

# Geochemical Processes at Mineral Surfaces

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## Potassium Fixation in Smectite by Wetting and Drying

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Potassium-smectites with various layer-charge densities and layer-charge locations were subjected to as many as 100 wetting and drying cycles, thereby producing randomly interstratified illite/smectite that contained illite layers stable against exchange by 0.1 N SrCl<sub>2</sub> or 1 N NaCl. The percentage of illite layers formed by this process in montmorillonite was proportional to layer-charge and, based upon very limited data, their stability with respect to subsequent exchange was inversely proportional to alpha, the angle of tetrahedral rotation. Most of the illite layers were produced during the first 20 cycles. Sodium-smectites treated in wetting and drying experiments that contained potassium-minerals (e.g. feldspar) formed illite layers by fixing potassium released from dissolution of the potassium-minerals. The presence of NaCl, KCl, and HCl in the experimental solutions had little effect on reaction rates, but CaCl<sub>2</sub> decreased and KOH increased the rate of illitization. The reaction with KOH increased layer charge, whereas, in all of the other experiments, layer charge remained constant. Oxygen isotope data confirmed the conclusion drawn from chemical data that the reaction mechanism for illite formation at high pH (chemical reaction of 2:1 layers) differed from that found at more acid pH (mechanical rearrangement of 2:1 layers around potassium). The wetting and drying process may be responsible for producing mixed-layer illite/smectite from smectite at surface temperatures, and for accelerated dissolution of sparingly soluble potassium-minerals in sediments and soils.

One method for studying reactions that occur at the mineral-water interface is to concentrate the interface by drying a clay mineral slurry. Certain reactions are promoted by this process, for example, reactions that respond to Brønsted acidity (1, 2). Repeated

wetting and drying (WD) cycles may be used to increase reaction yield.

Another type of reaction that responds to WD cycles is the fixation of K and  $\text{NH}_4$  ions by smectite (3-7). The fixation of K in smectite has been studied extensively by soil scientists because of its effect on the availability of plant nutrients. The reaction also decreases smectite's ability to swell, decreases its cation exchange capacity (CEC), and modifies its Brønsted acidity. Therefore, an understanding of this phenomenon is applicable to many fields of study that are concerned with swelling clays, fields such as soil fertility, soil mechanics, waste disposal, clay catalysis, and the geochemistry of ground and surface waters.

#### Previous Work

A review of the literature concerning K-fixation by smectite reveals the following patterns of reaction:

(1) *Simple K-exchange of smectite without WD forms illite-like layers in the clay, but this reaction is completely reversible with respect to exchange by cations having substantial hydration energy.* For example, Weaver (8) reported that smectite derived from the weathering of muscovite (Womble shale) collapsed to 1.0-nm during K-saturation, but re-expanded completely during Ca-exchange as long as heat was not applied. K-Ca exchange isotherms for smectite (9-11) show complete reversibility, even though absorption sites with enthalpies similar to mica and vermiculite are present, and even after heating to 300°C. When K-exchanged smectite is exchanged by cations with minimal hydration energy, however, some of the K may remain fixed (i.e. non-exchangeable with respect to a standard cation exchange procedure) even though the clay has not been subjected to WD cycles. For example,  $\text{NH}_4$ , a cation with a hydration energy similar to that of K, also becomes fixed, and, therefore, replaces only part of the K, trapping the rest in collapsed interlayers. Both K and  $\text{NH}_4$  are completely replaced, however, by exchange with Na, Mg, and Ca (12, 13). Simple K-exchange may produce an interlayering of three types of layers in smectite (14). For example, K- and  $\text{NH}_4$ -smectites investigated by direct Fourier analysis of their X-ray diffraction (XRD) patterns (15) were determined to be composed of randomly interstratified 1.0/1.26/1.56-nm layers (air-dry) or 1.0/1.4/1.68-nm layers (ethylene-glycol treated). More of the contracted (1.0-nm) layers were found in air-dry samples than in glycolated samples, thereby confirming earlier work on the sensitivity of the structure of K-smectite to solvent type (16). The structure also is sensitive to relative humidity (17).

(2) *The percentage of illite layers produced by K-exchange in smectite is proportional to the CEC of the clay (18-21).* Schultz (22) determined that among 83 smectites studied, only minerals of the Wyoming type [charge less than about -0.40 equivalents per  $\text{O}_{10}(\text{OH})_2$ ] do not change XRD characteristics after K-exchange and heat treatment, and that total layer charge, rather than charge location, is the important factor in determining the extent of layer expansion. Yaalon and Koyumdjisky (23) reported that high-charge smectites fix K by simple exchange with respect to subsequent  $\text{NH}_4$ -exchange, but that neither cations are fixed in low-charge materials.

(3) *Wetting and drying of K-exchanged smectite may fix K irreversibly, fixation being defined as a lack of K-exchange with respect to a standard-exchange procedure, such as shaking overnight in 1 N NaCl.* Wetting and drying experiments, performed with several different smectites and four cations (K, Na, Ca, Mg), indicated that only K is fixed, and that the original CEC of the smectite is decreased by as much as 52% by K-fixation (18). Small quantities of K are fixed without drying by illitic material, but WD is necessary for irreversible fixation by smectite (19). One complication is that interlayer Al- and Fe-complexes can block K-fixation (19).

(4) *The mechanism of K-fixation appears to be a trapping of dehydrated K-ions in "hexagonal" holes between 2:1 layers.* Wetting and drying may mechanically rearrange 2:1 layers around K into more stable configurations; i.e., line up "hexagonal" holes across interlayer space and change the coordination of interlayer K-ions from prismatic to octahedral by rotating adjacent 2:1 layers by  $\pm 60^\circ$ . The reaction appears to result from an interaction between cation-hydration energy, 2:1 layer-charge density, and structural arrangements between adjacent 2:1 layers.

Page and Baver (24) suggested that the unique ability of K to be fixed by smectite is related to its ionic size, the dehydrated K-ion having the correct radius to fit into "hexagonal" holes in the basal oxygen planes of the 2:1 layers. However, potassium's minimal hydration energy also has been considered to be the major factor in K-fixation (25, 26). The latter hypothesis is consistent with experiments (27, 28) that determined that Cs and Rb also are fixed by smectites and vermiculites, even though these ions are too large to fit comfortably into the "hexagonal" holes. In addition, others (29, 30) have determined that K may not fit well into these holes because of distortions related to tetrahedral rotations in the 2:1 layers. Eberl (31) presented a hypothesis for cation fixation and selectivity by smectite, based on a consideration of cation-hydration energies and smectite surface-charge density. The possibility that a mechanical rearrangement of 2:1 layers during WD is responsible for greater stability is supported by structural studies of K-smectites that showed that K-fixation by WD is accompanied by the development of tridimensional ordering of the initially turbostratic smectite structure (32, 33).

#### Aims of the Present Study

Previous studies have shown that elevated temperatures, such as those prevailing during deep burial, and long reaction times are required to produce illite/smectite (I/S) from smectite by chemical reaction (34-38). However, mixed-layer illite/smectites that have not been recycled from older materials occur in sediments that have never been exposed to elevated temperatures (39, 40), thereby indicating that another mechanism may be responsible for producing I/S at low temperatures. The studies discussed previously suggest that this mechanism is WD. Thus, WD was investigated systematically to discover how smectite-crystal chemistry and how chemical environment affect illite-layer formation by this mechanism. Recent methods for XRD analysis of mixed-layer clays (41-43) permitted a study in greater detail than was possible previously.

### Materials and Methods

Smectites with a range of layer charges and a variation in layer-charge location were chosen for experimentation (Table I). Chemical analyses for some of these smectites, which had been purified and size-fractionated after the methods of Jackson (44), are given in Table II; structural formulae are presented in Table III. The formulae in Table III are average compositions for all of the smectite layers in a given smectite, although each smectite probably has a heterogeneous layer-charge distribution. The starting smectites were analyzed for 2:1 layer chemistry by X-ray spectroscopy (45); starting smectites and experimental products were analyzed for interlayer chemistry by atomic-absorption spectroscopy (46). Coarse-grain K-minerals (Table I) were ground, and then washed by shaking in distilled water overnight, then washed several more times to remove readily soluble K and to clean the samples of very fine (<5 $\mu$ m) material. K-, Na-, or Sr-saturation of the starting smectites was achieved by shaking overnight in 1 N chloride solutions, followed by two more 1 N chloride exchanges, by several washings in distilled water, and finally by dialysis, until chloride could not be detected by the AgNO<sub>3</sub> test. The first Sr-exchange of the experimental products was accomplished by shaking in 0.1 N SrCl<sub>2</sub> overnight; subsequent Sr-exchanges were accomplished by shaking for about 1 hour in 0.1 N solutions. Experimental products then were washed and dialyzed as discussed previously.

WD experiments were conducted at 30°, 60°, and 90°C in a drying oven, by putting 300 mg of clay together with 20 mL of solution in polyethylene-weighing boats. Most experiments were conducted without shaking; 2 WD cycles were completed each day at 60°C. In several experiments, clays were dispersed completely by shaking prior to each drying cycle, and 1 WD cycle was completed per day at 60°C. A Na-K exchange isotherm was determined for the Kinney montmorillonite by overnight shaking of 150 mg of clay dispersed in 100 mL of 0.05 N solutions having different NaCl/KCl ratios.

Solid-experimental products were investigated by powder XRD (automated Siemens D-500 system; the use of trade names in this paper is for identification only and does not constitute endorsement by the U.S. Geological Survey) of oriented, glass-slide preparations solvated with ethylene glycol (42). Clays subjected to WD cycles in distilled water were investigated with no additional treatment, and after exchange with Na or Sr. Clays processed in electrolyte solutions were washed prior to analysis, and then given additional exchanges by dispersion, centrifugation, and dialysis. Clays processed with K-minerals largely were separated from these K-minerals prior to XRD analysis.

Illite contents of the run products were measured by the techniques of Srodoń (43, 44) using crystallite thickness determined from XRD characteristics of the starting smectites. Most illite contents were measured using the 003 and 005 XRD peaks (smectite reflections), but the 003 and 006 peaks (47) were used in the runs that contained muscovite.

Oxygen isotopes were analyzed using the technique of Clayton and Mayeda (69). Data are presented using the standard  $\delta$  notation relative to Standard Mean Ocean Water (SMOW).

Table I. Description of Minerals<sup>1</sup> Used in Wetting and Drying Experiments

Mineral	Source	Size Fraction ( $\mu\text{m}$ )	Pretreatment
<b>Smectites</b>			
Black Jack	Smithsonian Institution	Bulk	None
Cheto	SCMR <sup>2</sup> , SAz-1	<0.2	NaOAc buffer
Ferruginous	SCMR, SWa-1	<0.2	NaOAc buffer
Garfield "A"	Wards <sup>3</sup> , #33B	<0.2	NaOAc buffer
Hectorite	SCMR, SHCa-1	<0.2	1 N NaCl
Kinney	D. D. Eberl (14)	<0.2	NaOAc buffer
Montmorillon	R. E. Grim	<0.2	NaOAc buffer
Otay	SCMR, S-Ca-2	<0.2	None
Texas	SCMR, STx-1	<0.2	1 N NaCl
Umiat	J. Hower	<2.0	None
Wyoming	SCMR, SWy-1	<0.2	1 N NaCl
<b>K-Minerals<sup>4</sup></b>			
Microcline	C. V. Clemency	120 to 5.0	Washed in H <sub>2</sub> O
Muscovite	C. V. Clemency	37 to 5.0	Washed in H <sub>2</sub> O
Phlogopite	C. V. Clemency	37 to 5.0	Washed in H <sub>2</sub> O
Glauconite	J. Hower, #39 (47)	<2.0	None
Illitic material	D. J. Morgan, #M8 (53)	<5.0	1 N CaCl <sub>2</sub>

<sup>1</sup>For other data concerning the clays, see compilations in (57-59).

<sup>2</sup>Source Clay Mineral Repository, University of Missouri, Department of Geology, Columbia, Missouri 65211.

<sup>3</sup>Ward's Natural Science Establishment, Inc., Rochester, New York.

<sup>4</sup>For data on the K-minerals, see (60-62, 47, 53).

Table II. Chemical Analyses of Some Starting Smectites<sup>1</sup> Used in Wetting and Drying Experiments

Smectite	Weight Percent									
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	Li <sub>2</sub> O	Na <sub>2</sub> O	K <sub>2</sub> O	SrO	TiO <sub>2</sub>	LOI <sup>2</sup>
Cheto	56.0	16.2	1.49	5.25	NA <sup>3</sup>	0.12	0.39	6.17	0.23	16.9
Ferruginous	49.0	10.8	21.7	1.22	NA	0.04	0.89	4.31	0.58	15.0
Garfield "A" <sup>4</sup>	41.9	5.9	30.4	0.85	NA	0.25	0.09	4.71	0.05	20.0
Hectorite	52.3	0.52	0.17	23.2	1.31	0.13	0.93	3.49	0.03	20.7
Montmorillon	53.0	20.7	0.64	2.83	NA	0.13	0.09	5.25	0.02	19.4
Otay	54.2	15.6	1.55	6.86	NA	0.12	0.59	6.19	0.24	19.1
Texas	57.8	17.5	1.20	3.75	NA	0.09	0.09	5.01	0.26	17.3
Umiat	53.9	20.3	3.39	2.83	NA	0.07	0.17	4.92	0.17	18.8
Wyoming <sup>4</sup>	57.5	20.1	4.25	3.07	NA	0.31	1.11	3.28	0.09	11.7

<sup>1</sup>Sr-saturated. Analysis for Si, Al, Fe, Mg, and Ti by X-ray fluorescence, A. J. Bartel, K. Stewart, and J. Taggart, analysts. Analysis for Li by induction-coupled plasma spectroscopy, S. Wilson, analyst. Analysis for Na, K, and Sr by atomic-absorption spectroscopy, D. D. Eberl, analyst.

<sup>2</sup>Loss on ignition at 900°C.

<sup>3</sup>Not analyzed.

<sup>4</sup>Treated by WD for 100 cycles prior to Sr-saturation and to chemical analysis for interlayer cations.

Table III. Structural Formulae for Smectites Used in Wetting and Drying Experiments, Based on  $O_{10}(OH)_2$   
 [Formulae Calculated from Data in Table II, Unless Noted Otherwise]

Smectite	Tetrahedral <sup>1</sup>			Octahedral			Interlayer			Total Layer Charge (Equivalents)		
	Si (Equivalents)	Al	Fe <sup>3+</sup>	Al	Fe <sup>3+</sup>	Mg	Li	Na (Equivalents)	K		Sr	
Black Jack <sup>2</sup>	3.48	0.52	0	1.99	0.02	0.01	NA <sup>3</sup>	0.46	0	0	0	0.47
Cheto	4.00	0	0	1.36	0.08	0.56	NA	0.02	0.04	0.25	100	0.56
Ferruginous	3.68	0.32	0	0.64	1.22	0.14	NA	0.01	0.09	0.18	30	0.46
Garfield A	3.46	0.54	0	0.03	1.89	0.11	NA	0.04	0.08	0.23	4	0.56
Garfield B <sup>2</sup>	3.45	0.39	0.16	0.15	1.83	0.02	NA	0.57	0	0	4	0.57
Hectorite	3.95	0.05	0	0	0.01	2.61	0.40	0.02	0.09	0.15	85	0.41
Kinney <sup>2</sup>	3.97	0.03	0	1.47	0.07	0.46	0	0.47	0	0	96	0.49
Montmorillon	3.87	0.13	0	1.65	0.04	0.31	NA	0.02	0.01	0.22	67	0.44
Otay	3.92	0.08	0	1.25	0.08	0.74	NA	0.02	0.06	0.26	87	0.61
Texas <sup>4</sup>	4.00	0	0	1.52	0.07	0.41	NA	0.01	0.01	0.21	100	0.41
Umiat	3.83	0.17	0	1.53	0.18	0.30	NA	0.01	0.02	0.20	61	0.44
Wyoming	3.89	0.11	0	1.49	0.22	0.31	NA	0.04	0.09	0.13	69	0.36

<sup>1</sup>Ti is considered to be present as discrete anatase.

<sup>2</sup>Formulae for Black Jack from (63), for Garfield B from (51), and for Kinney from (14).

<sup>3</sup>Not analyzed.

<sup>4</sup>3.5% SiO<sub>2</sub>, presumably present as amorphous material, subtracted from the analysis in Table II to give an ideal tetrahedral occupancy.



## Experimental Results

Behavior of K-Exchanged Smectites Without Wetting and Drying. All of the smectites (Table I) gave XRD patterns characteristic for randomly interstratified (RO) mixed-layered minerals upon K-exchange. Those of low layer charge (e.g. Wyoming) gave patterns for I/S with a few percent illite layers. Those of higher layer charge were identified as 3-component 1.0/1.4/1.7-nm interstratifications. This heterogeneous swelling probably is related to heterogeneous layer-charge distributions in the smectites. XRD patterns for the 3-component interstratifications differed from those of the 2-component, in that the 001 was displaced toward higher angles; the 002 was much more diffuse; the 003 was displaced toward higher angles; and the 005 was displaced slightly towards lower angles of two-theta. The latter two peaks for the 3-component system plot on the extreme left side or outside of the graph used to identify mixed-layer I/S (see Figure 8A in 43). Saturation of K-smectite with an ion of higher hydration energy led to complete re-expansion, in agreement with previous studies. For example, XRD patterns for K- and Na-Black Jack smectite are given in Figure 1.

A Na-K exchange isotherm was determined using Na-Kinney smectite to study the evolution of 3-component mixed-layering with increasing K content. This evolution was followed by plotting the changing positions of the 003 and 005 XRD peaks as a function of K/Na ratio for the exchange solution on a graph used to determine illite contents and glycol spacings for I/S (Figure 2). From a K/Na ratio of 0 to about 25/75, the illite content of the sample increased from 0 to about 49%, and the glycol spacing of the expanded layers increased, as is expected for Na-K exchange (42). At K/Na ratios between 25/75 and 35/65, illite content remained nearly constant, and glycol spacing continued to increase, which is interpreted as a continued replacement of Na by K in expanded layers. At K/Na ratios greater than 40/60, the XRD spacings evolved out of the two-theta range possible for I/S; as discussed above, characteristics of 3-component interstratification could be observed. In particular, the 001 reflection began to migrate towards greater angles at Na/K of 35/65, as is expected for the development of 1.4-nm layers.

All of the K-exchanged smectites (Table I) re-expanded completely when exchanged four times with 1 N NaCl solution. Then it was determined that a single, overnight exchange with 0.1 N SrCl<sub>2</sub> is the mildest treatment sufficient to restore the K-Kinney to a 100% smectite structure, which means reexpanding to 1.7-nm on glycol saturation both the vermiculite-like (1.4 nm) and the unstable illite-like (1.0 nm) layers. This treatment subsequently was used as a standard test because, unlike Na, Sr is not replaced by hydronium ions during dialysis (49); therefore, Sr gives a better measure of CEC during chemical analysis. Illite layers formed by burial diagenesis are not affected significantly by either the Na- or the Sr-exchange procedures.

Response of K-Smectites to WD Cycles in Water at 60°C. Results of these WD experiments are given in Table IV; sample XRD patterns are given in Figures 3 and 4. The following patterns of reaction are evident from Table IV:

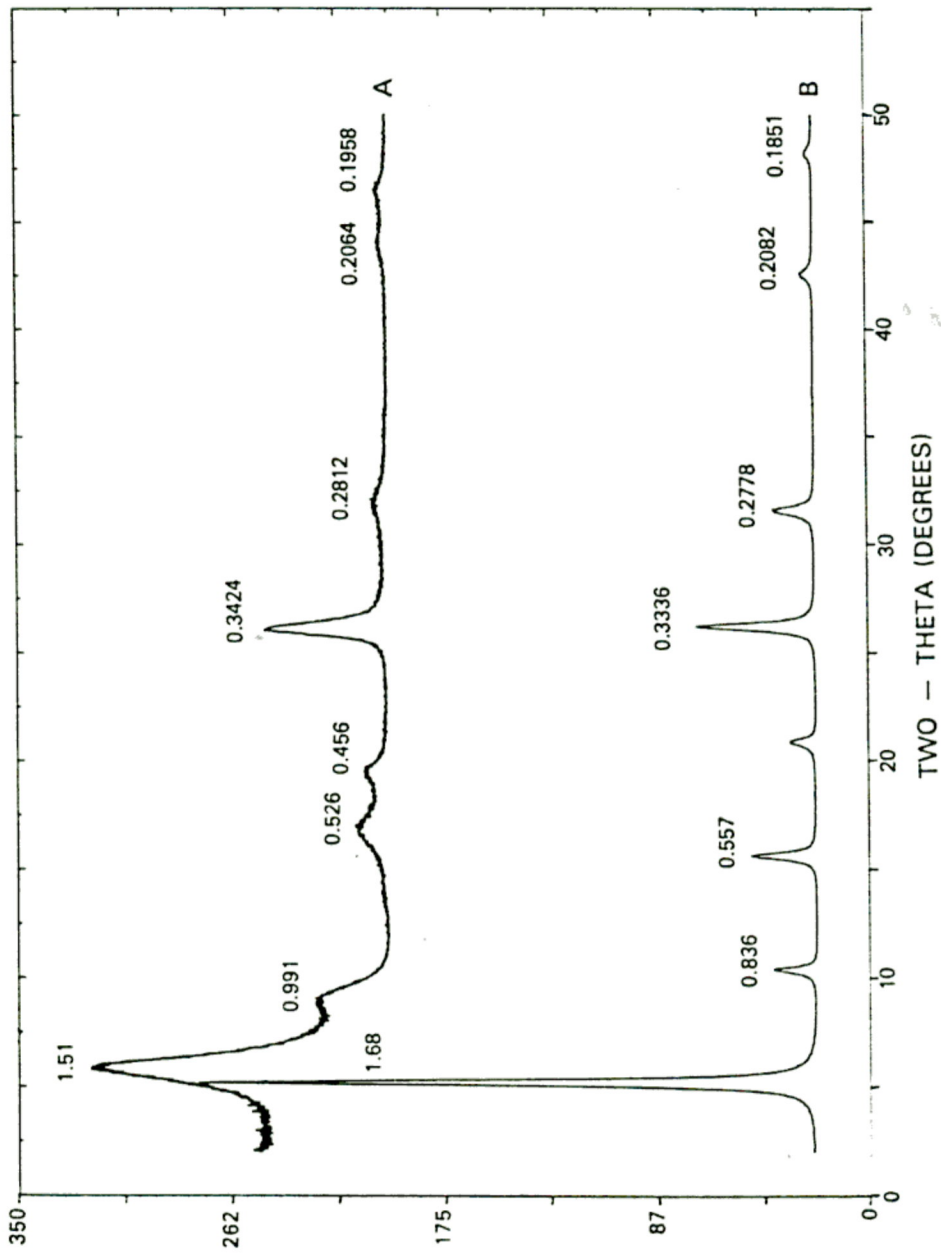


Figure 1. XRD patterns (CuK $\alpha$  radiation; ethylene glycol-solvated samples) showing effect of K-exchange on Black Jack smectite. A = K-exchanged sample; B = identical patterns were found for Na-exchanged sample and K-exchanged sample that was then Na-exchanged. Peaks labeled in nm.

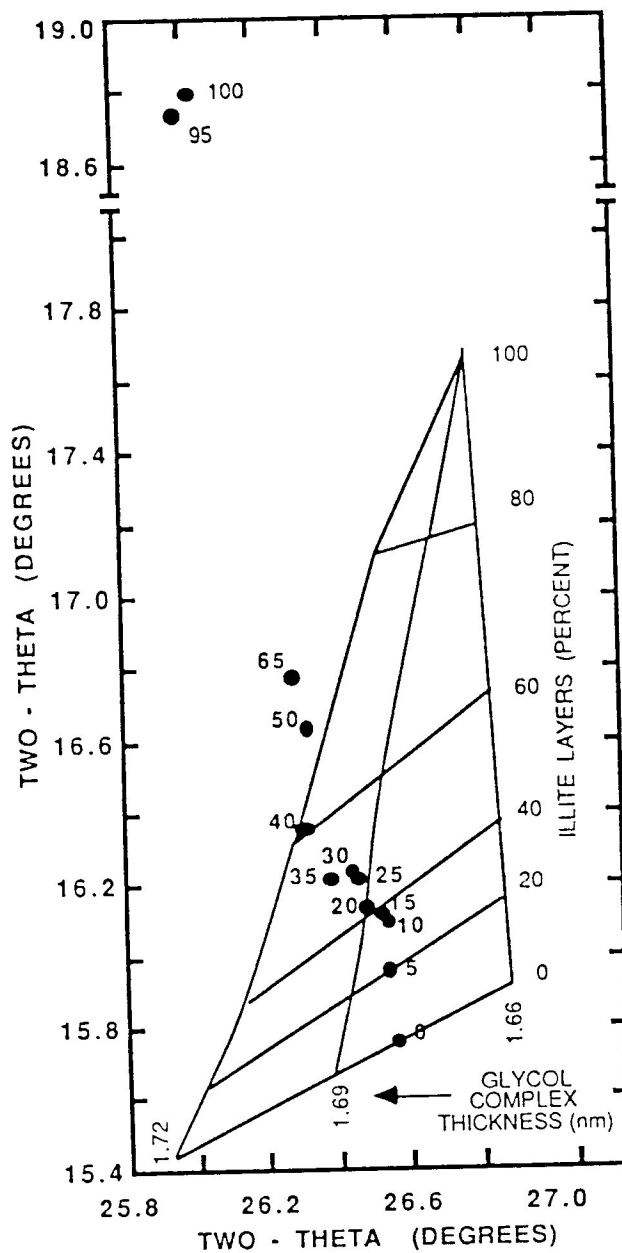


Figure 2. Plot of XRD peak positions ( $\text{CuK}\alpha$  radiation; ethylene glycol-solvated samples) for Kinney smectite treated with 0.05 N Na + K exchange solutions. Experimental points are labeled with percentages of K in solution. The graph, used to determine percentage illite layers and glycol-spacing for illite/smectites having crystallite thickness of 1-14 layers, is from (42).

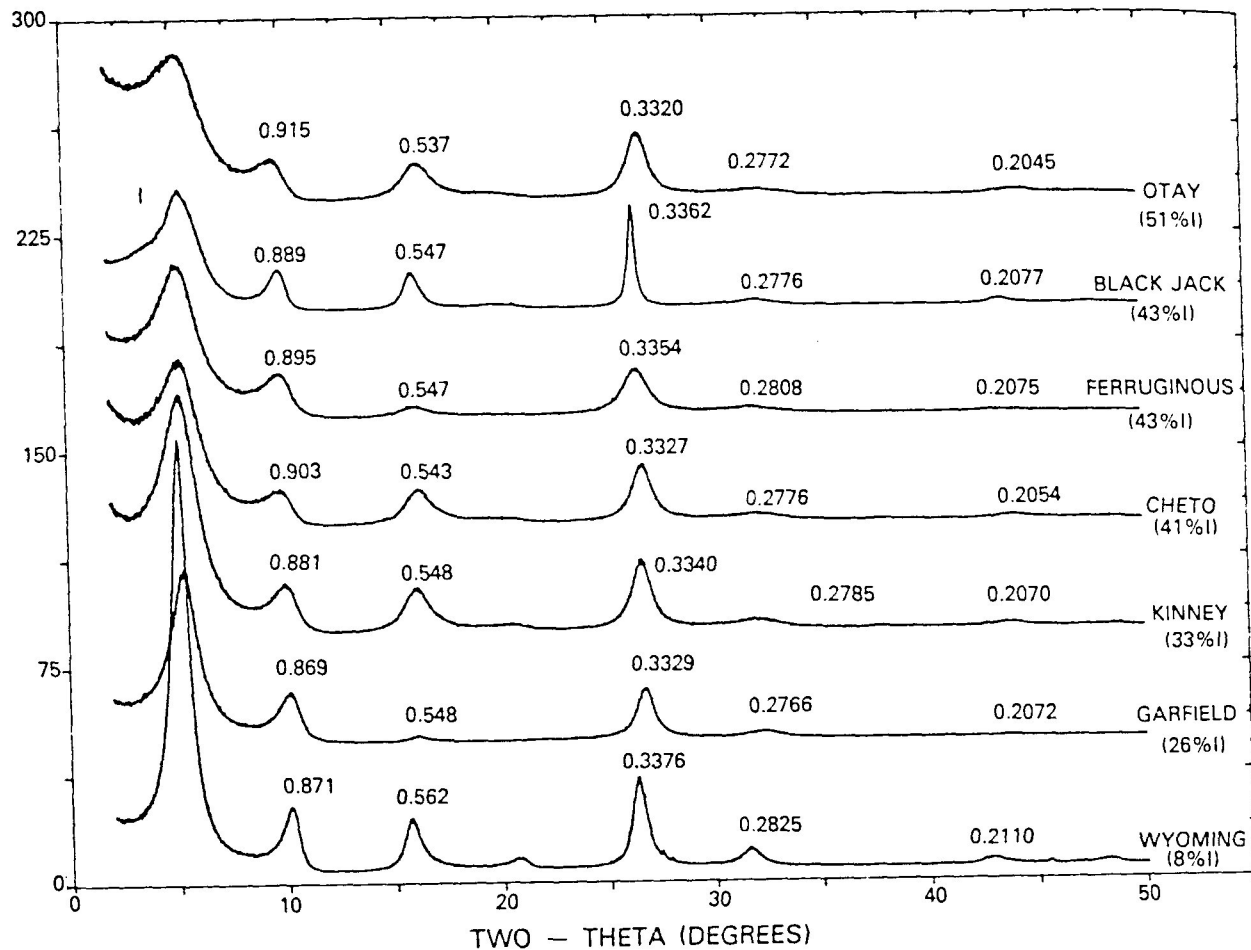


Figure 3. XRD patterns ( $\text{CuK}\alpha$  radiation; ethylene glycol-solvated samples) for Sr-exchanged K-smectites that have been subjected to 100 WD cycles in water at  $60^\circ\text{C}$ . A low-angle shoulder that indicates a trace of R1 ordering is marked by a tick on the Black Jack pattern. Peaks labeled in nm.

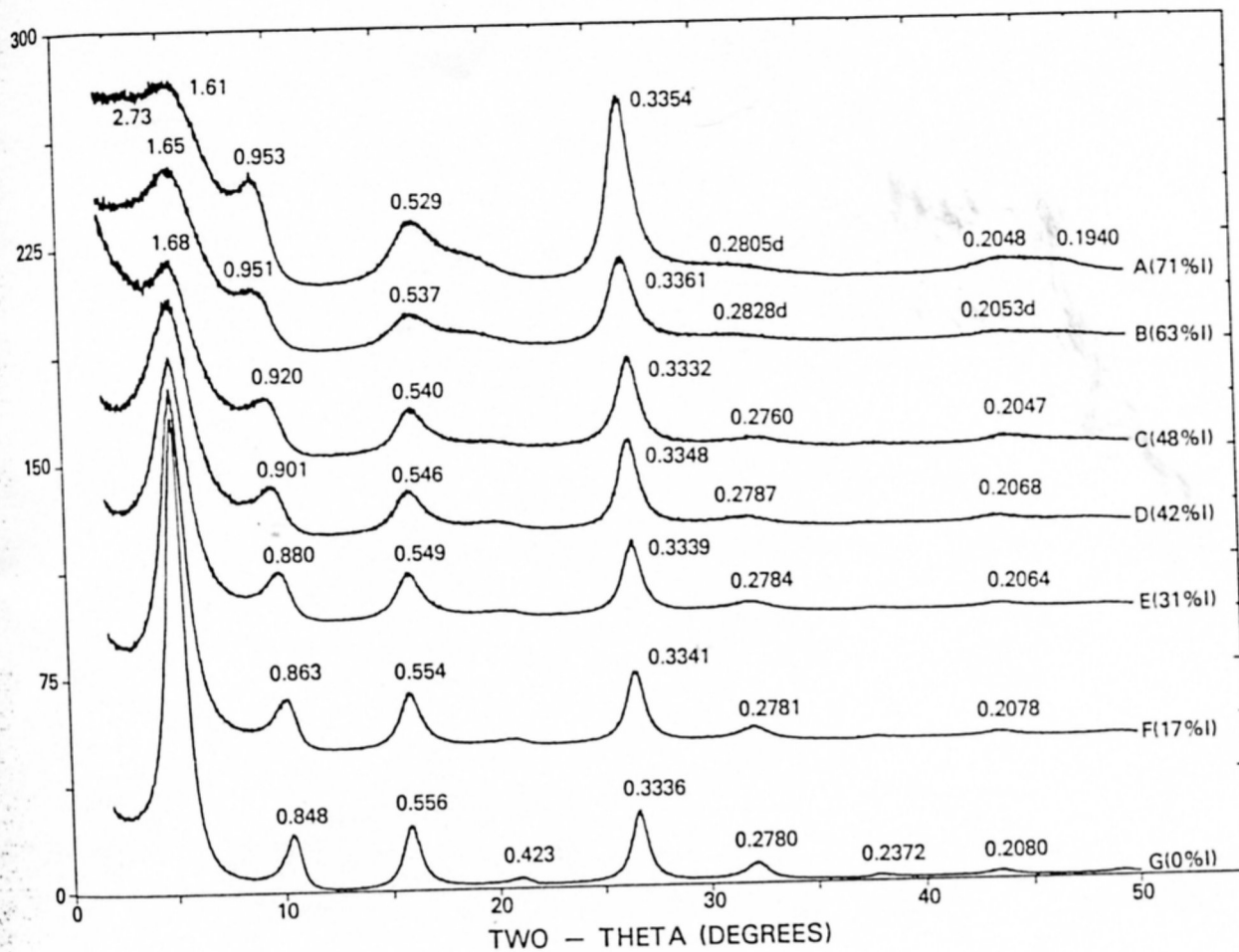


Figure 4. XRD patterns ( $\text{CuK}\alpha$  radiation; ethylene glycol-solvated samples) showing a range of illite contents for K-Kinney smectite that has been subjected to various treatments. A = 100 WD cycles in 0.5 N NaCl; B = 40 WD cycles in 0.5 N NaCl; C = 100 WD cycles in 0.5 N KOH, with 1 Sr exchange; D = 100 WD cycles in 0.5 N  $\text{CaCl}_2$ ; E = 100 WD cycles in 0.5 N KCl, with 1 Sr-exchange; F = 100 WD cycles in 0.5 N  $\text{CaCl}_2$ , with 1 Sr-exchange; G = clay left in suspension for a time equivalent to 100 WD cycles, with 1 Sr-exchange. Peaks labeled in nm.

Table IV. Percentage of Illite Layers and Interlayer Chemistry of K-Smectites Subjected to Wetting and Drying Cycles in Water at 60°C, and Then Exchanged with 0.1 N SrCl<sub>2</sub>

Reference Number	Sample	Number of		Meq per 100 g Oxide				Illite Layers (Percent)
		WD Cycles	Sr Exchanges	Na	K	Sr	Total	
1	K-Black Jack	100	1	0	52	80	132	43
2		100	3	6	9	122	137	0
3	K-Cheto	0	1	4	8	119	131	0
4		100	1	3	51	81	135	41
5		100	3	4	23	93	120	15
6	K-Ferruginous	0	1	1	19	83	103	0
7		5	1	0	31	71	102	33
8		10	1	1	32	72	105	38
9		15	1	5	28	64	97	36
10		20	1	0	30	66	96	36
11		25	1	0	33	68	101	37
12		30	1	1	34	66	100	41
13		40	1	3	35	68	106	41
14		50	1	0	34	66	100	41
15		75	1	0	36	68	104	41
16		100	1	0	35	68	103	43
17		100	3	6	21	78	105	29
18	K-Garfield	100	1	8	16	91	115	26
19	K-Hectorite	100	1	4	20	67	91	12
20	K-Kinney	5	1	4	29	92	125	22
21		10	1	3	33	89	125	26
22		15	1	3	36	87	126	26
23		20	1	4	34	80	118	28
24		25	1	4	35	83	122	28
25		30	1	4	35	86	125	29
26		40	1	4	37	83	124	30
27		50	1	4	37	82	123	30

25  
26  
27  
30  
40  
50  
1  
1  
1  
4  
4  
4  
53  
37  
37  
60  
83  
82  
123  
124  
123  
29  
30  
30

28		75	1	4	40	79	123	32
29		100	1	3	39	85	127	33
30		100	3	NA <sup>1</sup>	NA	NA	---	9
31	K-Montmorillon	0	1	4	2	101	107	0
32		100	1	2	40	69	111	27
33		100	3	3	21	88	112	17
34	K-Otay	0	1	4	13	120	137	5
35		100	1	4	56	71	131	51
36		100	3	8	51	73	132	26
37	K-Texas	0	1	3	2	97	102	0
38		100	1	4	38	63	105	22
39		100	3	3	22	81	105	11
40	K-Umiat	0	1	2	4	95	101	0
41		100	1	6	29	74	109	10
42		100	3	3	20	79	102	3
43	K-Wyoming	100	1	10	24	63	97	8

<sup>1</sup>Not analyzed.

- (1) WD cycles stabilize 1.0-nm layers against exchange by a cation with substantial hydration energy.
- (2) A regular decrease in CEC (meq Sr) occurs as the percentage of fixed K and percentage of illite layers increases.
- (3) The quantity of illite layers formed after 100-WD cycles and 1 Sr-exchange is proportional to layer charge (data from Tables III and IV plotted in Figure 5), although smectites with a large component of octahedral charge (montmorillonites) follow this relation better than do those that have a large component of tetrahedral charge (beidellites and one montmorillonite with 61% octahedral charge). A perfect correspondence between the quantity of illite layers formed by WD and layer charge is not expected, however, because this reaction may also depend on other factors, such as layer-charge distribution. Figure 5 may indicate that charge distribution is more heterogeneous for the beidellitic smectites.
- (4) The total milliequivalents of interlayer cations is not changed significantly by the WD process, thereby indicating that 2:1 layer charge does not change. These data suggest that the reaction to illite is a transformation reaction caused by simple dehydration and rearrangement of smectite layers, rather than by an increase in 2:1 layer charge.

All of the I/S produced by WD are randomly interstratified, with the possible exception of the Black Jack sample (Figure 3) and the most illitic Kinney sample (Figure 4), both of which show signs of partial R1 ordering between illite and smectite layers. For these samples, the 001 XRD reflections are displaced towards larger angles, and a very weak superlattice reflection is visible at small angles.

The stability of the illite layers produced by WD was investigated further by applying two additional 0.1 N SrCl<sub>2</sub> exchanges to WD smectites for which sufficient sample was available (Table IV). The quantity of illite layers decreased significantly with this treatment, but measurable illite layers were preserved in all samples except the Black Jack smectite. Exchange experiments with a WD Kinney sample showed that the use of three 0.1 N SrCl<sub>2</sub> exchanges is a slightly stronger treatment than the use of four 1 N NaCl exchanges used to study diagenetic I/S (44). Thus, the illite layers remaining in the WD clays after three Sr-exchanges may be of comparable stability to those formed by burial diagenesis.

The percentage change in illite layers between one and three exchanges with 0.1 N SrCl<sub>2</sub>, which is a measure of the stability of the illite layers formed by WD, correlates neither to original smectite-layer charge, nor to layer-charge location, but, based on very limited data, does correlate roughly to the mean angle of tetrahedral rotation of the original smectite (Figure 6). Angle of tetrahedral rotation ( $\alpha$ ) was calculated from structural formulae (Table III) and measurements of  $b$  (Table V) by the following equations (29, 50):

$$\cos \alpha = b_{\text{observed}} \div b_{\text{ideal}}$$

where

$$b_{\text{ideal}}(\text{Si}_{1-x}\text{Al}_x) = 9.15 + 0.74x$$



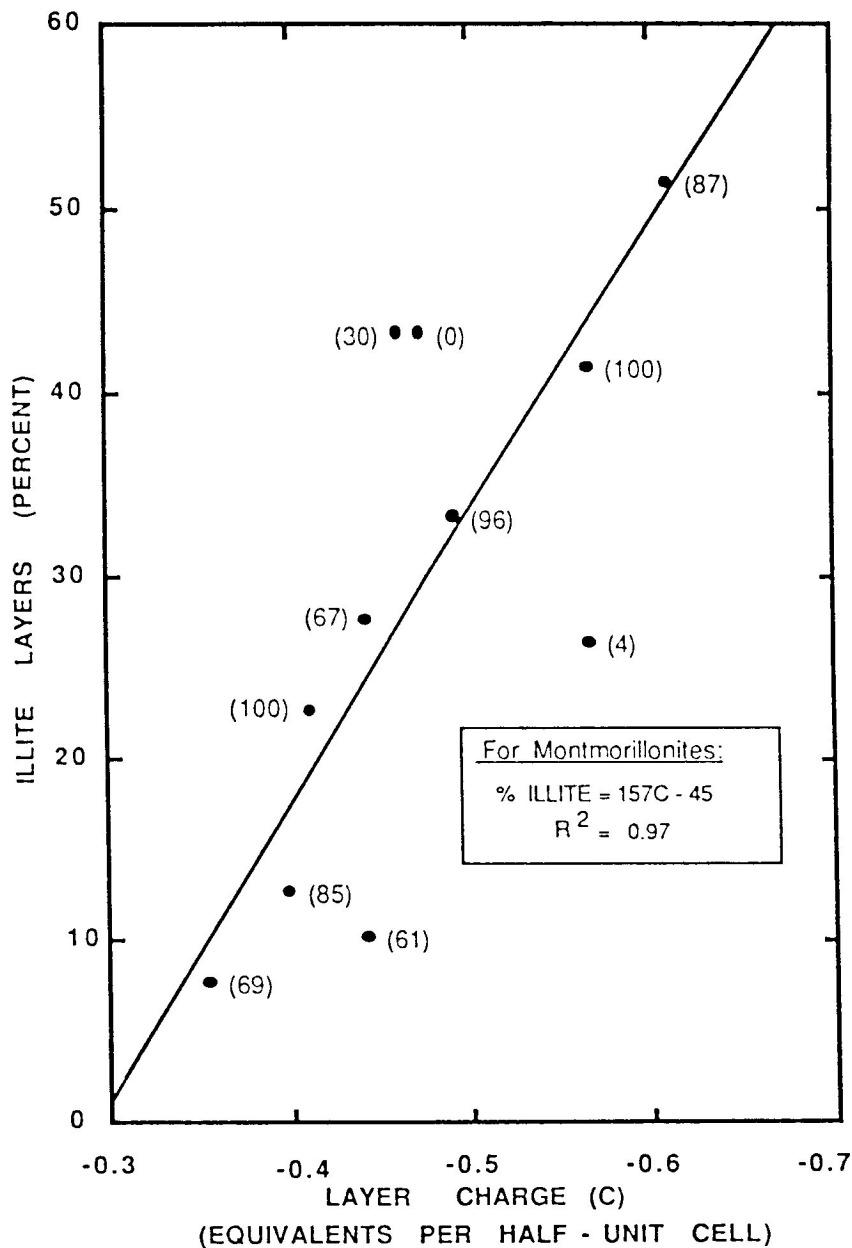


Figure 5. Percentage illite layers versus layer charge for K-smectites subjected to 100 WD cycles in water at 60°C and 1 Sr-exchange. Numbers in parentheses refer to percentage of octahedral charge. Best fit line is for montmorillonites having 69% or more octahedral charge. Data from Tables III and IV.

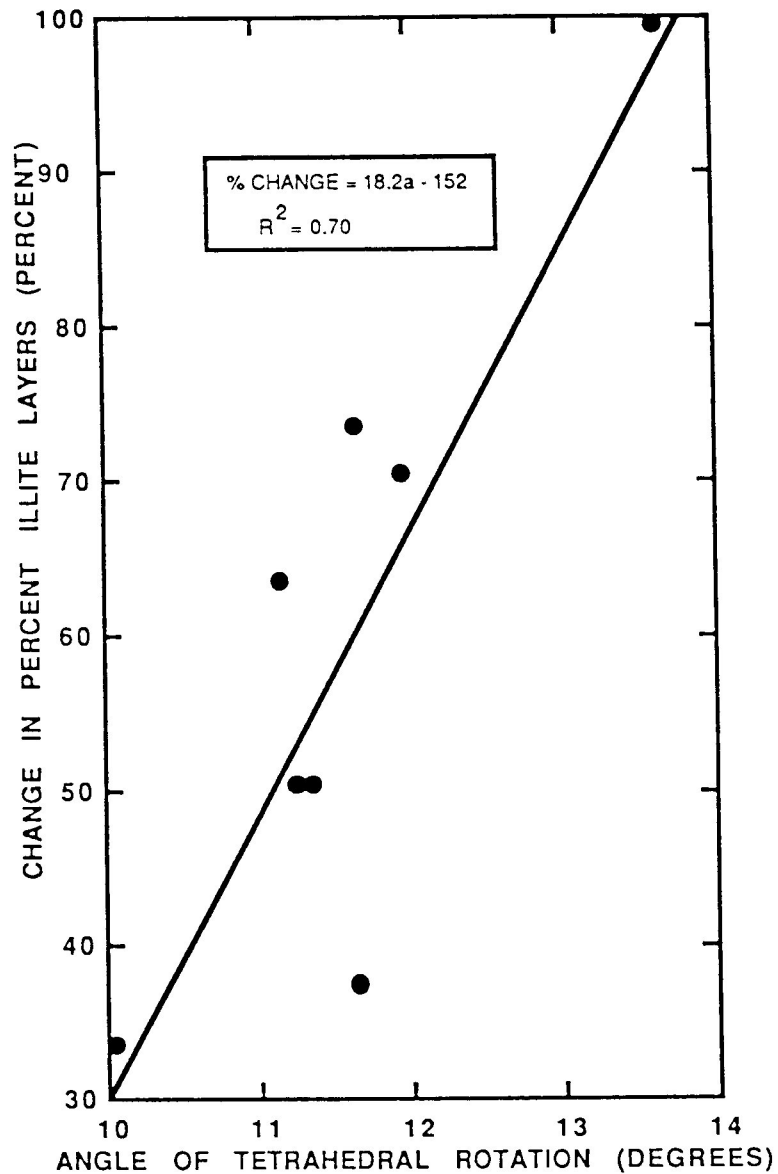


Figure 6. Stability of illite layers formed by WD mechanism: percentage of change in percentage illite layers between 1 and 3 Sr-exchanges is plotted against  $\alpha$ , the angle of tetrahedral rotation. Data from Table V.

This method for estimating  $\alpha$  applies generally if  $\alpha$  is greater than about  $7^\circ$ , and assumes an ideal 0(apical)-Si-0(basal) angle of  $109^\circ 28'$ . A relationship between  $\alpha$  and illite layer stability is expected, because the larger the  $\alpha$  is, the smaller the ditrigonal holes are in the basal oxygen planes of the 2:1 layers. The smaller the holes are, the less deeply dehydrated K ions can penetrate into 2:1 layers; thus, the more susceptible the K ions are to Sr-exchange. Alpha is only an approximate indicator of hole size; it would be better to measure directly the hole size, or the K-O bond lengths for the illite layers. But such a detailed structural analysis is beyond the scope of the present work.

Tetrahedral rotations in dioctahedral clays are required to adjust for a misfit in size between the normally larger tetrahedral sheet and the octahedral sheet. Rotation angles of  $30^\circ$  close the holes completely. The hole is so large for small angles of  $\alpha$  that the hole approaches hexagonal symmetry; in this case, interlayer K enters more nearly into 12-fold coordination, rather than into the 6-fold coordination of ditrigonal holes (30). Thus, perhaps the reason that the Garfield sample, with a small, measured  $\alpha = 6^\circ$  (51), does not lie on the curve in Figure 6 is because it belongs to an energetically different system. But other factors, in addition to  $\alpha$ , could influence, or even play a dominant role, in affecting the availability of K to Sr-exchange. Two such factors are the presence of heterogeneous layer charges, which would tend to bind K more strongly in highly-charged interlayers, and the presence or absence of three-dimensional ordering in the WD smectite-crystal structures, which could lead either to prismatic or octahedral coordination for K in the dehydrated interlayers, and to various distortions in the 2:1 layers that could affect K availability (V. A. Drits, personal communication).

The kinetics of the transformation towards illite for Ferruginous and Kinney smectites are shown in Figure 7. Most of the illite layers are formed in the first 20 WD cycles, although illite content appears still to be increasing slightly after 100 WD cycles. The Ferruginous smectite produces more illite layers for a given number of WD cycles than the Kinney does even though the Ferruginous smectite has a slightly smaller layer charge (Table III). This effect may be related to the much larger component of tetrahedral charge, to the slightly smaller degree of tetrahedral rotation for the Ferruginous sample, and to the other factors mentioned above. Similar experiments with other iron-rich smectites are needed to resolve this question.

Shaking in water prior to each drying cycle speeds reaction. For example, a K-Kinney smectite subjected to 64 WD cycles produced 42% illite layers, with shaking, compared with 30% for K-Kinney subjected to 50 WD cycles, and 32% for K-Kinney subjected to 75 WD cycles, without shaking.

The equivalents of fixed-interlayer cations per illite layer decrease with increasing illite content for the WD samples (Figure 8). Fixed cations are K, with a very small component of Na that was not removed by Sr-exchange (Tables IV and VI). The relation roughly fits a power curve, as depicted in the figure. Calculations for samples that plot on the extreme lower end of the curve (at 1.0 equivalents) actually gave equivalents of fixed-interlayer cations greater than one, which is impossible structurally, because there are not enough holes in the basal oxygen planes to accommodate more

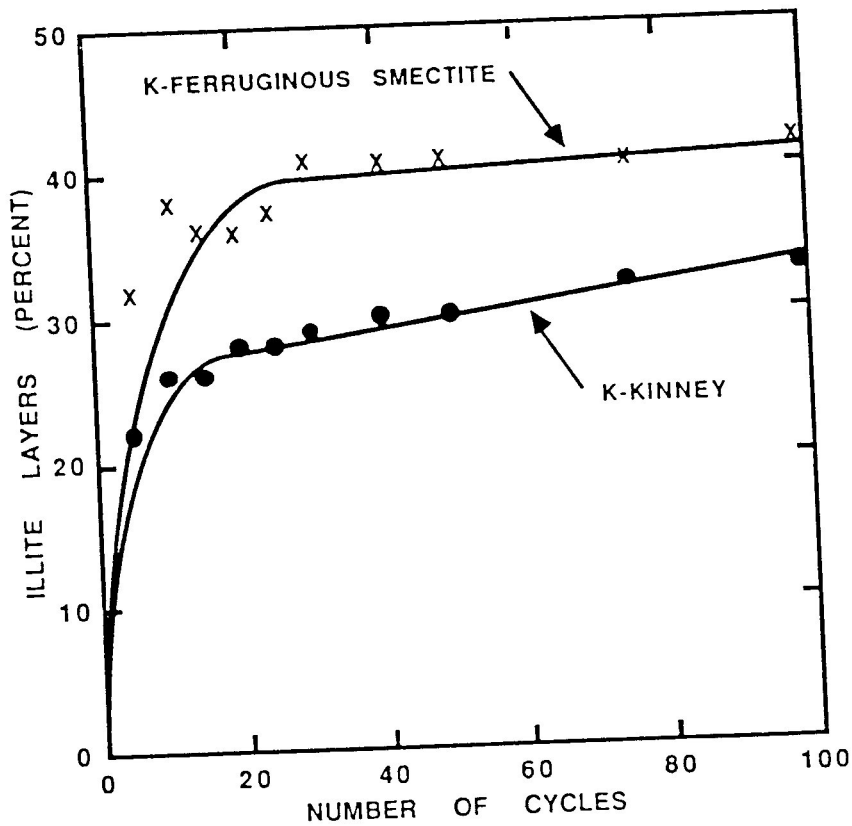


Figure 7. Kinetics of WD illitization: percentage illite layers versus number of WD cycles for Ferruginous and Kinney smectites after 1 Sr-exchange. Data from Table IV.

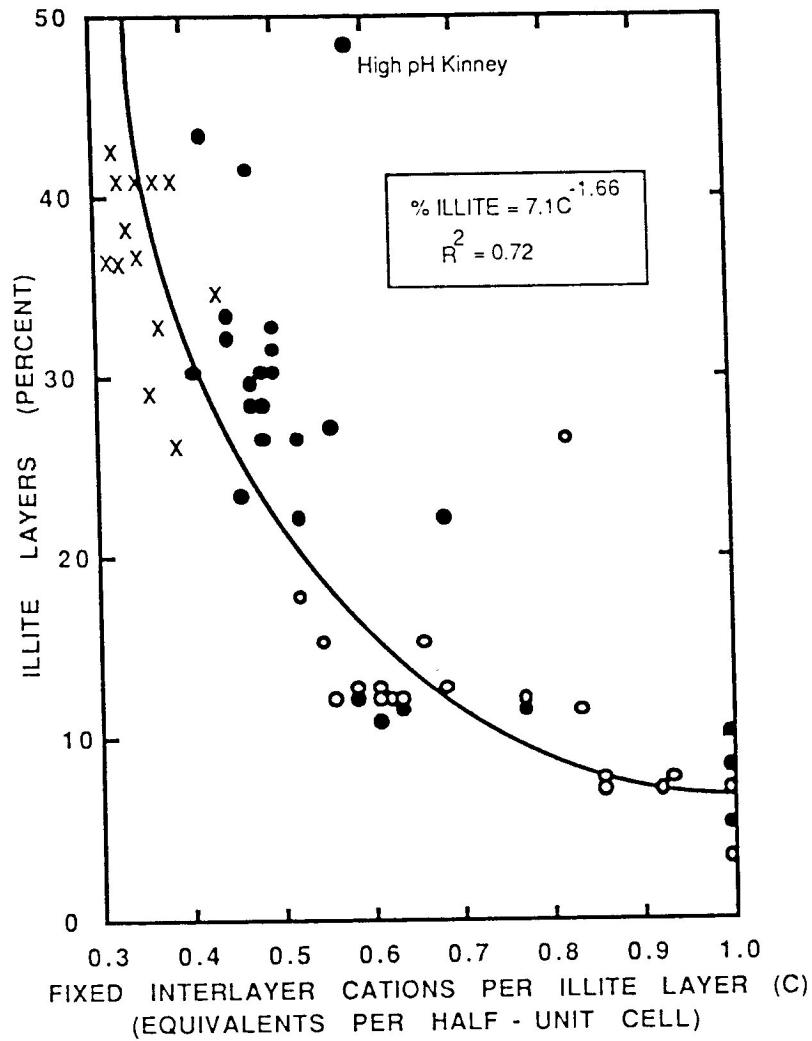


Figure 8. Percentage illite layers versus equivalents of fixed interlayer cations (Na + K) per illite layer [based on  $O_{10}(OH)_2$ ]. Solid circles = aluminous smectites with 1 Sr-exchange. Open circles = aluminous smectites with 2 or 3 Sr-exchanges. X = iron-rich smectites with 1 Sr-exchange. Points calculated from data in Tables III, IV, VI, and VIII.

than 1.0 equivalents of K-ions. The excess is attributed to errors in determining illite contents in highly smectitic clays. The data in Figure 8 indicate, from a consideration of the increase in illitic content with increasing WD cycles (Table IV and Figure 7), that a greater number of WD cycles is required to stabilize low-charge illite layers.

The iron-rich samples plot mostly to the left of the curve in Figure 8, thereby indicating that iron-rich clays tested in these experiments can form illite layers by WD at a lower fixed cation content than aluminous clays can. A similar observation has been made for iron-rich illite layers (glauconite) produced by diagenesis (52). This effect may be related to the deeper penetration of K<sup>+</sup> into the larger basal holes found in iron-rich 2:1 clays, as well as to the other factors mentioned above.

The pattern in Figure 8 is distinct from that for randomly interstratified I/S produced from bentonite by burial diagenesis (Figure 9). Fixed interlayer cation content for the latter clays is relatively constant at about 0.55 equivalents per illite layer for clays that contain less than 50% illite layers (53).

Effect of Solution Composition. The effect of changing solution composition on the reaction of K-Kinney is given in Table VI. The

Table VI. Effect of Solution Composition on the Reaction of K-Kinney Submitted to 40 Wetting and Drying Cycles at 60°C, and Then Exchanged Once With 0.1 N SrCl<sub>2</sub>

Reference Number	Solution	Meq per 100 g Oxide				Illite Layers (Percent)
		Na	K	Sr	Total	
26	Water	4	37	83	124	30
44	0.5 N NaCl	5	35	82	122	32
45	0.5 N KCl	3	40	81	125	31
46	0.5 N CaCl <sub>2</sub>	3	27	96	126	23
47	pH 3.6 (HCl)	3	32	85	121	30
48 <sup>1</sup>	0.5 N KOH	6	71	77	154	48

<sup>1</sup>Average of two analyses.

presence of 0.5 N NaCl, 0.5 N KCl, and HCl (pH 3.6) had no effect on reaction rate as compared with experiments made in water. The 0.5 N CaCl<sub>2</sub> solution significantly slowed the rate of reaction, whereas the 0.5 N KOH solution increased the rate. With one exception, the data in Table VI indicate that total layer charge did not change significantly during reaction. The exception is the high pH run (KOH) in which layer charge increased, thereby indicating that the composition of the 2:1 layer was altered. The average charge for illite layers in this sample (0.57) is plotted in Figure 8, and is greater than that expected for clays of this expandability formed by WD. It fits better on the diagenetic curve (Figure 9). In addition, the average charge for expanded layers increased from -0.49 for untreated Kinney to about -0.52.

Oxygen isotope data (Table VII) support conclusions drawn from the chemical data (Tables IV and VI) that clay in the high pH, WD experiments underwent significant chemical reaction, whereas clay

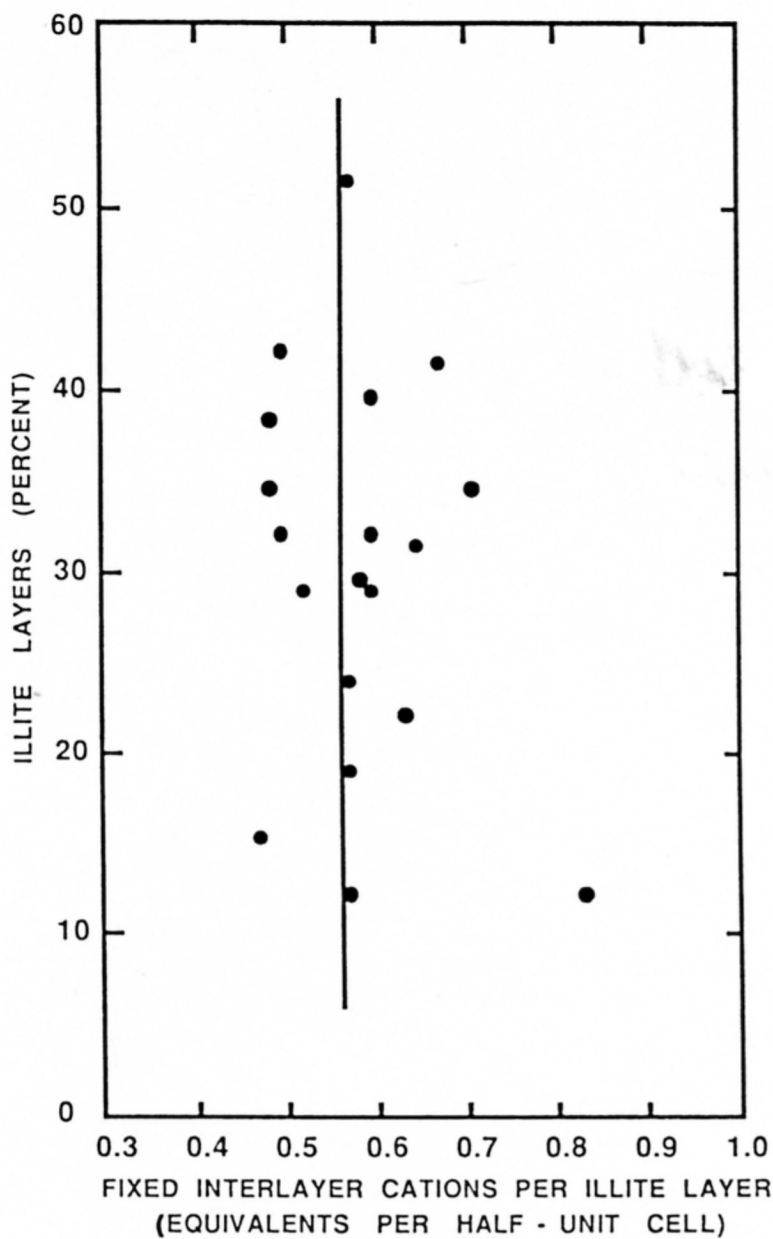


Figure 9. Percentage illite layers versus equivalents of fixed interlayer cations per illite layer [based on  $O_{10}(OH)_2$ ] for R0 illite/smectites formed by diagenesis in bentonites. Calculated from data in (53).

Table VII. Oxygen Isotope Data for Various Smectites

Smectite	Number of WD Cycles	Solution Composition	Measurements of $\delta^{18}\text{O}$	Average $\delta^{18}\text{O}$
Kinney	0	Water	13.8, 13.4, 14.6, 14.4	14.1
	64	Water	13.8	13.8
Black Jack	100	Water	13.9, 14.1, 14.2	14.1
	40	0.5 N KOH	15.9, 16.5, 15.7	16.0
	0	Water	1.6, 1.6, 1.4, 1.5, 2.1	1.6
	100	Water	2.0, 1.2, 1.3, 1.2, 2.0	1.5
Otay	0	Water	17.0, 17.8	17.4
Montmorillon	100	Water	16.9, 16.5	16.7
	0	Water	26.3	26.3
Texas	100	Water	25.0	25.0
	0	Water	26.2, 25.4, 25.5, 26.8	26.0
Hector	100	Water	26.0, 25.5, 25.6, 25.8	25.7
	0	Water	22.2, 22.3, 21.7, 21.7, 21.9, 22.0	22.0
	100	Water	21.5, 20.8, 21.7, 21.7, 21.2	21.4
	0	Water	15.2, 14.5, 14.3	14.7
Umiat	100	Water	13.8, 14.2, 13.7	13.9
	0	Water	17.1, 17.2, 17.4	17.2
Cheto	100	Water	17.4, 16.9, 17.0	17.1
	0	Water	12.8, 12.7	12.8
Ferruginous	100	Water	12.7, 12.6	12.7
	0	Water		



wetted and dried in other experimental solutions did not. Data in Table VII indicate that clay subjected to WD cycles in distilled water either remained unchanged isotopically, thereby indicating that the 2:1 layer chemistry did not change, or became slightly lighter, which is, perhaps, related to an exchange of oxygen atoms on crystal edges (54), or to experimental difficulties that were encountered in removing all of the interlayer water from the Sr-exchanged samples. The latter possibility is favored by the finding of larger oxygen yields (micromoles  $O_2$  per mg clay reacted) for the Sr-saturated clays, and of a decrease in scatter for  $\delta^{18}O$  values for clays subjected to increased drying times. The Kinney smectite, however, became 2 per mil heavier after 40 WD cycles in the high pH experimental solution, thereby indicating substantial alteration of 2:1 layer chemistry.

In other experiments, K-Wyoming and K-Otay smectite were subjected to 20 WD cycles in 0.5 N KOH, and then Sr-exchanged. The Wyoming reacted to form greater than 50% illite layers, giving a weak XRD pattern after the treatment, and the Otay clay was destroyed. Otay in suspension for the same length of time with 0.5 N KOH, but without WD, reacted to form about 42% illite layers, thereby demonstrating that WD is not essential for the reaction to illite at high pH. Previous studies (8, 55) have shown that a significant number of illite layers can be formed in low-charge smectites by boiling them in 1 N KOH. The increased solubility of Al and Si at high pH may lead to a chemical reaction in which layer charge is increased by Al for Si substitution. More work is needed to confirm this suggestion.

The KCl, HCl, and KOH experimental products (Table VI), when X-rayed prior to Sr-exchange, have characteristics of 3-component 1.0/1.4/1.7-nm interstratification. The NaCl and  $CaCl_2$  experimental products prior to Sr-saturation, however, were two component 1.0/1.7-nm interstratifications, containing 1.0-nm layers well in excess of the number remaining after one Sr saturation. WD experiments with more cycles than those given in Table VI showed that illite content (no Sr-exchange) increased from 63 to 71% between 40 and 100 WD cycles for the NaCl experiments, and from 30 to 42% for the  $CaCl_2$  experiments. But the stability of these additional illite layers did not increase with the number of WD cycles: after one Sr-exchange, the 40- and the 100-cycle runs differed by only a few percent illite.

Effect of Temperature. Temperature had little effect on the percentage of illite layers formed from K-Kinney, which was subjected to as many as 6 WD cycles at 30°, 60°, and 90°C, and then saturated twice with 0.1 N  $SrCl_2$  (Table VIII). Unfortunately, the experimental products were not X-rayed after a single Sr-saturation; therefore, results in Table VIII are not directly comparable to those in Table IV. The erratic data resulting from the 90°C experiments are unexplained.

Reaction with K-Bearing Minerals. WD experiments with mixtures of Na-Kinney and sparingly soluble K-minerals were undertaken to simulate natural conditions. When K-feldspar was shaken with Na-Kinney at room temperature without WD for as long as 1 year, no illite layers were found in the experimental product. Nor were illite layers formed when muscovite was shaken with Na-Kinney for

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<sup>1</sup>Dried<sup>2</sup>Not

Table VIII. Effect of Temperature on the Formation of Illite Layers in K-Kinney Submitted to Wetting and Drying Cycles, and Then Exchanged Twice With 0.1 N SrCl<sub>2</sub>

Reference Number	Temperature (°C)	Number of WD Cycles	Meq per 100 g Oxide				Illite Layers (Percent)	
			Na	K	Sr	Total		
49	30 <sup>1</sup>	0	4	9	113	126	0	
50		1	4	13	110	127	7	
51		2	3	15	107	125	7	
52		3	NA <sup>2</sup>	NA	NA	---	12	
53		4	3	18	110	131	12	
54		5	3	16	108	127	12	
55	60	6	3	18	106	127	12	
56		0	3	4	116	123	0	
57		1	NA	NA	NA	---	4	
58		2	3	16	110	129	11	
59		3	3	17	106	126	11	
60		4	3	17	106	126	12	
61		5	NA	NA	NA	---	11	
62		6	3	21	104	129	11	
63		90	0	3	5	117	125	0
64			1	2	15	108	125	7
65	2		3	17	107	127	12	
66	3		3	19	105	127	7	
67	4		3	20	103	126	12	
68	5		3	20	103	126	15	
69		6	3	18	108	129	8	

<sup>1</sup>Dried under vacuum.<sup>2</sup>Not analyzed.

100 days. Phlogopite, however, formed about 4% 1.0-nm layers when shaken with Na-Kinney for 100 days, but these layers disappeared after Sr-exchange.

All WD experiments, however, produced a significant percentage of illite layers after 100 WD cycles. The rate of illite-layer formation was greatest for the potassium-feldspar systems, and least for the systems that contained illitic material. The final proportion of illite layers depended on the initial ratio of K-mineral/Na-Kinney in the system, and on the number of subsequent Sr-exchanges. With a ratio of 0.17, illite layers were unstable with respect to Sr-exchange. With ratios of 1 or more, and with the exception of the experiments containing illitic material and phlogopite, these systems formed illite layers at a rate equivalent to, or greater than, that found for K-smectite (Table IX).

### Conclusions

The experiments indicate that WD can have a major effect on reactions that occur at the mineral-water interface. This process can rearrange clay 2:1 layers into more stable configurations, can substantially alter smectite selectivity for competing exchange cations, and can weather sparingly-soluble K-minerals in the presence of smectite.

The experiments also indicate that WD may be an important mechanism for producing I/S at low temperatures in nature by a transformation mechanism (56). The percentage of illite layers formed by this mechanism is proportional to the number of WD cycles, and to the layer charge of the original smectite. Simple K-exchange does not produce stable illite layers in smectite; therefore, these layers probably form by WD prior to deposition in subaqueous environments. The exception is found in high pH environments where illite layers may form without WD by chemical reaction, as has been reported previously for alkaline lakes (64, 65).

Illite layers form relatively quickly by WD (most in less than 20 WD cycles), and the reaction rate is not affected greatly by changes in solution compositions or temperatures that are typical of near-surface environments. Thus, that which has been studied in the laboratory also may occur abundantly in nature.

The fixation of K is expected to occur wherever smectite and K-minerals are subjected to the wetting and drying process. This process occurs, for example, in soils, deltas, flood plains, and playas. Thus, the patterns of reaction described here could be used geologically in studies of sediment cores to discover when a lake was dry, or to find the surface of a fluctuating, ancient water table. From a geochemical perspective, WD concentrates K in the unsaturated zone, whereas other cations are released to ground water and surface runoff. Agriculturally, the WD process can free K from sparingly soluble K-minerals, and then store it with varying degrees of availability in expanding clay, with availability depending on smectite-layer charge and on the angle of tetrahedral rotation. Availability also may be influenced by factors other than those investigated in these experiments, factors such as heterogeneous layer-charge distribution (66), and three-dimensional ordering of the 2:1 layers (67, 68). Finally, WD should be considered in the design of swelling clay barriers used to contain toxic chemical and radioactive wastes, because the process could

Table IX. Percentage of Illite Layers Found in Na-Kinney Subjected to 100 Wetting and Drying Cycles in the Presence of a Potassium Mineral at 60 °C

Reference Number	Potassium Mineral	Ratio of weight K-Mineral to Na-Kinney	Illite layers (%)	
			No Sr-exchange	1 Sr-exchange
70	Microcline	0.17	19	0
71		1.00	NA <sup>1</sup>	43
72		5.00	48	40
73	Muscovite	0.17	25	0
74		1.00	NA	37
75		5.00	47	NA
76	Glauconite	0.17	30	0
77		1.00	NA	37
78		0.17	28	0
79	Phlogopite	1.00	NA	31
80		0.17	30	0
81		1.00	NA	24

<sup>1</sup>Not analyzed.

cause barriers to crack, or, at least, to lose some of their absorptive properties.

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