallization of the clay material with an initial ^{143}Nd/^{144}Nd in agreement with a hydrothermal context. The quite large analytical error is mainly due to the fact that Sm and Nd do not fractionate significantly, which is increasing the analytical uncertainty. An « artifact » to increase the fractionation ratio has therefore been used by leaching the particles with dilute acid (HCl 1N) and analyzing separately the untreated, leachate and residue fractions (Figure 7). The data points of all aliquots plot on the same isochron, which strengthens the interpretation of an homogeneous ^{143}Nd/^{144}Nd ratio during clay recrystallization at 3.1 Ga.
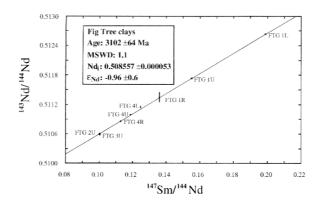

FIGURE 7. *Sm-Nd isochron dating of the oldest illite-type clay minerals of Earth Barberton Greenstone Belt (from Toulkeridis et al., 1994).*

Dating illite from multi-episode hydrothermal activity

In gas and hydrocarbon reservoirs

Permian sandstones have been drilled extensively in northern Germany because they host hydrocarbons and gas. The illite K-Ar ages scatter between 210 and 165 Ma (Figure 8), with most results between 200 and 175 Ma (Zwingmann et al., 1999). It can be seen that they are not related to maximum burial, meaning that they were not induced by burial diagenesis as their isotopic ages would be very recent, at 5-7 Ma, in this case. Alternatively, the authigenic illite necessarily precipitated at a temperature higher than 165°C, which is that for maximum burial, because if they would have crystallized at a lower temperature, the isotopic ages would have been partly reset or even completely erased.

Some illite of these Permian reservoirs were K-Ar dated on the basis of a detailed SEM study (Liewig and Clauer, 2000). The tangential illite (described as illite 1 in Figure 9) yields K-Ar ages at about 200 Ma and $\delta^{18}O$ from +17 to +18 per mil, whereas the radial illite (described as illite 2 in Figure 9) is younger with K-Ar ages at about 180 Ma with $\delta^{18}O$ slightly lighter, from +15 to +17 per mil. The two types of illite result either from one event extending over 20 Ma, or more probably from two distinct events at similar temperatures, but at different water/rock ratios: lower during event 1 (compressive) than during event 2 (extensive). This latter interpretation is supported by studies on similar rock types from western Europe.

In uranium deposits

K-Ar, $\delta^{18}O$ and δD isotope data of illite from sandstone cover and underlying basement close to and distant from Shea-Creek uranium deposit (Athabasca Basin, Canada) show that in the barren areas away from deposit, illite is mainly of the cv-1M polytype occurring as relatively coarse-grained lath-shaped particles, while it occurs as fine-grained particles of the tv-1M polytype next to the uranium mineralization (Laverret et al., submitted). The tectonic-induced hydrothermal system responsible for illite crystallization was multi-episodic at about 1430, 1290 (Figure 10) and 1150 Ma. These episodes of illite mineralizing occurred at the same time as those of the associated uranium oxides dated independently by the U-Pb method.
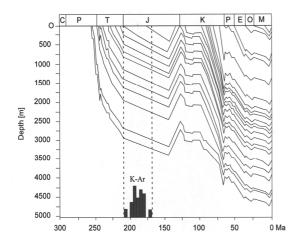

FIGURE 8. *K-Ar data of authigenic illite from Rotliegende sandstones in northern Germany relative to the reconstructed burial history of the sediments; the results are far from maximum burial seen from simulated burial curves (after Zwingmann et al., 1999).*
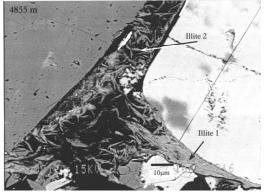
FIGURE 9. *Authigenic illite in the pore system of a Rotliegende sandstone from northern Germany; illite 1 is palisadic and illite 2 is fibrous (after Liewig and Clauer, 2000).*
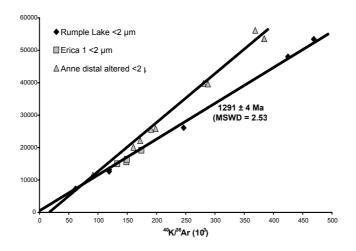
FIGURE 10. *K-Ar isochron plot of illite data points from distant barren Rumple Lake sandstones, from barren Erica 1 drilling nearby the ore and from distant Anne altered basement (after Laverret et al., submitted).*

No relationship was reported between the illite types and ages, meaning that crystallization of each illite polytype did not occur relative to a specific event, but formed during the same event at different physical and chemical conditions. In some cases, as in the Anne basement, clay-sized fractions consist obviously in mixtures of different generations leading to a line on the diagram plot that intersects the abscissa at an abnormal negative value for the $^{40}Ar/^{36}Ar$ ratio, which is impossible in nature. The $\delta^{18}O$ values of illite increase with the distance to the uranium deposit, which is interpreted as resulting from a combined decrease in temperature and increase in water-rock interaction with the barren rocks.

Isotope dating and tracing of illite-type fundamental particles

Isotopic dating and tracing was also completed on «fundamental particles» in the sense of Nadeau et al. (1984). These fundamental particles consist in illite sheets separated from illite-smectite mixed-layers that have particle sizes of 20 to 30 nm in ab and 0.20 to 0.30 nm in c. They represent the smallest clay particles technically separable. In the East-Slovak Basin, fundamental particles from bentonite beds of different drillings having varied burial histories were K-Ar and Rb-Sr dated and $\delta^{18}O$ traced (Clauer et al., 1997; Clauer et al., 2003). The hydrothermal bentonites from nearby Zempleni Mountains were also studied for comparison. At Cicarovce, burial diagenesis induced one episode of illite nucleation at about 130°C considered to have been the maximum paleotemperature. The K-Ar data range from 8 to 4 Ma, at about the middle of the theoretical duration of illitization, which outlines a constant illite-growth rate. About 20 Km away, near Throviste, burial diagenesis induced an episodic illitization at about 165°C, during temperature and water/rock ratio decrease. The K-Ar data range between 11 and 8 Ma, close to the end of the theoretical duration of the process. This can be interpreted as a slow rate of illite crystal-growth at the beginning of burial, which seems to have improved towards the end of illitization, probably due to a renewed nucleation at different P, T, X conditions. At Zempleni, the hydrothermal activity appears to have been fast, with K-Ar data narrowly scattered at 14.5 Ma, during temperature and/or water/rock ratio increase.

Illitization appears therefore to be possibly episodic during burial and an evolutionary model was proposed (Clauer, 2006) that relates illitization episodes relative to its burial-induced theoretical duration, based on the data obtained on illite-type fundamental particles from bentonites of different drillings in the East-Slovak Basin (Figure 11).
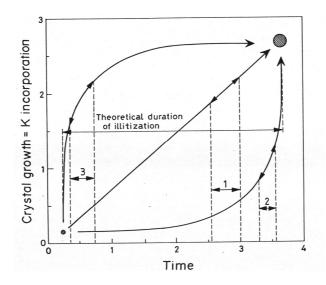
FIGURE 11. *Modeled crystal nucleation (lower left corner) and growth (upper right corner) of illite-type fundamental particles relative to time, with three periods of isotope dated illitization (1 to 3) depending on kinetics (after Clauer, 2006).*

Which application to the illitization process?
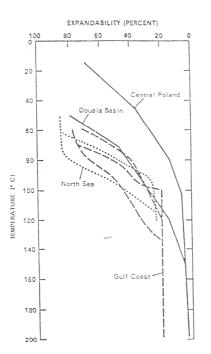
In burial-related sandstones

Illitization is considered to be a reliable tool to identify the impact of burial diagenesis in sediments. It is often represented by an « expandability » factor (% of smectite layers), and is believed to be a long-lasting, on-going process in the upper basin sequences (Figure 12). The varied evolution curves of illite expandability (negatively correlated to K_2O content) relative to temperature, suggest that each basin evolution depends on the local history, which is probably agreeable to many, but which is difficult to demonstrate. This may due to varied illite crystal-growth and kinetic rates depending on specific P, T, X conditions. Crystal growth depends also on rock porosity, permeability, mineralogy, and on the basin history.
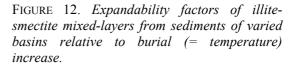
On the basis of the data reported for the fundamental particles of bentonites, the questioning is about K_2O incorporation: always considered to be continuous with burial (being mainly monitored by temperature increase), can it be also or instead episodic because of changing influence of other parameters, such as porosity, fluid chemistry,…? Illitization may proceed differently than considered for decades. This change in the basic concept might be determining in the understanding of its impact on the physical and chemical characteristics of sediment sequences, and on the extent and history of the economically important migrating fluids.

During tectonic-related hydrothermal activity

Precise geometrical and time constraints are essential to understand the evolution of fold and thrust belts. Combined structural studies including mineralogical, morphological and K-Ar isotopic investigation of clay-rich, < 0.2 μm and 1-2 μm size-fractions from fault- and host-rocks of selected fault zones can provide new information about these constraints.

For instance, lack of such constraints in the allochthonous of the Northern Appalachian mainland limits the comprehension in their kinematic evolution. New structural and K-Ar data define five age groups at: (1) ca. 490 Ma, (2) 465 to 450 Ma, (3) ca. 410 Ma, (4) ca. 370 Ma, and (5) ca. 360 Ma (Sasseville et al., submitted). These constraints challenge the traditional view of a single and gradual piggyback progression of faulting in the allochthonous fold and thrust belt of this region between Middle and Late Ordovician.

FIGURE 12. *Expandability factors of illite-smectite mixed-layers from sediments of varied basins relative to burial (= temperature) increase.*

The recognition of the distinct contraction pulses during the Taconic Orogeny shows that deformation (D_1) started at about 490 Ma and culminated with the out-of-sequence imbrication (D_2) of nappe stacking at ca. 465 and 450 Ma. At ca. 410 Ma, a brittle strike-slip extension (D_{3b}) evolved simultaneously with a ductile hinterland-directed shear zone (D_{3a}). At ca. 370 Ma, imbrications (D_4) exhumed D_{3a} shear zones and M_3 metamorphic facies in the allochthonous. Finally, normal-sense reactivation (D_5) of D_4 structures and related hydrothermal activity (M_5) at ca. 360 Ma, were also identified in the allochthonous mainland.

Structural observations combined with mineralogical and isotopic dating of clay material from selected rocks allowed for the first time to document the incremental evolution of the Taconic Orogeny and the occurrence of Late Silurian-Early Devonian strike-slip extension and Late Devonian imbrications in the allochthonous of mainland Canada. This is potentially possible in other complex tectonic areas.

Conclusions

Isotopic dating and tracing of clay minerals has been proved useful in many circumstances on the basis of stratigraphic applications and comparisons with the isotopic ages of contemporaneous ore minerals. However, this application is reliable only in following basics in the separation and the characterization of the separated clay fractions.

A new determining step has recently been made by the application of several isotopic methods to fundamental illite-type particles from illite-smectite mixed layers and in combining detailed structural observations with mineralogic and isotopic data on precisely identified rocks. They allow providing new insights on (1) the duration of burial-induced illitization, the continuous or episodic nucleation of illite, and the varied kinetic rates of growing illite particles. They also allow deciphering complex histories of tectonic regions in distinguishing the different episodes of their evolution.

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