

CRYSTALLIZATION CONDITIONS OF FUNDAMENTAL PARTICLES FROM MIXED-LAYER ILLITE-SMECTITE OF BENTONITES BASED ON ISOTOPIC DATA (K-Ar, Rb-Sr AND $\delta^{18}\text{O}$)

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Abstract—Rb-Sr and oxygen isotope studies, in addition to K-Ar isotopic determinations published previously, are reported on diagenetic and hydrothermal fundamental particles (particle thickness of 0.03 to 0.05 nm and particle *ab* size of 0.02–0.05 μm) of the East-Slovak Basin. The combined data set allows us to ascertain the crystallization conditions of the illite material from two bentonite units collected at two basinal sites located ~20 km apart, and characterized by prolonged diagenetic conditions induced by progressive burial. A bentonite rock characterized by a short hydrothermal event from the Zempleni mountains to the SW of the East-Slovak basin is also studied.

For the two first sites, the $\delta^{18}\text{O}$ values increase in one case and decrease in the other, when the size of the diagenetic fundamental particles from bentonite samples increases. These variations suggest that temperature increased in one and decreased in the second of the two samples collected in the basin, while the particles were growing. In the case of the hydrothermal bentonite, the $\delta^{18}\text{O}$ values of the different size-fractions consisting of fundamental particles remain about constant, suggesting constant temperature and fluid chemistry.

The Rb-Sr dates of the fundamental particles of the three bentonite rocks were systematically higher than the corresponding K-Ar ages. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, which are initially involved in the particle nucleation, appeared higher than that of contemporaneous sea-water. In all cases, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio decreases when particle size increases, which implies supply of external Sr into the bentonite units. This external Sr seems to have had an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio close or identical to that of the contemporaneous sea water. This means that Sr, probably of sea-water origin, progressively diffused from host shales into the bentonite units, during burial diagenesis. In turn it favors the suggestion made previously about diffusion of K from shales into the bentonite layers during illitization of the smectite from these units.

Key Words—Bentonites, $\delta^{18}\text{O}$, East-Slovak Basin, Fundamental Particles, Isotopic Tracing, Rb-Sr.

INTRODUCTION

The work of Clauer *et al.* (1997) was the first on K-Ar dating of fundamental particles that were separated from mixed-layer illite-smectite (I-S) of bentonites. These particles were separated by high-speed centrifugation after infinite osmotic swelling of the mixed-layer crystals achieved by Na exchange and dispersion in distilled water. A major conclusion of this study was that the thinnest fundamental particles from a sample may yield older K-Ar ages than thicker particles, implying that clays do not necessarily lose radiogenic ^{40}Ar just because of their extremely small particle size. This study also showed that illitization probably entails a crystal-growth process of long duration during burial diagenesis. Thus, K-Ar ages of pure authigenic fundamental particles from mixed layers extracted from any volcano-sedimentary unit could very easily represent an integrated age in the whole history of illite mineralization over longer or shorter periods of time that are dictated by the thermal and chemical history of the host rocks.

Different studies have addressed the theoretical aspects of the nucleation and growth of fundamental particles (*e.g.* Eberl *et al.*, 1998) and also of other minerals (Kile *et al.*, 2000). However, documentation on natural conditions that have the potential to adequately describe the crystal-growth process is rare. The present study provides a fresh perspective on crystal-growth conditions by examining Rb-Sr and oxygen isotope characteristics of some of the fundamental particles that were previously K-Ar dated by Clauer *et al.* (1997). As preparation and separation of fundamental particles from I-S are extremely time consuming, this complementary study has been completed, as a pioneering attempt, on the size-fractions which were K-Ar dated and which still yielded enough material to allow completion of $\delta^{18}\text{O}$ and Rb-Sr determinations. It is clear to us that the limited number of samples and size-fractions is a shortcoming of this study, but we did expect, given the detailed information about these samples from previous studies, that the collective isotope data would at least help to provide additional information about the growth process of fundamental particles, and about the chemistry of the fluids involved. This information might help to guide future studies on the same topic.

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The mechanism of illitization is a powerful determinant of the isotopic system of clay material, and consequently of the age relationship among size-fractions of I-S. Although many models favor dissolution of smectite layers followed by crystallization and growth of illite crystals (*i.e.* sets of layers bound permanently by fixed K; Nadeau *et al.*, 1984; Inoue *et al.*, 1987; Eberl and Środoń, 1988), the specific paths in the crystal-growth processes have yet to be constrained by a detailed geochemical approach. Such illite crystals are referred to hereunder as 'fundamental particles' after Nadeau *et al.* (1984). Detailed mineralogical and geochemical studies on such particles are now possible, because a separation technique according to particle thickness has been developed (Clauer *et al.*, 1997; Środoń and Clauer, 2001).

SAMPLE DESCRIPTION AND PREVIOUS RESULTS

Three bentonite samples were the subjects of this investigation. Two samples come from cored boreholes

of the molassic East-Slovak Basin which belongs to the Alpine-Carpathian orogenic belt, and which contains numerous bentonite beds recording a calc-alkaline type of volcanic activity during Middle to Late Miocene (Rudinec, 1978). One sample (CIC1/20) belongs to a core taken at a depth of 2495 m in drill hole CIC-1 near Cicarovce in the southeastern region, and the second (TRH1/37) was taken in the northwestern part of the basin, at a depth of 3015 m in the drill hole TRH-1 near Trhoviste (Clauer *et al.*, 1997, and Figure 1). The burial and thermal history of the basin was presented in Clauer *et al.* (1997); it was simulated using forward modeling software based on the principles of Welte *et al.* (1981). The compaction process was treated as a porosity decrease controlled by lithology, permeability, sedimentation rate and pore-fluid expulsion. The paleotemperatures were modeled as a function of heat flow, thermal capacity and conductivity of the rocks, while the present-day borehole temperatures are from Kral *et al.* (1985). The simulated data of the diagenetic alteration of the sediments were also compared to parameters measured in the boreholes, mutual agreement being a

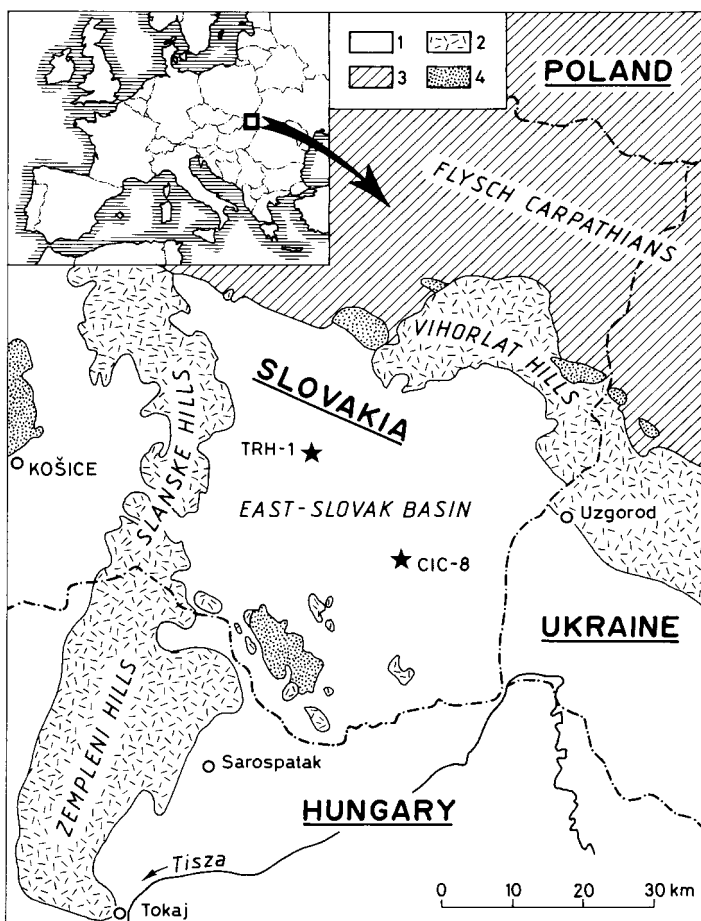


Figure 1. Sample locations in the East-Slovak Basin (after Clauer *et al.*, 1997). 1: Neogene sediments; 2: Neogene volcanic rocks; 3: Paleogene sediments/flysch; 4: pre-Paleogene sediments.

prerequisite for the validity of the burial and thermal evolutionary model. The paleotemperatures were consistent with the beginning of the illitization process at $\sim 70^\circ\text{C}$, based on a detailed study by Šučá *et al.* (1993), where the transition of smectite to illite in both the bentonite and shale units characteristically shows a good correlation between the content of expandable layers in the I-S and the burial depth. Consequently, illitization of

the studied bentonite level in the TRH1/37 hole lasted from ~ 15 Ma to 7 Ma, during temperature decrease. In the borehole of CIC1/20, illitization of the studied bentonite lasted from ~ 11.5 Ma to the present day, as the temperature never decreased markedly (Figure 2).

The third sample is an extremely pure, hydrothermal clay from nearby Zempleni Hills in northeastern Hungary (Figure 1). It was chosen because it is very

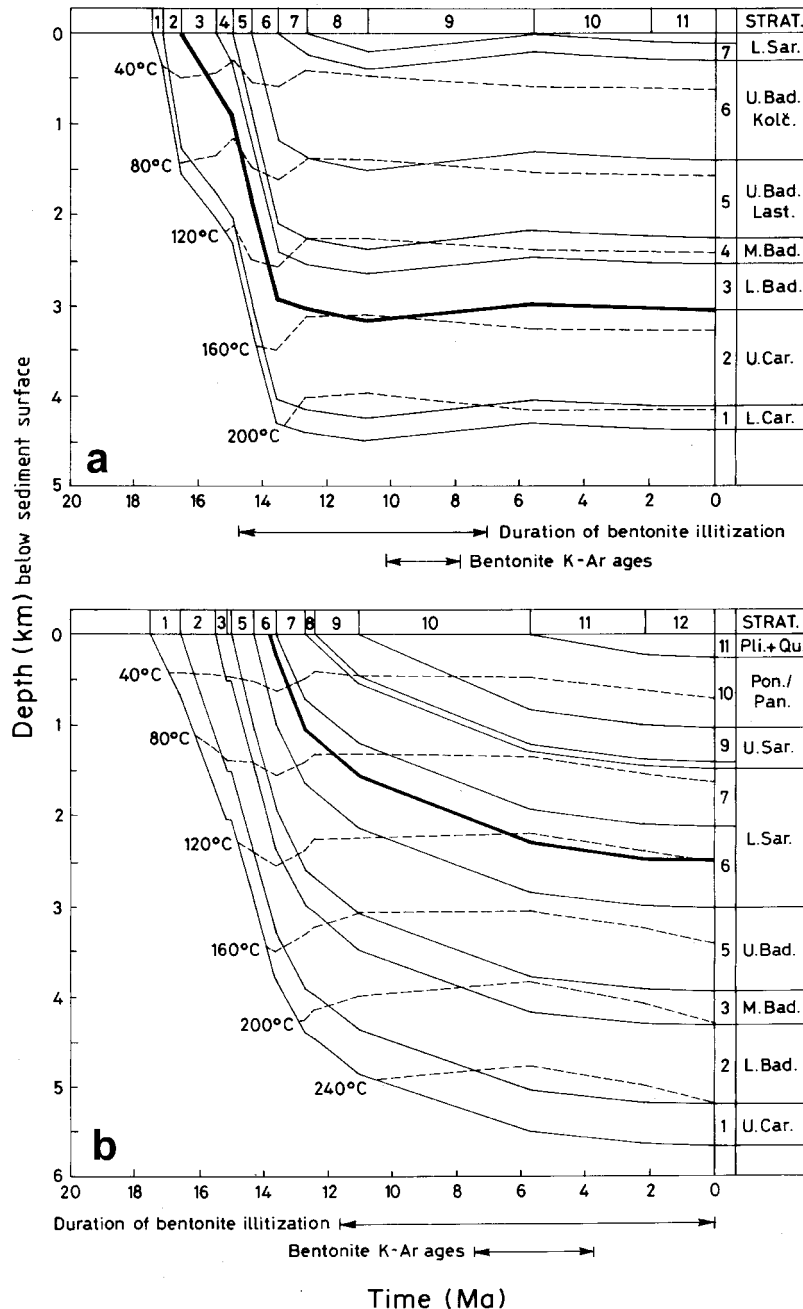


Figure 2. Reconstruction of the burial histories of the Trhoviste-1 (a) and Cicarovce-8 (b) boreholes from the East-Slovak Basin starting at the Carpathian stratigraphic unit. The studied bentonite level of both boreholes is represented by the thick bold curve. The time-related isotherms are identified by the dashed lines. The bentonite K-Ar ages (also given in Table 1) and the estimated duration of bentonite illitization are from Clauer *et al.* (1997).

well known and because it represents an alternative hydrothermal material to the diagenetic minerals from bentonite samples of the basinal drill cores (ref. in Clauer *et al.*, 1997). It probably comes from the well known Fűdzéradvány I-S deposit near Sarospaták, as this is the only mixed-layer occurrence in the Zempleni area (Vicizian, pers. comm., 1995).

The different size-fractions each consisted of almost monomineralic I-S mixed layers identified by XRD, with a few impurities of quartz, plagioclase, kaolinite and chlorite reported in some of the larger size-fractions (Clauer *et al.*, 1997). It could also be determined that the amount of smectite layers (%S) increases in the I-S as the particle size decreases. The XRD patterns also showed that the separation procedure allows dispersion of mixed-layer crystals into free fundamental particles and concentration of the thinnest fundamental particles in the finest size-fractions. A concentration of the thinnest mixed-layer crystals of the same fundamental-particle composition would have induced the opposite result, namely a decrease in %S in the finest size-fractions. Intermediate %S in the coarser fractions seems to result from the occurrence of aggregates of mixed-layer crystals, strongly suggesting that these coarser fractions might contain several classes of fundamental particles. The Zempleni hydrothermal sample contains almost exclusively fundamental clay particles in the <0.3 μm size-fractions, while aggregates of the same particles are dominant in the >1 μm fraction. The electron microscopic observations (Clauer *et al.*, 1997) also emphasized the occurrence of aggregates in the coarser fractions of the other samples. This means that the results of these size-fractions may have been partly biased by the mixing of smaller and/or thinner particles sticking together or on larger ones.

The K-Ar dates of the TRH1/37 size-fractions increase slightly with the thickness of the particles from 7.9 Ma to ~10.2 Ma, the coarser aggregates (0.3–0.5 and 0.5–2 μm) yielding an average of 10.6 \pm 0.7 Ma. This relationship between increasing thickness and K-Ar dates is not evident in the CIC1/20 size-fractions for which the K-Ar values decrease from 7.4 to 3.7 Ma when the particle thickness increases, the aggregates again yielding a high value of ~8.0 Ma, similar to that of the thinnest particles. A reasonable explanation for the unexpected decrease in the K-Ar dates from 7.4 to 3.7 Ma, which has since been found in fundamental particles of other basinal bentonite units (Clauer, unpublished data), while the grain size of the fundamental particles increases, might be based on the fact that if all nucleating germs of fundamental particles do not grow in their environment, those remaining very small will necessarily yield higher K-Ar dates than those which grew. This is due to the continuing integration of K during growth, which reduces the K-Ar values. The K-Ar dates of the size-fractions of the Zempleni hydrothermal sample appear very similar, ranging from

15.6 \pm 0.5 to 13.5 \pm 0.5 Ma. No clear trend could be found between the K-Ar dates and the corresponding particle sizes.

ANALYTICAL PROCEDURE

The analytical procedure for separation of the fundamental particles has been described elsewhere (Clauer *et al.*, 1997). The whole-rock samples were crushed and processed using Na acetate and Na dithionite techniques (Jackson, 1975) to remove carbonates and iron oxides. The <2 μm fractions were separated by continuous-flow ultra-centrifugation, after repeated settling in distilled water. The <0.1 μm suspensions were diluted to a concentration of 1 g/40 L to ensure an infinite osmotic swelling (Środoń *et al.*, 1992) and three fractions <0.1 μm were collected using a high-speed centrifuge. The equivalent spherical diameters were not calculated, the fraction limits being marked with the letters X and Y (Table 1). The finest fractions were collected by flocculating the suspensions with NaCl and then removing the excess electrolyte by dialysis. The size-fractions were X-rayed as random powders to determine the mineral composition, and as oriented slides after glycolation to identify the clay minerals. Expandability of the I-S was determined using the techniques of Środoń (1980, 1981, 1984).

Several size-fractions of the three samples were analyzed for their $\delta^{18}\text{O}$ and Rb-Sr systematics. The oxygen-extraction technique is based on BrF₅ digestion at 600°C under vacuum in Ni reaction vessels, according to the technique of Clayton and Mayeda (1963). Oxygen was converted into CO₂ and analyzed in a double collecting mass spectrometer. The results represent

Table 1. Oxygen isotope results of the studied size-fractions separated from the Trhoviste, Cicarovce and Zempleni bentonite samples, together with the XRD, and K-Ar data of the study by Clauer *et al.* (1997).

Samples	Size (μm)	$\delta^{18}\text{O}$ (‰ V-SMOW)	%S	K-Ar age (Ma \pm 2 σ)
TRH 1/37	Y–X	+17.0	37	7.9 (0.4)
	X–0.1	+17.9	31	10.2 (0.4)
	0.3–0.5	+17.6	–	11.3 (0.4)
	0.5–2	+18.5	–	9.9 (0.4)
CIC 1/20	<Y	+11.8	79	7.4 (2.4)
	X–Y	+11.0	63	3.8 (2.0)
	X–0.1	+12.2	66	3.7 (2.1)
	0.5–2	+9.6	–	7.8 (1.8)
Zempleni	Y–X	+7.8	26	n.d.
	X–0.1	+7.6	27	15.6 (0.5)
	0.2–0.3	+7.2	15	14.3 (0.5)
	>1	+7.2	–	14.0 (1.4)

%S: smectite layers in the size-fractions

average values of systematic independent duplicate analyses, which never exceeded $\pm 0.2\%$, and they are expressed in the usual δ notation in per mil (‰) relative to the V-SMOW standard. The average $\delta^{18}\text{O}$ of 16 independent determinations of the NL615 interlaboratory reference was found to be 17.5 ± 0.8 (2σ), while its accepted reference value is 17.95 ± 0.20 (2σ) relative to the V-SMOW. The Rb-Sr systematics were applied here more as a tracing tool, on the basis of the previously obtained K-Ar results, in order to identify the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the clay minerals and of the soluble authigenic minerals intimately associated with the clay particles. This was done by gentle acid leaching of the clay size-fractions with dilute HCl (1 N), in order to remove the adsorbed elements from particles and to dissolve any soluble contaminant mineral phase mixed with the clay particles into a leached phase, as reported by Clauer *et al.* (1993). This technique has been used often, because it provides information about the crystallization environments of the clay particles (*e.g.* discussion in Clauer and Chaudhuri, 1995), and about the chemistry of the fluids that interacted directly with the clay particles while forming and growing (Ohr *et al.*, 1991; Clauer *et al.*, 1992). After HF-HNO₃-HClO₄ digestion of the residues and evaporation of the acid leachates of the different illite fractions, Rb and Sr were separated by resin chromatography following a technique described elsewhere (Dequincey *et al.*, 1999; Riotte and Chabaux, 1999). The Sr was analyzed by thermal-ionization mass spectrometry with a multi-collector having five mobile collectors. The analytical precision of the procedure was periodically controlled by analysis of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the NBS 987 standard which averaged 0.710262 ± 0.000014 (2σ) for four independent determinations made during the course of the study. The Rb and Sr concentrations were determined by ICP-MS with a precision of $\pm 5\%$ (2σ). The Rb-Sr dates were calculated with the usual decay and fractionation constants (Steiger and Jäger, 1977).

RESULTS

The $\delta^{18}\text{O}$ values of the TRH1/37 fundamental particles increase irregularly, but significantly, from +17.0‰ for the thinnest X-Y μm fraction to +18.5‰ for the thickest 0.5–2 μm fraction (Table 1). Those of the CIC1/20 fundamental particles decrease irregularly from +11.8‰ for the <Y μm fraction to +9.6‰ for the 0.5–2 μm fraction. The irregular decrease or increase could be attributable to the impurities identified earlier, the amounts of which might vary slightly. Evaluation of the minute amounts of the impurities and knowledge of their oxygen isotope fractionations, allow us to discard the effects of such contamination on the results. On the other hand, the Zempleni illite fractions yield almost no trend in the $\delta^{18}\text{O}$ values from +7.8‰ for the X-Y μm fraction to +7.2‰ for the >1 μm fraction (Table 1).

The Rb and Sr contents vary randomly among the different size residues of the two basinal TRH1/37 and CIC1/20 samples and of the hydrothermal Zempleni sample, as well as among the leachates of the different size-fractions (Table 2). No clear trend relates the Rb and Sr contents to the particle size. The individual Rb-Sr dates constructed from combined leachate and residue data of each TRH1/37 fraction are scattered between 26.0 and 29.2 Ma (Table 2). In the case of the CIC1/20 sample, the range of the Rb-Sr dates based on the leachates and residues is wider, from 11.3 to 40.4 Ma. For the Zempleni sample, the Rb-Sr data are again significantly above the K-Ar data from 38.3 to 56.0 Ma. The Rb-Sr data of the three sets of size-fractions from which three data points including the leachate (denoted L), residue (denoted R) and untreated fractions (denoted U) could be determined, provide fairly linear trends in an isochron diagram (Figure 3). These good-quality trends only reflect the care taken with the analytical procedure, not the validity of the date extracted from alignment (see discussion in Clauer and Chaudhuri, 1995). Relative to the K-Ar dates obtained previously, the Rb-Sr dates for each of the analyzed fractions are significantly higher in the three samples (Table 1). Roughly, the trend in the variations of the Rb-Sr dates follows the K-Ar trend for each sample: the Rb-Sr dates increase or decrease with increase or decrease of the K-Ar dates. In detail, the trends do not follow each other perfectly, especially for the 0.3–0.5 μm fraction of sample TRH1/37. This is probably due to the fact that the Rb-Sr values have no geological meaning, whereas the K-Ar ones have. Indeed, the Rb-Sr values are systematically above the stratigraphic age of the samples, making it clear that they cannot have a geological meaning as such. Furthermore, the fact that the Rb-Sr values calculated from combined leachate and residue data yield values beyond stratigraphic ages of the samples, probably reflects leachates not in Sr isotopic equilibrium with the clay residues during crystallization. This might also explain varied scatter among the Rb-Sr data, and among the K-Ar and Rb-Sr data for each fraction.

DISCUSSION

The previous mineralogical and K-Ar isotopic study of the selected bentonite fractions (Clauer *et al.*, 1997) showed that: (1) the fundamental particles of the I-S yield K-Ar dates that appear to have bearing on their diagenetic evolution, and (2) the thinnest fundamental particles can, in some instances, yield older K-Ar ages than the thicker fundamental particles, implying that the illitization process proceeds as a single crystal-growth mechanism. In this case, each particle consists of layers that individually might yield different apparent ages. As a result, a K-Ar age of fundamental particles becomes an integration over a varied span of crystallization time, depending on the thermal history of the rock sample.

Table 2. Rb-Sr data of the studied size-fractions separated from the Trhoviste, Cicarovec and Zemleni samples.

Samples	Size	Fraction	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ ($\pm 2\sigma$)	Rb-Sr age (Ma)	$^{87}\text{Sr}/^{86}\text{Sr}_{\text{in}}$ (Rb-Sr age)	$^{87}\text{Sr}/^{86}\text{Sr}_{\text{in}}$ (K-Ar age)	$^{87}\text{Sr}/^{86}\text{Sr}_{\text{SW}}$	
TRH1/37	X-0.1	Leachate	5.0	35.2	0.41	0.709320 (10)	29.1 (L-R)	0.70915	0.72348	0.70870	
		Untreated	72.0	22.3	9.37	0.711750 (11)					
	0.3-0.5	Residue	48.3	2.6	53.4	0.731214 (24)					
		Leachate	n.d.	n.d.	n.d.	0.709385 (12)	22.6 (L-R)	0.70939	0.71347		
	0.5-2	Untreated	13.2	3.3	11.4	0.711468 (12)					
		Residue	15.2	1.6	28.4	0.718502 (12)					
		Leachate	2.4	29.4	0.23	0.709493 (10)	26.0 (L-R)	0.70941	0.71050		
		Untreated	37.0	39.4	2.72	0.710404 (17)					
	CIC 1/20	<Y	Residue	47.9	28.9	4.79	0.711173 (21)				
			Leachate	1.6	8.9	0.30	0.708687 (12)	40.4 (L-R)	0.70840	0.72280	0.70878
X-0.1		Residue	13.8	1.3	30.7	0.726020 (17)					
		Leachate	2.6	25.3	0.30	0.709223 (12)	11.3 (L-R)	0.70918	0.72112		
0.5-2	Residue	15.7	0.4	111	0.726968 (14)						
	Leachate	4.3	7.4	1.69	0.709124 (10)	40.0 (L-R)	0.70817	0.70952			
Zemleni	Y-X	Residue	13.1	12.7	2.97	0.709852 (10)					
		Leachate	3.8	9.0	1.24	0.709224 (12)	51.9 (L-R)	0.70831	n.d.	0.70875	
	X-0.1	Residue	285	18.4	44.9	0.741355 (23)					
		Leachate	4.5	6.4	2.03	0.709438 (12)	56.0 (L-R)	0.70782	0.73208		
	0.2-0.3	Residue	397	27.2	42.3	0.741434 (10)					
		Leachate	5.3	8.0	1.91	0.710229 (13)	38.3 (L-R)	0.70936	0.71170		
Residue	410	128	9.27	0.713581 (09)							

$^{87}\text{Sr}/^{86}\text{Sr}_{\text{in}}$ stands for the initial ratio $^{87}\text{Sr}/^{86}\text{Sr}$; $^{87}\text{Sr}/^{86}\text{Sr}_{\text{SW}}$ for sea-water $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, 2σ for a 2σ mean uncertainty; L for leachate, R for residue, in. for initial, SW for sea-water, and n.d. for not determined

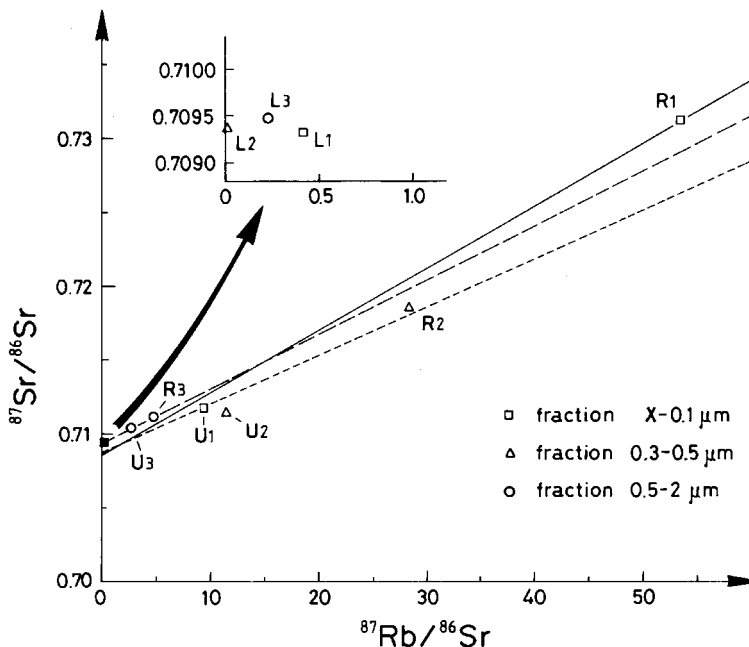


Figure 3. Rb-Sr isochron diagram including the untreated (U), leachate (L) and residue (R) aliquots of the different size-fractions of TRH1/37 sample. The lines are the best fits through the three data points (L, U, R) of each size-fraction.

Two types of fundamental particles were analyzed here for their $\delta^{18}\text{O}$ and Rb-Sr systematics: (1) those of the TRH1/37 and CIC1/20 basinal bentonite units which underwent prolonged burial evolutions; and (2) those of the Zempleni bentonite which formed during a short-lasting hydrothermal activity. Therefore, the studied fundamental particles belong to very similar bentonite units, which were affected by different thermal evolutions and might have been in contact with contrasted fluids. All these could have varied effects on their isotopic systems

Oxygen isotope compositions

The oxygen isotope composition of any authigenic mineral in an aqueous environment is controlled by fluid isotope composition, temperature and degree of fluid-mineral interaction. Experiments by O'Neil and Kharaka (1976) suggested a lack of isotopic exchanges between structural oxygen of clay particles and that of fluids for tens of million years in burial diagenetic environments. The variations in $\delta^{18}\text{O}$ as a function of K content in fundamental particles may, therefore, be explained as reflecting either changes in the oxygen isotope composition of the fluids responsible for the mineral crystallization and/or growth, or changes in temperature. Variations in $\delta^{18}\text{O}$ values of fundamental particles reflecting changes in the water/rock ratio during illitization could probably be discarded because of the known impermeability of bentonite units, even if increasing K contents in the I-S needs to be explained by a supply of K from host shales into the bentonite units. However, the range of variations in the $\delta^{18}\text{O}$

values for the fundamental particles with differing K contents may be inconsistent with the variations in relatively high temperatures, as Savin and Lee (1988) showed for mixed-layer I-S. It has also been reported from studies in sedimentary basins, that the $\delta^{18}\text{O}$ values of formation waters are temperature dependent, increasing with temperature (Taylor, 1979; Sheppard, 1986; Kharaka and Thordsen, 1992).

As mentioned above, the $\delta^{18}\text{O}$ values of the fundamental particles studied here were found to either (1) change (increase or decrease) with respect to particle size increase in the basin, or (2) remain the same in the hydrothermal site. Progressive depletion of $\delta^{18}\text{O}$ values of clay particles from sedimentary rocks has already been reported, while K increases (Eslinger and Yeh, 1981; Whitney and Northrop, 1988). Such a relationship of increasing K content and decreasing $\delta^{18}\text{O}$ value suggests a progressively more pronounced interaction between K-rich fluids and the clay material which could, in turn, indicate higher temperatures and/or water/rock ratios. Here, no consistent relationship could be observed among the $\delta^{18}\text{O}$ values of the studied size-fractions from the East-Slovak Basin and the expandability or K content. It is, therefore, necessary to provide an explanation other than temperature or water/rock increases to explain the data.

East-Slovak Basin. The $\delta^{18}\text{O}$ values of the TRH1/37 fundamental particles increase by 1.5‰ when the particle size increases, whereas those of the CIC1/20 particles decrease by 2.2‰ when particle size increases. These changes are analytically significant and, despite

similar basinal evolution, burial history and illitization process, these opposite trends suggest different illitization conditions at the two sites. Estimates of the $\delta^{18}\text{O}$ of the fluids in both cases might be made by assuming an average $\delta^{18}\text{O}$ value for the fractions and an average temperature of the crystal-growth process given by the thermal evolutionary model (maximum temperatures of 160°C in TRH-1 borehole and 130°C in CIC-1 borehole taken from Kral *et al.*, 1985). These parameters provide values at +9.3‰ for an average fluid in TRH-1 borehole, and +0.7‰ for an equivalent average fluid in CIC-1 hole, meaning that the fluids could have been close to meteoric (surface-derived) water in the case of the CIC-1 hole, while such an origin cannot be envisaged for the fluids having percolated the TRH-1 bentonite level. Obviously, illitization had to proceed differently in the two samples which are located only ~20 km apart and which were buried in the same basin to depths of 2495 and 3015 m.

As illitization occurred in bentonite units which are generally characterized by low permeabilities, fluid migrations may be considered to have been of limited scale, inducing negligible changes in the water/rock ratios during the process, even if it were very long. Such a low permeability of the rocks further induced almost no change in the $\delta^{18}\text{O}$ of the fluids, provided that no diffusion-related fractionation of the fluid $\delta^{18}\text{O}$ occurred. Thus, the change in the $\delta^{18}\text{O}$ of the fundamental particles may be assumed to have been mainly temperature dependent.

The $\delta^{18}\text{O}$ values of the TRH-1 and CIC-1 fundamental particles describe two different trends relative to size (thickness) increase. Interpretations of the trends may be as follows: (1) the decrease in the $\delta^{18}\text{O}$ value with increase in the size might correspond to an overall temperature increase during crystallization, as for the CIC1/20 fundamental particles, and (2) the increase in the $\delta^{18}\text{O}$ value with increase in the size might correspond to an overall temperature decrease during the same crystallization, as for the TRH-1 fundamental particles. The previous K-Ar study of the same fractions (Clauer *et al.*, 1997) showed that the data represent an integration over the whole duration of the illitization process that started at ~70°C, as shown by Šuchá *et al.* (1993) elsewhere. Illitization occurring at a constant rate might result in an integrated age that would be skewed more towards the middle of the mineral-growth period, reflecting progressive increases of the K and radiogenic ^{40}Ar contents in the crystal structures. By contrast, very rapid illitization followed by a limited incremental growth over a relatively long period would result in an integrated K-Ar data range clearly locating the main growth span in the early phase of the mineralization. Yet again, a small incremental growth over a long period of time followed by a rapid illitization during the end phase of the growth should result in an integrated K-Ar age that would mark the major growth span in a late phase of the mineralization.

(1) On the basis of the burial and thermal history of the basin, which was simulated using modeling software based on principles of Welte *et al.* (1981), illitization of TRH-1 I-S particles started nearly 15 Ma ago at ~70°C and may have continued until ~7 Ma ago (Figure 2a). The K-Ar dates range from ~11.3 to 7.9 Ma, whereas the simulation based on organic matter maturation data points to a model age of ~10.5 Ma for the maximum temperature. The $\delta^{18}\text{O}$ values of the fundamental particles agree with this temperature model, as they suggest that illitization occurred during a marked temperature decrease after maximum was reached.

(2) In the case of the CIC-1 hole, illitization seems to have started at ~11.5 Ma at the same temperature of 70°C, and to have lasted since (Figure 2b). The K-Ar dates range from 7.4 to 3.7 Ma, which is consistent with the period of maximum temperature based on the model of organic matter maturation. The $\delta^{18}\text{O}$ values of the CIC-1 fundamental particles appear to relate to a temperature increase during illitization.

Therefore, the illitization rate was probably higher for the CIC-1 bentonite fundamental particles, as it occurred during temperature increase, than for the TRH-1 bentonite fundamental particles which grew during temperature decrease.

The calculated $\delta^{18}\text{O}$ for the fluid involved in the illitization process of CIC-1 hole, was found to be very low at +0.7‰, considering the temperature was 130°C. Surface-derived water expelled from shales underlying the bentonite unit during maximum or advanced burial (close to maximum temperature and during maximum compaction), could explain this low $\delta^{18}\text{O}$ value, unless fractionation occurred by diffusion. This value seems reasonable, because in taking a $\delta^{18}\text{O}$ close to the +9.3‰ obtained for the calculated $\delta^{18}\text{O}$ of the fluid present during illitization in the TRH-1 bentonite, the crystallization temperature of the illite particles would become as high as ~300°C, which is clearly unrealistic.

Zempleni hydrothermal sample. Very similar K-Ar dates among the fundamental particles and the aggregates of particles (14.0±1.0 Ma) of the Zempleni bentonite favor a thermal event of short duration inducing simultaneous crystallization and growth of the clay material. The narrow range of $\delta^{18}\text{O}$ values with only a slight shift of -0.6‰ from thinnest to thickest particles supports such a rapid episode without significant changes in the chemical composition of the migrating fluids. It is yet difficult to assume a temperature for the fluids and therefore evaluate a calculated $\delta^{18}\text{O}$ value. It is, however, known that hydrothermal waters may yield low $\delta^{18}\text{O}$ shifts, such as in the Wairakei area (Taylor, 1979; Sheppard, 1986). If the temperature remained below 200°C, the $\delta^{18}\text{O}$ of the fluid could have been as low as +1.7‰, close to the $\delta^{18}\text{O}$ value of the calculated value for the fluid related to illitization in CIC-1 hole. The fluid could, again, have been expelled 'surface-

derived' water, unless the reaction temperature was significantly higher.

Rb-Sr isotope systematics

The Rb-Sr values obtained for the different size-fractions of the three bentonite samples were significantly larger than the K-Ar ages, based on the use of the leachate and residue data points. It is well known that this means that both the leachates – representing the adsorbed Rb and Sr, and the Rb and Sr trapped in soluble mineral phases intimately mixed with the clay particles – were not in chemical and isotopic equilibrium with the residual Rb and Sr trapped in the clay material (e.g. review in Clauer and Chaudhuri, 1995). The fact that the K-Ar and Rb-Sr values are positively correlated leads us to believe that the leachable Sr represents a mixture of two types of Sr: one in equilibrium with that in the clay particles with an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio equaling the value calculated on the basis of the K-Ar age determinations, and the second one of different origin. This can be shown graphically in an $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{87}\text{Rb}/^{86}\text{Sr}$ diagram where a composite line consisting of a leachate data point (denoted L) and a residue data point (denoted R) yields a 'higher age' when the L data point moves towards either lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios or higher $^{87}\text{Rb}/^{86}\text{Sr}$ ratios. The first shift implies addition of Sr to a lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, whereas the second implies either subtraction of Sr of the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as the measured one, or addition of Rb. If addition of Rb appears plausible, as addition of K is needed for illitization of the original smectite, removal of Sr from the bentonite unit is difficult to consider as it would imply diffusion from a depleted medium represented by the bentonite into a concentrated medium represented by the host shales.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the leachable Sr in equilibrium with that trapped in the fundamental particles can be calculated by assuming that the Rb-Sr and K-Ar ages are identical. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the different size-fractions are reported in Table 2. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the TRH 1/37 fractions decreases from 0.72348 for the thinnest analyzed X–0.1 μm fraction, to 0.71050 for the thickest analyzed 0.5–2 μm fraction. The same ratio decreases from 0.72280 for the thinnest <Y μm fraction to 0.70952 for the thickest 0.5–2 μm fraction of sample CIC 1/20. For the Zempleni sample, it decreases from 0.73208 for the X–0.1 μm fraction to 0.71170 for the 0.2–0.3 μm fraction. The fact that the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio systematically decreases as particle size increases suggests that (1) the Sr available at the beginning of the illitization process was clearly enriched in radiogenic ^{87}Sr , probably at 0.7220–0.7235 in the basinal bentonite units, and at 0.7321 in the Zempleni site, (2) the Sr progressively decreased its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio when illitization progressed, *i.e.* when the fundamental particles grew in any of the three environments studied. There are not many straightforward explanations for

such a decrease in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the immediate environment of the clay particles. Either some Sr with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios left the bentonite units, or some Sr with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios was supplied to it. There is no obvious reason to consider that Sr with abnormally high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios left the volcanogenic units, as already considered, but Clauer *et al.* (1997) showed that K was supplied progressively in thicker bentonite units of Montana, so it could be that Rb and Sr were supplied in the same way into the thinner TRH-1 and CIC-1 bentonite units. This external Sr had to have a smaller $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than the Sr originally in the bentonite rocks, allowing the overall ratio to decrease almost until sea-water value.

The Sr external to the bentonite unit did indeed have to have an $^{87}\text{Sr}/^{86}\text{Sr}$ value close to that of the sea-water contemporaneous with bentonite deposition. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the leachates probably represent varied mixtures of this external Sr and of Sr initially released from precursor minerals and glass altered concomitantly to the illitization process. If it were the case, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the external Sr (originally the sea-water Sr) was 0.70870 for the Lower Badenian TRH1/37 sample, 0.70878 for the Lower Sarmatian CIC1/20 sample, and 0.70875 for the Zempleni sample for which the stratigraphic age is unknown but may be defined by the K-Ar age (Hodell *et al.*, 1991). With these values and a range of 0.7228–0.7235 for the initial $^{87}\text{Sr}/^{86}\text{Sr}$ of the fundamental particles, rough estimates might be made for the amounts of external Sr associated with the interstitial Sr of the clay particles. These amounts would vary from 0 to 88% for the TRH1/37 material, from 0 to 94% for the CIC1/20 fractions, not taking into account the Sr contents of the respective fluids. For the Zempleni bentonite, the problem is different, as the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is difficult to assert, as in any hydrothermal system.

CONCLUSIONS

Oxygen and Rb-Sr isotopic determinations, in addition to previous K-Ar analyses of diagenetic to hydrothermal illite fundamental particles of bentonite units from the East-Slovak Basin, allow consideration of the crystallization conditions of these particles either during prolonged burial or episodic hydrothermal activity. The limited number of samples and size-fractions studied certainly does not allow us to draw general conclusions from the results obtained. However, we consider that they are of importance to support fresh thoughts about the physical and chemical conditions of the nucleation and growth processes of fundamental particles from I-S mixed layers in bentonite units.

The $\delta^{18}\text{O}$ values either increase or decrease when the size of the diagenetic particles increases. If one considers that the fluid chemistry remained constant during the process, these changes in the $\delta^{18}\text{O}$ mean that

temperature could have increased or decreased while the particles were growing. In the case of the hydrothermal material, the $\delta^{18}\text{O}$ remains constant, suggesting constant temperature and fluid chemistry during nucleation and growth of the fundamental particles. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, which were initially involved in the particle nucleation of the different bentonite rocks, were systematically significantly high relative to the contemporaneous sea-water Sr isotopic value. In all cases, this initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio decreases when particle size increases, which implies supply of Sr external to the bentonite units. This external Sr could have had an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio close or identical to that of the contemporaneous sea-water. If this was the case, it means that K needed for illitization of the smectite in the bentonite units, was probably from the same source, *i.e.* sea-water, and that it probably diffused progressively from host shales into the bentonite units.

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