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K/Ar SYSTEMATICS OF AN ACID-TREATED ILLITE/SMECTITE: IMPLICATIONS FOR EVALUATING AGE AND CRYSTAL STRUCTURE

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Abstract—On the basis of progressive acid dissolution the Thompson-Hower model states that mixed-layer glauconite/smectite and illite/smectite contain potassium in two structural sites: a mica-type K position (site 1) and a position of uncertain structural status more prone to dissolution (site 2). Site 2 was thought not to retain radiogenic argon ($^{40}Ar^*$). Using extensive progressive acid dissolution and K/Ar studies on a sized illite/smectite (I/S), determining the amount of K in site 2 is shown to be somewhat more complicated than previously thought because the dissolution pattern depends on acid normality. More important, site 2 fully retains $^{40}Ar^*$, and no age correction is thus necessary as is required by the Thompson-Hower model, further affirming the geochronologic value of illite in mixed-layer clay. These data are also relevant to understanding the crystal and particle structure of I/S. Site 2 is probably a partly filled K interlayer that develops as an intermediate kinematic step on the way to being fully filled during the transformation of smectite to illite.

Key Words—Acid dissolution, Age dating, Glauconite, Illite/smectite, Interstratification, Ordering, Potassium.

INTRODUCTION

The progressive acid-dissolution procedure for silicates is a step-wise process in which the dissolved constituents are determined after fresh batches of acid are added to the same silicate residue. The technique can be useful to determine if an element exists in more than one structural site in a given crystal structure (Brindley and Youell, 1951; Osthaus, 1956; Grandquist and Sumner, 1957). Together with other data, such as radiogenic argon retentivity, information about the structural nature of those sites can then be obtained.

In a large excess of acid, the dissolution of silicates similar to chlorite, which dissolves congruently, is a first-order reaction (Ross, 1969). This means that a plot of the log of the proportion of the original amount of an element still remaining in the solid vs. time will be linear. The proportion remaining is expressed as α, the percentage of the original content. The slope of the line in such a log concentration plot is the first-order rate constant of dissolution. If, on the other hand, a crystalline solid dissolves incongruently, in which an element in one part of the structure (site 2) dissolves more rapidly than the element in the main part of the structure (site 1), a log concentration plot of that element vs. time will be a curve that is a composite resulting from the first-order removal of each of the two components (Figure 1). The early part of the dissolution curve will be dominated by the rapid dissolution of materials in site 2 which soon become depleted. At this point, the curve becomes asymptotic to the line representing the dissolution of the more slowly dissolving component, i.e., the materials in site 1. The total dissolution curve can be deconvolved by subtracting the site-1 dissolution line from the total curve. The remainder, normalized to 100%, is a line on the log concentration plot whose slope is the first-order rate constant of the dissolution of materials in site 2.

Thompson and Hower (1973) used progressive acid dissolution of K from mixed-layer glauconite/smectites (G/S) and illite/smectites (I/S) to show that in general non-exchangeable K exists in two sites. Typically, about 10–20% of the total K is in the site more prone to dissolution (site 2), and the remainder is in site 1. At the time of Thompson and Hower's work, glauconite pellets containing glauconite or G/S typically gave K/Ar and Rb/Sr *measured* ages (or "dates") that were 10–20% too low compared with independent assessments of their depositional age. It is now known that many such glauconite materials give K/Ar dates which are close to their depositional age, and criteria are being developed to recognize and select such materials (Odin and Hunziker, 1974; Odin and Rex, 1982).

Thompson and Hower (1973) proposed that a prime cause of low dates for G/S (and by analogy, for the mineralogically similar I/S) is that site 2 for K is not structurally capable of retaining Ar. They proposed that K/Ar measured ages on G/S and I/S must be routinely corrected by acid dissolution determination of the proportion of K in site 2 and then substracting that from the total measured K. Because of the long half life of ^{40}K, the K/Ar date is nearly a linear reflection of the ratio of radiogenic Ar to K, thus the proposal of Thompson and Hower causes the measured age to

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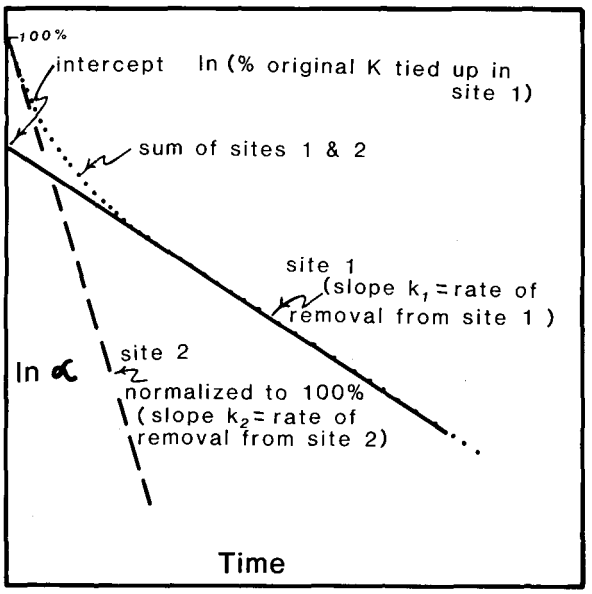


Figure 1. General form of a log concentration vs. time acid-dissolution plot for K being removed from two different structural sites at two different first-order rates. The dotted curve plots ln α vs. time, where α is the percentage of the initial K content still remaining in the solid as deduced by subtracting the running total of dissolved K in the dissolution increments from the initial content. At a given time t, $\alpha_t = \alpha_{1,t} + \alpha_{2,t}$, where $\alpha_{1,t}$ and $\alpha_{2,t}$ present the percentage of the original K that still remains in sites 1 and 2, respectively, at time t. The solid straight line is the first-order dissolution plot for site 1 alone, produced simply by extrapolating the linear asymptote of the dissolution curve back to t = 0. Its initial y intercept, $\alpha_{1,0}$, is the percentage of the original K content that initially existed in site 1; $\alpha_{2,0}$ (=100% − $\alpha_{1,0}$) is the initial percentage in site 2. The first-order dissolution of site 2 (dashed line) is conveniently plotted on the same graph by normalizing $\alpha_{2,t}$ such that $\alpha_{2,0}$ = 100%. Thus, this process deconvolves the ln α curve into its two components; note however, that the curve is *not* the sum of the ln α_1 and ln α_2 lines.

be adjusted upwards. The correction for the samples they investigated would increase their measured age by about 10–20%, which matched the discrepancy at that time thought to exist for glauconite dates. The Thompson-Hower model has remained in the literature, and the correction factor has been applied in at least one geochronological study to correct the ages of illitization of I/S in meta-bentonites (K-bentonites) formed by tectonic burial during overthrusting (Hoffman *et al.*, 1976).

A test of the Thompson-Hower model and the applicability of their age correction factor are the subjects of the present paper. Progressive acid-dissolution studies were conducted on aliquots of 0.2–0.5-μm-size I/S separated from the identical meta-bentonite sample LT-109 examined by Hoffman (1976). In addition to monitoring dissolved K in the acid increments, the solid residues of individual dissolution steps were also analyzed for their K and $^{40}Ar^*$ (radiogenic component of the total extracted argon) contents. Furthermore, following a suggestion in Thompson and Hower (1973), tests were made at two different acid normalities for which theoretically the same site distributions should result. All of Thompson and Hower's (1973) experiments were conducted at a single normality, 0.5 N.

EXPERIMENTAL PROCEDURE

Sample LT-109 is from a 30-cm-thick bentonite of upper Cretaceous age that underwent burial metamorphism to become a K-bentonite during Laramide thrusting of the Lewis thrust plate over the disturbed belt in Montana (Hoffman, 1976). The sample was collected just downstream from the Swift Reservoir on the Marias River.

About 10 g of the 0.25–0.5-μm-size range (equivalent spherical diameter) of sample LT-109 was separated using a Sharples supercentrifuge. The separate consisted of R=1 I/S, interpreted by the Reynolds and Hower (1970) method to contain 65% illite (Hoffman, 1976). This bentonite was re-collected by Eslinger *et al.* (1979) who reported their sample to be R=1 I/S, containing 78% illite layers. The sized sample was saturated with Na, extensively dialyzed in deionized water, dried, and divided into about 20, 200-mg aliquots. The progressive acid-dissolution procedure was identical to that employed by Thompson and Hower (1973) and Hoffman *et al.* (1976), except (1) the studies were performed in nitric acid, and (2) the experiments were conducted such that the residue of many of the dissolution intervals could be analyzed for K and $^{40}Ar^*$. Nitric acid was used instead of HCl to avoid complications in the argon mass spectrometry caused by chloride contamination. In addition, Janet Hoffman made available to us the results of her 0.5 N HCl dissolution of the same size fraction independently obtained from her piece of sample LT-109. Her results are included for comparison.

All trials were conducted for a 12-hr period during which samples were magnetically stirred at 80°C in 50 ml of acid. At the end of every 30-min interval the hot acid was quickly replaced with fresh acid, following a rapid contrifuging and pipeting off of the previous batch for analysis. Three trials were conducted, the first of which was a pilot trial carried out in 1.0 N HNO_3 in which data were obtained during the early dissolution period. Unfortunately, the amount of K in some residues in the pilot trial was not measured because the entire sample was used for argon analysis. These values had to be interpolated from adjacent intervals. Two detailed trials were then conducted, one in 0.5 N and one in 1.0 N HNO_3. These trials focused on the time intervals after 4 hr; complete K and $^{40}Ar^*$ measurements were made on the residues.

In a standard progressive acid-dissolution trial, only

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the solution is analyzed, thereby requiring only one aliquot of sample. Progressively examining the residues greatly complicated the procedure by requiring that many aliquots be tested in parallel. A *complete* 12-hr trial (which was never conducted) sampled at 30-min intervals would have required starting with 24, 200-g aliquots of clay. For example, the 3.5-hr residue would have been the residue after the seventh 30-min interval, which would then have been retired from further dissolution so that it could be dialyzed, dried, partitioned, and analyzed separately for K and $^{40}Ar^*$. In such a trial, the standard dissolution data obtained from the solution would have been collected only for the 24 acid changes for the one 12-hr sample that endured through the whole trial.

The K content of the solutions and solid residue is reported as wt. % K_2O and was measured in the 50-ml acid batches on an IL 143 flame photometer, using an internal Li standard. The blank represented only 1–5% of the lowest amount of dissolved K registered and was not significant in terms of the experimental goal. The K and $^{40}Ar^*$ contents of the residue were measured on separate aliquots of about 50–70 mg. For K_2O, the sample was fused in anhydrous $LiBO_3$. The separate aliquot for $^{40}Ar^*$ was fused in vacuum, and the extracted Ar was mixed with a calibrated ^{38}Ar spike. None of the samples were pre-baked. The radiogenic component of the total extracted Ar for all samples was between 70 and 88%, thereby allowing precise correction for the atmospheric component. Interlaboratory LP6 biotite standard was routinely run on the argon system and produced the accepted value of $19.3 \pm 0.2 \times 10^{-10}$ mole/g. Typical uncertainty in the K analyses was about 1%, and that for Ar, about 2% of the values reported. Unlike the K data for the residue which fell on a smooth curve vs. time, scatter was found for the Ar data vs. time in this study. This scatter implies that a few argon measurements may have had a random error as great as 10% of the reported value. Such errors are probably due to an unusual degree of analytical error related to the large amount of sample handling needed for this experiment and to the weighing and transferring of small amounts of clay into the Ar extraction packets.

RESULTS

Dissolved potassium vs. time, acid type, and acid normality

Thompson and Hower (1973) were able to deconvolve their K-dissolution curves into three component lines representing three sites. Because site 3 contained only a small amount of K and was very rapidly depleted, it clearly represented K in cation-exchangeable positions. No K was found in site 3 in the present experiments, because our pretreatment of the samples (and Hoffman's) included a Na-saturation step. Such pre-removal of exchangeable K should be a standard procedure for any K/Ar study of clays.

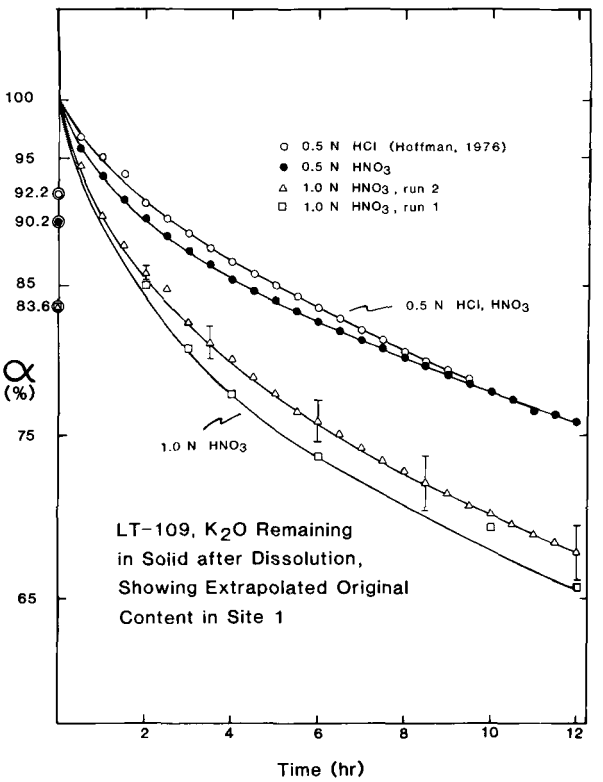


Figure 2. Acid dissolution curves for K (reported as K_2O) from four separate trials. Dissolution clearly correlates with acid normality, the curves at 1.0 N being displaced lower and retaining a concave-up shape to the end of the trial in contrast to the 0.5 N curves. The circled symbols on the y axis are initial intercepts, $\alpha_{1,0}$, extrapolated from a linear fit to the 6.0–12.0-hr segment of each curve. These represent the percentage of the total original K content that was in site 1, as interpreted by the two-site deconvolution.

Figure 2 shows plots of log concentration vs. time for three trials in nitric acid and for Hoffman's (1976) 0.5 N HCl dissolution. The curves agree closely for the two trials at 0.5 N HNO_3 and 0.5 N HCl and for the two trials at 1.0 N HNO_3, but these two sets of curves are strikingly different, demonstrating that the dissolution curve is strongly dependent on acid normality, but not on acid type. Of key importance is the fact that if one assumes incongruent dissolution for only two K sites, the initial intercept of the line to which the curve becomes asymptotic after long times (the site 1 part of the curve) is quite different for the two normalities: the 0.5 N dissolution curve indicates about 91% of the K is in site 1, whereas the 1.0 N curve indicates 84%. These data conflict with the assumption of the two-site dissolution model that a unique proportion of the K is in site 1.

A detailed examination of the 1.0 N curves reveals a slight concave-up character persisting to the end of

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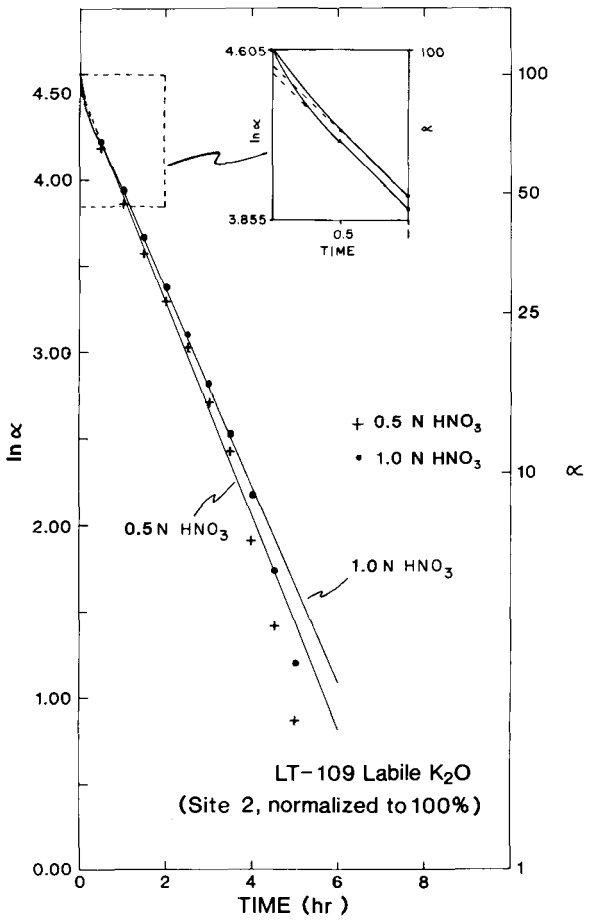


Figure 3. Acid dissolution plot for the site-2 component of K (reported as K_2O) in sample LT-109. The curves were derived from Figure 2 according to the procedure outlined in Figure 1, and assume a two-site distribution for K. As expected, the linear nature of these plots demonstrates that no exchange-site K is present.

Table 1. Proportion of K in each site (using either two- or three-site deconvolutions of log concentration curves) and first-order rate constants of dissolution.

Acid	Site 1	1A	1B	Site 2
0.5 N HCl (two sites)				
Fraction of total K_2O	0.922			0.078
k (hr^{-1})	0.017			0.61
0.5 N HNO_3 (two sites)				
Fraction of total K_2O	0.902			0.098
k (hr^{-1})	0.015			0.62
1.0 N HNO_3 (two sites)				
Fraction of total K_2O	0.836			0.164
k (hr^{-1})	0.023			0.58
1.0 N HNO_3 (three sites)				
Fraction of total K_2O		0.836	0.066	0.098
k (hr^{-1})		0.023	0.040	0.85

the trials, which is not evident in the 0.5 N curves. Two glauconites of the 10 samples Thompson and Hower (1973) investigated, both treated in 0.5 N HCl, showed an even more pronounced concave-up pattern, as opposed to the linear patterns of the other eight. These two samples are heterogenous mixtures with respect to I/S expandability, and the concave-up curvature is thus readily explained as representing part of a continuum of subsites in the site 1 category. Sample LT-109 has had a simple geologic history and is mineralogically homogeneous. As discussed below, the slight concave-up character of the 1.0 N dissolution curves probably resulted from site 1 actually comprising subtly differing subsites each having slightly varying rate constants. For example, the subsites could represent particle sizes distributed within the 0.2–0.5-μm range, the smaller clay sheets dissolving fast enough to be detected in the 12-hr trial in 1.0 N acid, but not in 0.5 N acid.

The sensitivity of the log concentration curve to acid strength clouds the assignment of K to site 1. For sample LT-109 the assignment of 83.6% of the total K to site 1 as determined for a two-site model of the 1.0 N trial is clearly too low a value because of the multi-site concave-up dissolution curve produced. Values of 90.2–92.2% for site 1 determined from the initial intercept of the 0.5 N dissolutions represent better estimates of the proportion of K in site 1 subsites because these curves become apparently linear after about 8 hr.

Figure 3 shows the dissolution of the rapidly dissolved components in site 2 after deconvolution of the curves in Figure 2 by subtracting the site 1 component and normalizing the remainder to 100%. The linear nature of these plots demonstrates that little or no K exists in such an easily dissolved exchange site (site 3).

The slopes of the component lines derived from Figures 2 and 3 for sites 1 and 2 represent the first-order rate constants of dissolution for these sites at 0.5 and 1.0 N acid, respectively, and 80°C. These values are tabulated in Table 1. Using the single site 1 model for the 1.0 N trial resulted in slopes that are virtually the same as for the 0.5 N trials. Such a similarity of slopes is illogical because it is the H ion that promotes dissolution of the clay. The lack of an increase in the rate constants at the higher normality is further evidence that the single-site model for site 1 in the 1.0 N acid trial is not correct, and that site 1 must represent a group of subsites of slightly decreasing solubility.

To rectify this situation, the 1.0 N log concentration curve was deconvolved on the basis of two simplifying assumptions: (1) that site 1 consists of two subsites 1A and 1B, with subsite 1A being the less vulnerable to acid attack, and (2) that the total fraction of the initial K in subsites 1A and 1B equals 0.902, as indicated by

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the 0.5 N dissolution data. The results of this three-component deconvolution of the 1.0 N trial are also tabulated in Table 1 (case 3b). The reasonably higher rate constants, by comparison with those obtained at 0.5 N, suggest that K distribution in the I/S sample LT-109 is effectively modeled by these results—9.8% of its K is in site 2, 6.6% in site 1B, and 83.6% in site 1A. Sites 1A and 1B are likely to be structurally similar, such that their rate constants of dissolution, although resolvable (0.04/hr vs. 0.027/hr) at 1.0 N, are not resolvable at 0.5 N over the duration and at the temperature employed here. We suggest that site 1B represents the smallest grains in our 0.02–0.5-μm-size spectrum, whereas site 1A represents the main bulk of the sample. In fact, site 1 is likely to be a continuum of slightly different subsites.

Potassium and radiogenic argon in the solid residue vs. time

Figure 4 shows (A) K_2O, (B) $^{40}Ar^*$, and (C) measured age vs. time in the three pertinent dissolution trials. The data for this illustration are listed in Table 2. Relatively smooth curves result except for fluctuations attributed to experimental error in the Ar measurement. The K in the residue exponentially declined from the initial 5.5% K_2O and leveled off at about 4.8% K_2O after about 6 hr at 1.0 N and about 9 hr at 0.5% N acid dissolution. A similar leveling off was detected in the $^{40}Ar^*$ data, but with more scatter.

Curves a and b in Figure 4C show ages expected for the residue from the 1.0 N and 0.5 N dissolution, respectively, vs. dissolution time using the Thompson-Hower model of no Ar retention by site 2. For simplicity, curves a and b were obtained by calculating the proportion of K in site 1 for each residue, without considering any subsites. The asymptotes of these curves, 69.5 and 75.4 m.y., are the ages calculated after all the K in site 2 has been removed, and thus is the corrected age proposed for these samples by the Thompson-Hower model. Of key importance is that after removal of the K from site 2, the actual measured age of the residue did not follow these model curves, but instead remained essentially constant and equal to the 62 m.y. measured age of the starting material. The measured age was equal to the starting value to the end of each trial, when 20 to 30% of the initial K has been removed. Thus, the K in site 2 must have had $^{40}Ar^*$ associated with it, and site 2 had to have been as retentive of Ar as site 1. Thus, the Thompson-Hower hypothesis that K in site 2 should not be counted in the age calculation is incorrect.

Potassium content of sites 1 and 2

The pattern in which wt. % K in the residue rapidly declined and then remained constant affirms that: (1)

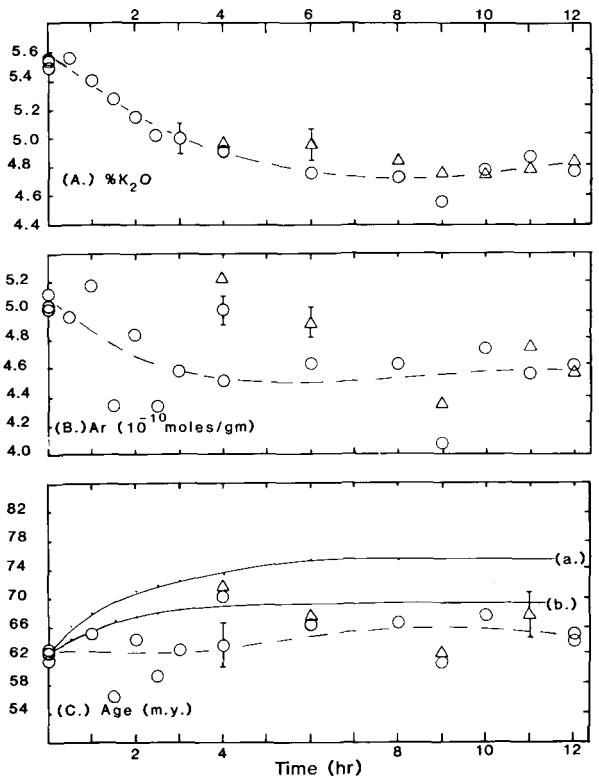


Figure 4. (A) K_2O, (B) radiogenic Ar, and (C) measured age of the solid residue vs. time during progressive acid dissolution. Dashed lines are fitted to the 1.0 N acid dissolution data (circles). Triangles are data for the 0.5 N acid dissolution. Part (C) shows curves of model ages expected for the residues using the amounts of K in sites 1 and 2 remaining in the sample deduced from the two-site deconvolution at (a) 1.0 N and (b) 0.5 N acid and employing the Thompson-Hower (1973) hypothesis that site 2 does not retain Ar. The asymptote values of curves (a) and (b) of 74.4 m.y. and 69.0 m.y., respectively, are the model ages that would be calculated by the Thompson-Hower hypothesis. The data do not match either curve and thus do not support the hypothesis. Use of a three-site deconvolution for (a) yields a curve very similar to curve (b).

at first, the dissolution was incongruent resulting in depletion of K from site 2, during which time some of the K in site 1 was dissolving; (2) once K was completely dissolved from site 2, the constant amount of K in the residue with continual removal of K into solution means that site 1 represented the congruent dissolution of the remainder of the mineral structure. This remainder (site 1) contained 4.8 wt. % K_2O, whereas site 2 must have contained more than 4.8 wt. % K_2O in order for its removal to have caused a reduction in the residue from a starting value of 5.5 wt. %. Material-balance equations can be applied to calculate the wt. % K in the material dissolved during a dissolution increment because data are available for the residues before and after any dissolution increment

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Table 2. K/Ar data for acid-treated residues of illite/smectite sample LT-109.

Time	K_2O Acid strength		$^{40}Ar^*$ Acid strength		Age (10^6 yr)[1] Acid strength	
	0.5 N	1.0 N	0.5 N	1.0 N	0.5 N	1.0 N
0.0	5.539	5.539	5.115	5.115	62.5	62.5
0.0	5.545	5.545	5.007	5.007	61.6	61.6
0.0	5.50	5.50	5.046	5.046	62.6	62.6
0.5	—	5.52	—	4.958	—	61.3
1.0	—	(5.40)	—	5.1701	—	(65.2)
1.5	—	5.28	—	4.344	—	56.2
2.0	—	(5.15)	—	4.830	—	(64.1)
2.5	—	5.03	—	4.345	—	59.1
3.0	—	(5.00)	—	4.590	—	(62.8)
4.0	—	(4.92)	—	4.512	—	(63.5)
4.0 (B)	4.98	4.92	5.244	5.075	71.7	70.3
6.0	4.96	4.77	4.914	4.642	67.9	66.4
8.0	4.84	4.74	—	4.634	—	66.6
9.0	4.78	4.56	4.360	4.092	62.3	61.0
10.0	4.75	4.79	—	4.745	—	67.6
11.0	4.79	4.87	4.755	4.570	67.6	—
12.0		(4.78)	4.570	4.617	—	65.0
12.0 (b)	4.84	4.78			—	64.3

Radiogenic argon ($^{40}Ar^*$) 10^{-10} mole/g; all extractions produced Ar between 70 and 88% radiogenic (the rest being atmospheric as precisely deduced from the extracted $^{40}Ar/^{36}Ar$ ratio). ( ) K_2O not measured, but interpolated, doubling the age uncertainty approximately to ±5 m.y.

[1] Calculated age using constants recommended by Steiger and Jager (1977); each has an uncertainty of about 2.5 m.y.

together with the weight of K dissolved in solution during that increment.[2]

In calculating the wt. % K_2O in the material that dissolved from site 2, data were collected only for the trial at 1.0 N HNO_3 during the early part of the dissolution when the bulk of the K in site 2 was dissolving. The mass-balance calculation is very sensitive to small errors in the measured amount of K in the residue before and after an increment of dissolution; thus, this value is more reliable if it is averaged over several contiguous increments. Such an average is tabulated in Table 3 for the one relevant trial. This average suggests that the material that dissolved during the first 6 hr contained 11.6 wt. % K_2O. Site 2 is richer in K_2O because the material that dissolved came not only from site 2, but from that part of site 1 that dissolved in the first 6 hr plus exchangeable material on the clay. For example, 200 mg of Na-saturated sample LT-109 was expected to contain 1.4 mg of readily dissolved, exchangeable Na.

To calculate the amount of K in site 2, the contribution from site 1 was calculated and subtracted from the net 11.6% K_2O, using three-component deconvolution involving subsites 1A and 1B. This calculation shows that site 1, which contained 4.8 wt. % K_2O, contributed 0.50 of the dissolved K in the first 6 hr, and that the non-site 1 material that dissolved contained 18.4 wt. % K_2O. Allowing for the expected exchangeable Na, which undoubtedly dissolved in the first 0.5 hr and further diluted the K in the dissolved material from site 2, the calculation yields a value of 20 wt. % K_2O for site 2, with an estimated maximum uncertainty of ±4 wt. %. The calculated value shifted to 17.5 wt. % K_2O if the two-component deconvolution was used for the calculation. The material-balance calculation reveals that 90% of the 4.8 wt. % K_2O in site 1 comes from site 1A and only about 10% from the slightly more acid vulnerable faster site 1B.[3]

DISCUSSION

Implications of the data for the crystal structure of I/S

Thompson and Hower (1973, 1975) showed the value of progressive acid dissolution studies for understanding cation distribution in G/S and I/S. They cited the difficulty in assigning a position in the mixed-layer structure for a site 2 whose dissolution rate was far too slow to be the exchangeable site, but faster than site 1, which they assigned to the interlayer position. The present study has produced further information about the K sites to guide the structural interpretation. Spe-

[2] Wt. % K_2O of dissolved material = grams of K_2O dissolved/grams of material dissolved, where, grams of material dissolved = grams of residue "before" − grams of residue "after" and grams of residue "after" = grams K_2O "before" − grams K_2O dissolved/wt. % K_2O "after", where "before" and "after" refer to a specified dissolution increment.

[3] Because the rate constants for sites 1A and 1B are so similar (Table 1) and because the K in site 1B comprises such a small fraction of the small amount of K released after the depletion of site 2, it was not possible to distinguish whether the wt. % K in site 1B in fact differs from that in site 1A.

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Table 3. Weight percent K_2O of dissolved material (by material balance) in 1.0 N HNO_3 trial.

Time interval (hr)	K_2O in total dissolved material (%)	Fraction of K_2O contributed by site 2[1]	Weight percent K_2O, site 2[2]
0–1.5	9.4[3]	0.73	
0–2.5	12.8	0.67	
0–4	11.6	0.59	
0–6	11.6	0.50	18.4

[1] Calculation utilizes the three-site deconvolution of the 1.0 N HNO_3 data; Table 1.

[2] Site 2 includes exchange sites, which here are saturated with Na^+ whose release dilutes the K_2O assigned to site 2.

[3] This initial interval shows strongest effect by release of exchangeable Na^+.

cifically: (1) Site 2 is argon-retentive, similar to site 1; (2) Site 1 represents dissolution of the whole crystal structure after removal of site 2; (3) Material that dissolves with site 1 contains 4.8 wt. % K_2O; and (4) Material that dissolves with site 2 contains 20 ± 4 wt. % K_2O.

The match of calculated and natural XRD patterns (Reynolds and Hower, 1970) shows that a typical I/S particle is about 10 tetrahedral-octahedral-tetrahedral (TOT) layers thick. Thus, a 65% illitic I/S (as in sample LT-109 which contains 5.5 wt. % K_2O) could consist of about 5 or 6 interlayers sandwiched within 10 TOT layers (assuming that a 10-layer 100% illite would contain about 9.4 wt. % K_2O). Sample LT-109 is similar in character and origin to the I/S in Cretaceous metabentonite Mb 235 (Cb) used by Nadeau *et al.* (1984a, 1984b), except that it is more illitic (65 vs. 52%). Those studies demonstrated by transmission electron microscopy (TEM) that sample Mb 235 consists of nearly 100% fundamental illite particles, 20 Å thick. Except for particle thickness, the consequences of the Reynolds and Hower (1970) continuous multi-layer model and the Nadeau *et al.* (1984a, 1984b) fundamental particle model for I/S are quite similar. For example, although not explicitly stated, both imply a lack of symmetry in tetrahedral Al distribution, there being 1 Al to 3 Si on the K interface of a TOT layer and none on the smectite interface. In the fundamental particle model, sample LT-109 should be like its geologically similar counterpart sample Mb 235, but instead of being 100% fundamental illite particles 20 Å thick, it should contain a significant number of particles 40 Å thick. In the present studies of sample LT-109, after prolonged dissolution (5–9 hr) and complete removal of site 2, the K_2O content of the I/S asymptotically approached 4.8 wt. %. This content is about what would be projected according to the fundamental particle model for a uniform population of 100% fundamental illite particles (or conversely, by the Reynolds and Hower (1970) continuous multilayer model, an I/S containing 50% illite layers). This projection results because 20-Å-thick fundamental illite has one K layer to every two TOT units in contrast to thick, well-crystallized illite containing 9.4 wt. % K_2O and (n − 1) K layers for n TOT layers, where n > 10 (Nadeau *et al.*, 1984b). Thus, this residue after removal of K from site 2 is probably composed of fundamental illite particles. This interpretation accounts for the uniformity with which K in site 2 congruently dissolves.

With respect to the more difficult problem of the structural position of K in site 2, Thompson and Hower (1973) proposed that K was present in "the tetrahedral layer surrounded by 6 oxygens." Basically this position is equivalent to the position along a smectite interface of a TOT layer that K occupies within illite layers (site 1); however, in illite, it is bound there because of Al substitution in the adjoining tetrahedral layers. The K site we propose to be site 2 is similar to that of Thompson and Hower. To be Ar retentive, however, the K in site 2 must be ionically bound so that the K cavity is closed from both sides and the rare radiogenic Ar atom is quantitatively retained there.[4] Thus, like Thompson and Hower, we interpret site 1 to be the mica-like K site in illite layers (or particles) of the I/S; however, we interpret site 2 to be the equivalent site in a *partly converted* interlayer between two smectite layers that happen to be in an *intermediate* structural stage. In such a partly converted interlayer, less than 25% of the Si in the tetrahedral layer will have been subsituted by Al and thus only a portion of the basal holes for K will have actually been filled by K. Such partly filled K layers should be easier targets for replacement by H ion and incongruent acid dissolution, as further discussed below.

Although mass-balance calculations show that site 2 has a high K content (20 ± 4 wt. % K_2O), the question arises about the nature and source of the other 80% of material. This material, in addition to K, must come from other ions residing in the partly converted interlayer or in some of the adjacent tetrahedral layers disrupted by the dissolution of K in site 2.[5]

Speculation about the structural character of site 2 in sample LT-109 has implications about the kinematics of how an I/S becomes more illitic in character during diagenesis. Our interpretation of site 2 implies that an intermediate step, in which the K interlayer is only partly filled, occurs prior to the development of

[4] In a 60-m.y.-old illite, only 1 in 4×10^6 K atoms will have decayed to $^{40}Ar^*$, meaning that typically one $^{40}Ar^*$ atom will be present for every 20, 0.2–0.5-μm fundamental clay grains.

[5] Compared with the dominant mass of ions in site 1, the non-K part of site 2 is such a small amount of material that even if one restores it all to site 1, the calculated K in site 1 would be impacted only slightly, shifting it from 4.8 to 4.65 wt. % K_2O.

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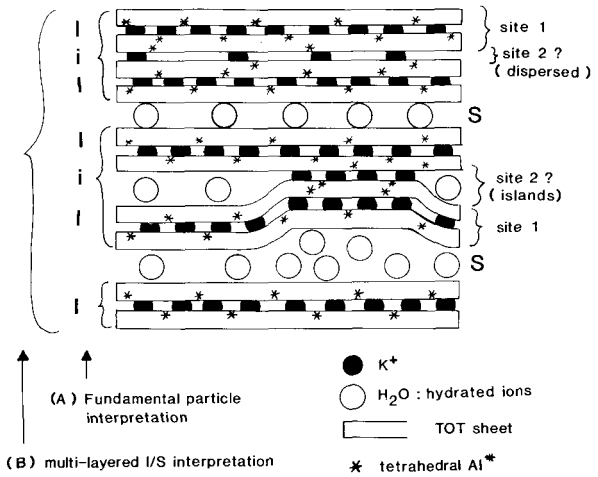


Figure 5. Schematic representation of K in sites 1 and 2 in the I/S crystal structure. The Ar retentivity of site 2 implies that this site represents an intermediate stage in the illitization of a smectitic interface, as discussed in the text. Two hypothetical forms of this intermediate stage are shown within the same grain at the right of the figure. Two prevailing views of I/S particle structure in the "c" direction are shown at the left. I = illite; i = intermediate-stage illite; and S = smectite. Note that the incomplete interlayer with dispersed K would register identically to a completely filled illite interlayer by X-ray powder diffraction, whereas the island interlayer would not.

a complete illitic interlayer having a full complement of K, balanced by tetrahedral Al substitution.

The Ar retentivity of this partly filled interlayer (site 2) argues that of two possible kinematic pathways for inserting a certain amount of K (and Al) into I/S, nature prefers to complete the filling of those smectitic interlayers which have already partly converted rather than widely distributing the same amount of K equally into virgin interlayers. In the latter product, the binding of the sheets near a site where ^{40}K has decayed to $^{40}Ar^*$ would probably be too weak to retain that Ar atom. Thus, during the illitization of smectite, once the process of Al and K insertion has started in a particular interlayer, succeeding insertions of Al and K are more likely nearby in that same interlayer.

Figure 5 shows schematically two possible forms of site 2 in which the K could be sufficiently dense in a partly filled interlayer to bind $^{40}Ar^*$ strongly. One possibility, shown in the upper part of the drawing, is that the K is confined to such a partly filled interlayer, but at relatively low density. The lower part of the drawing shows an alternate possibility in which the K is concentrated (along with the adjacent tetrahedral Al substitution) within the smectite interlayer in high-density "islands." The two mechanisms can be distinguished by XRD because the collapsed interlayer containing dispersed K would cause the adjacent TOT layer to be "counted" as a complete illite layer, whereas the interlayer containing K islands would not. The first possibility explains in part why R=0 I/S containing <50% illite layers is reported to have lower K contents per illite layer than R=1 I/S (Środoń and Eberl, 1984). The island mechanism (which we prefer) is similar to a nucleation-growth process.

With reference to their fundamental particle model, Nadeau *et al.* (1984b) addressed the question of how illitization proceeds, specifically referring to an I/S having <50% illite layers transforming to an ordered I/S having 50% illite layers. For such a reaction they categorically stated that fundamental smectite particles *dissolved* while fundamental illite precipitated. Sample LT-109 is sufficiently advanced in terms of illite content that in the fundamental particle model it essentially should no longer contain fundamental smectite particles. Thus, for sample LT-109, further illitization must proceed by fundamental illite particles becoming thicker (Nadeau *et al.*, 1984b). How this process occurs and whether it also involves solution was not specifically addressed by Nadeau *et al.* (1984b). We submit that solution may not be necessary at any level of illitization. Our interpretation of the existence of an intermediate, partly filled interlayer between two fundamental illites, at least for fundamental illite particles to become thicker, implies that illitization proceeds by conversion of the smectite interface or interlayer during which time the TOT structure remains assembled, not by solution and reprecipitation. That such a transformation can occur at the smectite-like *interface* between fundamental illite particles lends credence to the possibility that it could also happen for the interface between smectite fundamental *particles*. Solution and precipitation need not be involved in the illitization of I/S at any range of expandability.

Implication of results for K/Ar dating of illite clay

Sample LT-109 has two K sites whose degree of binding within the crystal can be differentiated into a relatively weak site (1) and a relatively strong site (2). Ar retentivity of these two sites, however, has been the same throughout this sample's geologic history. Following the reasoning of Thompson and Hower (1973), site 2 should retain less Ar than site 1. For sample LT-109, which formed during overthrusting and tectonic-burial metamorphism of a Cretaceous section (Hoffman *et al.*, 1976), the internal age concordance of site 1 and site 2 argues that neither site has preferentially lost Ar. Thus, the 62 m.y. measured age is the true *mean* age of formation of the illitic clay. Considering the tectonic-burial process, sample LT-109 could have formed over a period of time. The age concordance of the two sites suggests that the span of time over which this illitic clay formed (centered at 62 m.y. ago) was narrow, in agreement with Hoffman's (1976) modeling of that process. This is so because the K in site 2 might

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be expected to have been incorporated toward the end of that tectonic-burial process compared to the K in site 1. Finally, the dissolution treatment in the present study was harsh to the extent the clay underwent significant congruent dissolution, yet the residue was still fully Ar retentive. These results qualitatively support the integrity of the illite K/Ar clock. Evidently, once the two TOT sheets of illite are bound together about a ^{40}K atom that subsequently decays to $^{40}Ar^*$, the dimensions of the hole and of the $^{40}Ar^*$ (1.5 or 1.9 Å, depending on whether or not it is ionic) and the degree of binding of the sheets prevent Ar from escaping.

The evidence for the argon retentivity of site 2 in an I/S not only applies to all I/S, but also to mineralogically comparable glauconites (G/S). If samples of I/S and G/S have not subsequently been strongly reheated, their ability to retain argon is not a factor in causing low ages. Rather, geologic factors such as sustained growth over a long period of diagenesis or recrystallization in response to diagenesis are more likely causes of demonstrably low dates. Thus, illitic clays are extremely useful for timing those aspects in the history of sedimentary rocks which control the formation of the component.

CONSEQUENCES

Several consequences of the results obtained here are listed below:

1. No XRD observations were made of the residues, but the residue left after removal of K from site 2 should be similar to an ordered I/S with 50% illitic layers, because the residue probably consists entirely of fundamental illite particles.
2. If I/S containing 50% illite layers, similar to the sample Mb 235 discussed by Nadeau *et al.* (1984a), consists entirely of fundamental illite particles, progressive acid dissolution of such material should reveal no K in site 2.
3. I/S that contains $\ll$50% illite layers effectively represents an early stage of illitization and thus may have a relatively high proportion of its small K content in partly filled interlayers. If so, it should contain a higher proportion of K in site 2. Thompson and Hower (1973) obtained higher proportions of K in site 2 in I/S having a high percentage of smectite layers. The high proportion of K in site 2 in such I/S (and by analogy such G/S) may be related to their observed lower K content per illite layer (Thompson and Hower, 1975; Środoń and Eberl, 1984).
4. If illitization proceeds by transformation of smectite-like interfaces without dissolution of the smectite or illite, detrital I/S which contains initial illite layers will show Ar retention by those inherited layers during progressive diagenetic illitization. The data for I/S in the deeply buried Frio Shale was so interpreted by Aronson and Hower (1976), but an alternate interpretation was presented by Morton (1985).
5. Progressive acid dissolution studies combined with XRD, TEM, and K/Ar observations of a continuous series of I/S formed by progressive contact metamorphism of a single, thin bentonite bed sampled outward from a dike (Nadeau and Reynolds, 1981) or in a hydrothermal aureole (Inoue and Utada, 1983), or by burial metamorphism of a single, thick bentonite sampled inwards from the contact (Bystrom, 1956; Altaner *et al.*, 1984) could provide more information about the kinematic pathways that create new illite interlayers.

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