

Potassium fixation by smectites in wetting-drying cycles with different anions

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Four smectites were subjected to up to 120 wetting-drying (WD) cycles in the presence of K_2CO_3 , $KHCO_3$, $K_2C_2O_4$, KCO_3CH_3 or KCl . Microprobe and inductively coupled plasma analyses showed that WD cycles with all the reagents except oxalate did not appreciably change the ratios Si : Al : Mg : Fe of the smectite layers, indicating that these cations were not extracted from the layers. Samples cycled with K_2CO_3 or $KHCO_3$ contained more K that was not exchanged by Sr than those treated with acetate or chloride. Moreover, the total layer charge was greater than that of the original smectites. The products obtained with acetate and chloride were very similar. Oxalate appears to attack the clay layers. The additional K introduced by WD at elevated pH increases the proportion of collapsed layers, but the correlation between the amount of non-exchangeable K and the proportion of layers collapsed is poor. Infrared spectra and thermogravimetric analysis suggest that smectites exposed to WD cycles at high pH undergo partial deprotonation according to the scheme $K_x(SiAl)_4(AlMgFe)_2O_{10}(OH)_2 + yKM = K_x(SiAl)_4(AlMgFe)_2O_{10}(OH)_{(2-y)}(O...K)_y + yHM$ where M is the anion of the K salt. Deprotonation increases the layer charge, but the compensating K^+ ions seem to be bound differently from those in normal exchange positions.

Key words: Smectites, wetting-drying, K salts, pH.

INTRODUCTION

The decrease in K exchangeability of smectites and the concomitant collapse of their interlayers has been very extensively studied. K is rendered nonexchangeable by heating K-smectites. The present research focuses on layer collapse that occurs at earth surface temperatures. K fixation occurs when smectites are exposed to repeated wetting-drying (WD) cycles (Gaultier and Mamy 1979; Eberl *et al.* 1986; Sucha and Siranova 1991; Miklos and Ciel 1993). In such WD cycles the amount of K rendered non-exchangeable to repeated treatment with $SrCl_2$ solutions and the associated layer collapse increased with total layer charge of the smectite (Eberl *et al.* 1986), as was previously observed with heated samples (Schultz 1969).

Most of the WD experiments were performed with K exchanged samples and distilled water. Eberl *et al.* (1986) observed that the oxygen isotope composition of K-smectite remained unaffected by WD cycles in water, but was changed by WD in KOH solution, which also increased the proportion of collapsed layers. Later experiments (Eberl *et al.* 1993) showed that heating smectites at 60°C in 0.1-1M KOH solutions promoted layer collapse. Heating at 60°C in 3M KOH solution initially led to a drastic reduction in expanded layers, but more prolonged heating or 6 WD cycles in a KOH solution destroyed the smectites, leaving an amorphous product. In contrast, a limited number of WD experiments carried out with K_2CO_3 or $KHCO_3$ indicated that this treatment did not destroy the smectites, but led to a

higher proportion of collapsed layers than WD cycles of K saturated samples in pure water. These phenomena remained unexplained.

WD cycles may play a significant role in clay diagenesis. The high alkalinities of saturated KOH solutions are geologically unrealistic, but WD cycles in carbonate-bicarbonate systems may occur in arid regions. The principal purpose of the present investigation was to examine the changes that occur in smectites on WD in K containing solutions at elevated alkalinities and to attempt to rationalize some of the results reported in the literature.

In recent years the possible participation of organic anions in diagenetic processes has received increasing attention (Surdam *et al.* 1980). Small (1994) found that dilute solutions of K-acetate or oxalate at 200°C caused significant conversion of smectite to R1 or R2 ordered illite-smectite. He attributed this effect to the buffering action of the anions on fluid composition. We report the results of exploratory experiments on the effect of these organic anions on K-fixation by smectites in WD cycles, conditions that differ drastically from those prevailing in Small's experiments.

MATERIALS AND METHODS

The starting materials were four smectites from the Source Clay Mineral Depository: Wyoming (Wy), Cheto (Ch), Otay (Ot) and a ferruginous clay (Fe-clay), aliquots of the samples used by Eberl *et al.* (1986). The experiments were carried out with $<2\mu m$ fractions, except for the Ot sample,

Table 1. % collapsed layers and K, Sr and Ca content after 120 WD cycles (Sr exchanged samples)

No / Cycles	Clay	Salt	% Collapse		Atoms / 4 Si ¹			Σ Equiv.
			(M+R) ²	(S) ³	K	Sr	Ca	
1/120	Wy	K ₂ CO ₃	~9	~8	0.14	0.20		0.56
2/120	Wy	KHCO	~9	~8	0.14	0.18		0.50
3/120	Wy	KOx	<<10	<<10		E		
4/120	Wy	KAc	<<10	<<10		ND		
5/120	Wy	KCl	<<10	<<10	0.05	0.15		0.35
6/120	Ch	K ₂ CO ₃	50	52	0.23	0.16		0.54
7/120	Ch	KHCO ₃	55	46	0.24	0.19		0.62
8/120	Ch	KOx	30	32		E		
9/120	Ch	KAc	33	32		ND		
10/120	Ch	KCl	30	31	0.15	0.16		0.47
63/120	Ot	K ₂ CO ₃	68	65	0.27	0.15	0.01	0.59
64/120	Ot	KCl	42	37	0.17	0.15	0.02	0.51
65/120	Ot	KOx	42	37		E		
11/120	Fe-clay	K ₂ CO ₃	34			E		
12/120	Fe-clay	KHCO ₃	30			E		
13/120	Fe-clay	KOx	41			E		
14/120	Fe-clay	KAc	31			E		
15/120	Fe-clay	KCl	30			E		

¹ See text; ² Moore and Reynolds (1989); ³ Srodon (1980).

E erratic; ND not determined.

which was the whole rock specimen. The K salts K₂CO₃, KHCO₃, KO₂C.CH₃ (KAc), K₂O₄C₂ (KOx) and KCl were of analytical grade.

Five grams of clay were mixed with 5g salt and 100 cc H₂O, stirred and evaporated to dryness at 60°C with occasional stirring. For each subsequent WD cycle 20 cc of distilled H₂O were added to the dry mixture and the process was repeated.

After various numbers of WD cycles aliquots of the samples were withdrawn for investigation. Aliquots were washed with deionized water until free of excess salts. Fractions of most of these samples were cation exchanged by treating them twice with 0.5M SrCl₂ solution, followed by exhaustive washing with deionized water. Some of the samples were examined as obtained or after washing.

X-ray diffraction (XRD) analysis of glycolated samples was carried out as described by Eberl *et al.* (1986). The chemical composition was determined by electron microprobe analysis (EMPA) of several particles from each sample, with a Joel JXA 8600 instrument. The same instrument was used for obtaining electron micrographs. For control, two samples were analyzed by inductively coupled plasma (ICP) at the Geological Survey of Israel. Infrared spectra of 1mg samples embedded in 150 mg KBr were recorded on a Nicolet 740 FTIR spectrometer. Thermogravimetric curves (TG) were obtained on a Stanton-Redcroft thermoanalyser (STA 780), at a heating rate of 10°C per minute under a stream of dried air.

The XRD analyses were performed on Sr exchanged, glycolated samples, to determine the extent of layer collapse under standardized conditions. Chemical analyses were carried out on samples that had been washed and on Sr exchanged samples. TG curves were obtained on washed, nonexchanged samples. FTIR spectra were recorded of samples in the presence of excess salt as well as after washing or ion exchange, to establish whether these treatments affected the processes studied.

RESULTS AND INTERPRETATION

X-Ray Diffraction

WD cycles of smectites with various K salts caused partial collapse of the layers, as observed by previous investigators. Some representative patterns are shown in Fig. 1. The proportion of collapsed layers in Sr exchanged, glycolated samples, after 120 WD cycles, as determined by the methods of Moore and Reynolds (1989, Table 7.3) and Srodon (1980) are shown in Table 1. Srodon's method could not be applied to the ferruginous clay, because this contained too much quartz, whose 3.34Å spacing overlapped a diagnostic smectite reflection. For the other samples the agreement between the results obtained by the two methods is satisfactory. Moreover, the d₀₀₁ spacing of the expanded layers, deduced from Srodon's plots, is consistent for any one smectite, whatever the K salt used (16.9, 16.7 and 16.6Å

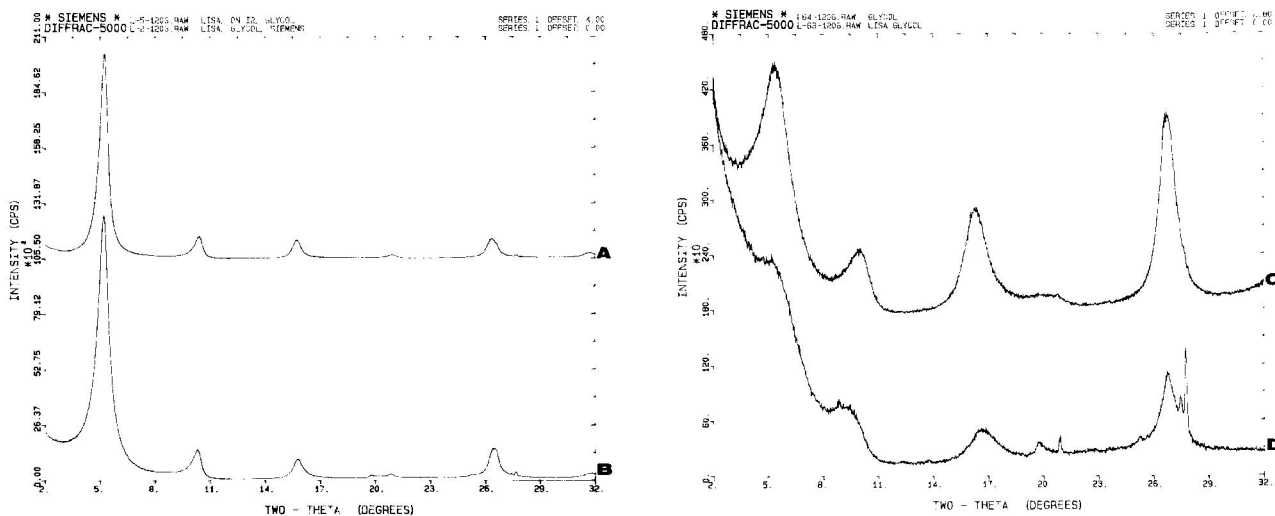


Fig. 1. XRD patterns of Wy (A and B) and Ot (C and D) montmorillonites after 120 WD cycles. A) KCl (5/120); B) KHCO_3 (2/120); C) KCl (64/120); D) K_2CO_3 (64/120). The samples were Sr saturated and glycolated ($\text{CuK}\alpha$ radiation).

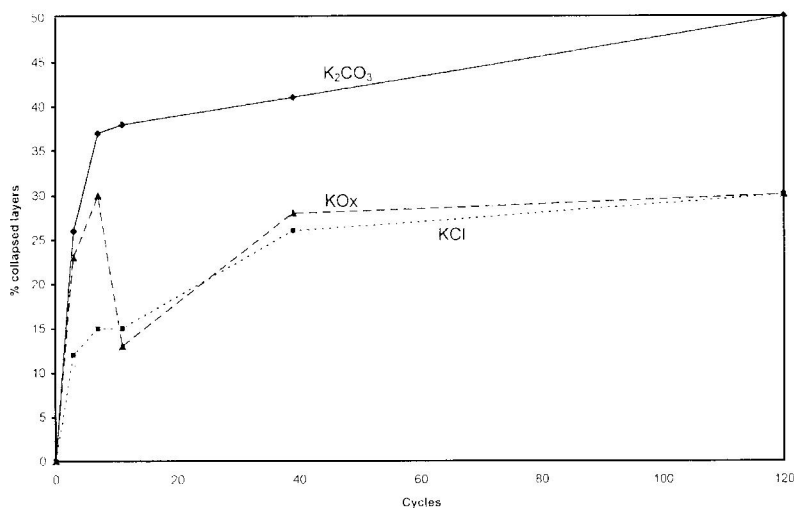


Fig. 2. Proportion of collapsed layers vs number of WD cycles of Cheto montmorillonite. The samples were Sr saturated and glycolated.

for Wy, Ch and Ot respectively). These results indicate that the products of WD treatment with different K salts, after Sr exchange and glycolation, are composed of $\sim 17\text{\AA}$ expanded and $\sim 10\text{\AA}$ collapsed layers, without significant contributions of other components.

The K salts can be divided into two groups on the basis of their effect on layer collapse of non-ferruginous smectites: K_2CO_3 and KHCO_3 in one group, KCl, KAc and KOx in the other. The effects on the ferruginous samples differed: the proportion of layers collapsed was similar with all the salts, but the X-ray patterns of samples cycled with K_2CO_3 or KHCO_3 became very weak, indicating extensive destruction of this iron-rich clay.

The proportion of layers collapsed by corresponding treatments increased in the order $\text{Wy} < \text{Ch} < \text{Ot}$, as previously observed by Eberl *et al.* (1986), who established a correlation between the proportion of collapsed layers of K smectites in WD cycles with water and the layer charge. Most of the collapse occurred in the first few WD cycles, as shown for representative samples in Fig. 2.

According to Srodon *et al.* (1992) the proportion of layers collapsed in the course of WD cycles may be overestimated, due to a decrease in the X-ray coherent scattering domain (short stack effect). However, they found that the values of N, the number of silicate layers per particle, were characteristic of a given smectite and did not change with solution chemistry. This suggests that whereas the proportions of collapsed layers given in

Table 1 and Fig. 2 may be overestimated, the differences between the effects of the solutions are genuine and are not artefacts due to changes in size of fundamental particles or to changes in the size of stacks of fundamental particles (MacEwan crystallites).

Chemical Composition

The chemical composition of samples after 120 WD cycles and Sr exchange and of two washed, but non-exchanged samples after 70 WD cycles are presented in Table 2. The interlayer population of the samples is also shown in Table 1. The results were obtained by EMPA and, for comparison, two samples were analyzed by ICP. The results are in good agreement.

Table 2. Chemical analyses* normalized to 4 Si (see text)

No / Cycles	Clay	Salt	Atom ratios (see text)						Equivalents $\Sigma(K+Sr+Ca)$	
			Si	Al	Fe	Mg	K	Sr		Ca
1/120	Wy	K ₂ CO ₃	4	1.67	0.26	0.27	0.14	0.21		0.56
2/120	Wy	KHCO ₃	4	1.55	0.22	0.30	0.14	0.18		0.50
5/120	Wy	KCl	4	1.57	0.20	0.25	0.05	0.15		0.35
6/70	Ch	K ₂ CO ₃	4	1.35	0.07	0.64	0.68	-		0.68
10/70	Ch	KCl	4	1.35	0.08	0.59	0.48	-		0.48
6/120	Ch	K ₂ CO ₃	4	1.38	0.08	0.58	0.22	0.16		0.54
7/120	Ch	KHCO ₃	4	1.36	0.05	0.61	0.24	0.19		0.62
10/120	Ch	KCl	4	1.37	0.07	0.59	0.15	0.16		0.47
63/120	Ot	K ₂ CO ₃	4	1.36	0.07	0.72	0.27	0.15	0.01	0.59
64/120	Ot	KCl	4	1.35	0.07	0.64	0.17	0.15	0.02	0.51

*The samples were Sr exchanged, except for samples 6/70 and 10/70, which were merely washed.

The advantage of EMPA over bulk chemical analysis is that it also probes the homogeneity of the samples. The ferruginous clay was found to be very inhomogeneous and was, therefore, not analyzed and was not investigated any further. The other clays, before and after treatment, were homogeneous within the limits of error of the method of measurement, except for the KOx treated samples, for which the chemical analyses were therefore not pursued further.

The presentation of the data in Table 2 requires explanation. All the analyses were normalized to 4 Si per unit. This corresponds to the actual composition per O₁₀(OH)₂ formula unit of Ch and Ot, untreated or cycled with KCl. The Wy sample is problematic, because it contains some tetrahedrally coordinated Al as well as quartz. However, to avoid arbitrary corrections and for convenience of comparison, the data for Wy were also normalized to 4Si. The interlayer population per formula unit is, therefore, slightly underestimated. The XRD traces and IR spectra showed that quartz was partly dissolved at the high pH of the K₂CO₃ solution. This accounts for the higher Al : Si ratio of the K₂CO₃ treated sample.

The objective of the chemical analyses was twofold: to establish whether the different treatments caused any significant changes in the chemistry of the clay layers and to determine the composition of the interlayer population. The method of presenting the data serves as a convenient basis of comparison for the differently treated samples of any one clay, except for the Wy sample cycled with K₂CO₃.

It is evident from Table 2 that, with the exception of K₂CO₃ treated Wy, the Si : Al : Fe : Mg ratios of the non-ferruginous clays did not change appreciably after the various treatments. This demonstrates that these treatments did not alter the bulk cation composition of the layers. In contrast, Tables 1 and 2 show that the amount of non-exchangeable K and the total interlayer cation population were significantly higher in samples cycled in the alkaline

K₂CO₃ or KHCO₃ than in those cycled in the neutral KCl or KAc systems. The difference between K₂CO₃ and KCl treatments is most apparent with samples that were not Sr exchanged, e.g. Ch samples 6/70 and 10/70, with 68 and 48 meq K respectively (Table 2). The interlayer charge of the KCl treated sample remained unchanged after 120 cycles and Sr exchange, but that of the corresponding K₂CO₃ treated one was reduced to 0.55 per 4 Si (Table 2). The proportion of collapsed layers of similarly treated samples cycled with K₂CO₃ increased steadily with progressive cycles (Fig. 2). The lower interlayer charge of the sample after 120 cycles must, therefore, be attributed to the effect of Sr exchange. It appears that the effect that caused the increased layer charge in the non-exchanged sample 6/70 was partly reversed on cation exchange of sample 6/120.

Exposure of a K₂CO₃ treated particle to the electron beam for 1-2 minutes caused a decrease of up to 10% in the intensity of the K radiation. A similar reduction in intensity was not observed with the KCl treated sample. This suggests that the additional K in the K₂CO₃ and KHCO₃ treated samples is bound less firmly than K introduced by cation exchange.

Electron Micrographs

Electron micrographs of the original Ch and of K₂CO₃ (6/70) and KCl (10/70) treated, washed samples are shown in Fig. 3. The morphology of sample 10/70 is indistinguishable from that of the starting material, but sample 6/70 has clearly undergone some change. The aggregates are smaller and more compact, with less edge-face contact. The particles do not appear to be digested.

Infrared Spectra

Selected data are presented in Table 3 and Fig. 4. The spectra of KCl, KOx or KAc treated samples were similar to those of the starting materials, whereas samples cycled with K₂CO₃

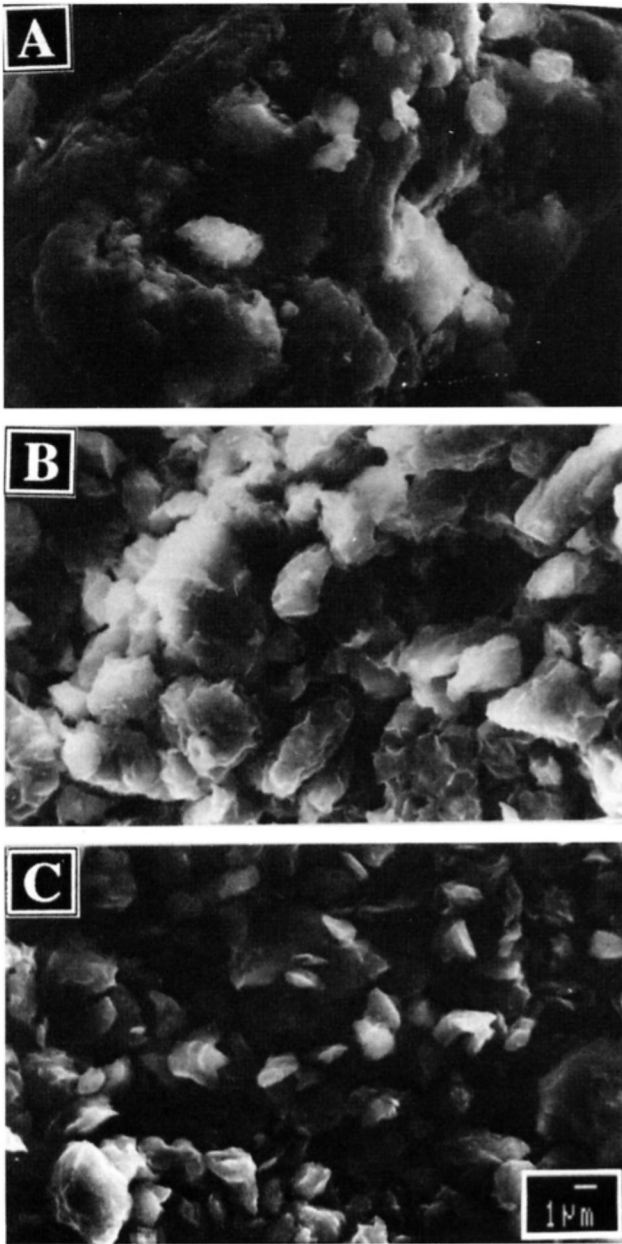


Fig. 3. Electron micrographs of Cheto montmorillonite A) untreated; and after 70 WD cycles with B) KCl (10/70); C) K_2CO_3 (6/70) (washed samples).

or $KHCO_3$ showed small shifts of the OH ($\sim 3630\text{ cm}^{-1}$) and the principal Si-O ($\sim 1030\text{ cm}^{-1}$) stretching bands towards lower wavenumbers. In addition, the Fe-OH-Al bending vibration ($\sim 880\text{ cm}^{-1}$) in the spectrum of Wy clay became weak or disappeared after WD cycles at high pH. This band was not observed in the spectra of the Ch and Ot clays, due to their low Fe content.

The changes observed in the spectra of clays cycled in alkaline solutions are similar to those reported for smectites that were heated with alkali halides (Heller-Kallai 1975) or for nontronites and ferruginous smectites treated with

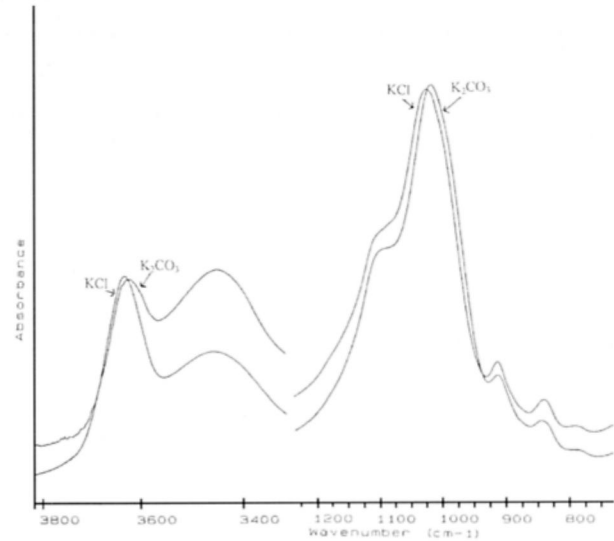


Fig. 4. Infrared spectra of Cheto montmorillonite after 70 WD cycles (washed samples).

alkaline solutions under milder conditions (Russell 1979; Heller-Kallai and Rozenson 1981). They were attributed to the effect of partial deprotonation of the structure. Features diagnostic for illite, i.e. vibrations at 825 and 750 cm^{-1} (Russell and Fraser 1994), were not observed in any of the spectra.

It is evident from Table 3 that deprotonation is partly reversed by washing the samples and by Sr exchange. The shifts observed with non-exchanged, washed samples after 7 WD cycles, and, even more so with the corresponding unwashed sample, were greater than those detected after 120 cycles and Sr exchange.

The infrared spectra of unwashed samples show that at most after 7 cycles K_2CO_3 was entirely converted to $KHCO_3$. Therefore, after the first few WD cycles the effect of these two reagents became identical.

Thermogravimetric Analysis

Fig. 5 shows weight loss curves for Ch samples 6/70 (K_2CO_3 treated) and 10/70 (KCl treated), which were subjected to 70 WD cycles, washed but not cation exchanged. The samples were stored under the same ambient conditions for about 44 months before analysis. It is evident that the weight losses differ mainly in two temperature regions: below about 200°C and above 565°C (Table 4). Although weight losses due to adsorbed and structural water obviously overlap in the intermediate temperature region, losses below 200°C and above 565°C may be attributed to adsorbed and structural water respectively. Both samples were saturated with K and sample 6/70 contained more collapsed layers than 10/70 (Fig. 2). The enhanced low temperature weight loss must, therefore, be attributed to differences in surface area, compatible with the changes in morphology observed in the electron micrographs. The smaller weight loss of sample 6/70

Table 3. Infrared spectra

No / Cycles	Clay	Salt	W	Sr	OH cm ⁻¹	Si-O cm ⁻¹	Fe-OH-Al* 880 cm ⁻¹
	Wy	-	-	-	3635	1049	+
1/70	Wy	K ₂ CO ₃	-	-	3617	1027**	-
1/70	Wy	K ₂ CO ₃	+	-	3625	1034	vw
1/120	Wy	K ₂ CO ₃	+	+	3628	1033	vw
5/120	Wy	KCl	+	+	3634	1049	+
	Ch				3624	1030	
6/70	Ch	K ₂ CO ₃	-	-	3617	1023**	
6/70	Ch	K ₂ CO ₃	+	-	3617	1023	
6/120	Ch	K ₂ CO ₃	+	+	3626	1024	
10/120	Ch	KCl	+	+	3626	1030	
63/7	Ot	K ₂ CO ₃	-	-	3608	1007**	
63/7	Ot	K ₂ CO ₃	+	-	3622	1024	
63/120	Ot	K ₂ CO ₃	+	+	3626	1024	
64/120	Ot	KCl	+	+	3628	1028	

Abbreviations: W = washed; Sr = Sr exchanged; v = very; w = weak, + = yes;

* see text; ** uncertain due to overlap of KHCO₃ absorption.

Table 4. Weight loss of Cheto smectite after 70 WD cycles, washed samples

Temp. °C	Weight loss %		Species
	K ₂ CO ₃ (6/70)	KCl (10/70)	
<200	4.9	3.0	H ₂ O
200-565	8.3	8.2	H ₂ O + OH
565-750	2.9	3.7	OH

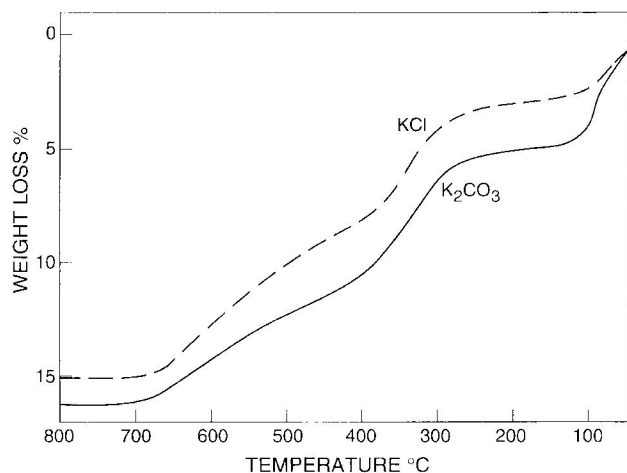


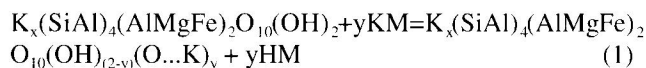
Fig. 5. Weight loss of Cheto montmorillonite after 70 WD cycles (washed samples).

in the last stage of heating may be due to one of two causes: destabilization of the structure, which reduces the dehydroxylation temperature, or a lower hydroxyl content. In view of the similarity of the weight losses of the two samples between 200 - 565°C the second explanation seems more

plausible. Thus, the observed weight losses are compatible with the conclusion that the K₂CO₃ treated sample was partially deprotonated.

DISCUSSION

In the course of WD cycles fixation of K and collapse of smectite interlayers occurred with all the K salts. The ferruginous clay was extensively destroyed at high pH and the residual samples resembled those treated with neutral salts. With non-ferruginous smectites a greater proportion of layers collapsed on WD treatments with K₂CO₃ or KHCO₃ solutions than with KCl, KOx or KAc. The results obtained indicate that at the high pH of the K₂CO₃ or KHCO₃ solutions some deprotonation of structural OH groups occurred, according to the equation:



where M is the anion of the K salt. This is compatible with the changes observed in the IR spectra and accounts for the higher layer charge, the enhanced K fixation and the concomitant increase in the proportion of collapsed layers of the carbonate treated samples. Deprotonation reduces the

amount of structural OH groups, in agreement with the lower weight loss at elevated temperatures.

The additional K, which neutralizes the charge due to deprotonation, seems to be bound differently from K introduced by K exchange. The correlation between the amount of fixed K and the proportion of collapsed layers of K-smectites after WD treatment in water observed by Eberl *et al.* (1986) does not extend to K introduced in the course of deprotonation. Table 1 shows that the amount of fixed K in Wy after WD in alkaline solutions was similar to that of Ch cycled in KCl, but the proportion of collapsed layers was much smaller. Moreover, this additional K was less resistant to exposure to the electron beam than that introduced by cation exchange.

Smectites subjected to WD cycles with KAc were similar to those treated with KCl. The effect of KOx treatment resembled that of KCl more than that of the carbonates, but the erratic results of the chemical analyses and of the proportion of collapsed layers in the early stages of cycling (Fig. 2) suggest that some complexing of Al and Fe may have occurred. This was particularly pronounced with the ferruginous clay. The reactions with oxalate require further investigation.

This study concentrated on the nature of the clay produced after the WD treatment. In the course of WD in the alkaline solutions some dissolution may have occurred, but the chemical composition of the bulk of the non-ferruginous clays remained unaltered, except for the changes inferred from equation (1). Extensive dissolution occurred with the ferruginous clay.

Eberl *et al.* (1993) found that WD cycles with KOH solutions destroyed smectites, as did prolonged heating with 3N KOH solutions without WD cycles, whereas smectites exposed to 1N KOH solutions at 60°C for 150 days without WD persisted. In the course of every WD cycle samples are exposed to the maximum alkalinity and ionic strength of a saturated solution. WD cycles with KOH are, therefore, not comparable with K₂CO₃ or KHCO₃ treatment, whatever the initial KOH concentration. The pH of the K₂CO₃ system at saturation was 13.68, that of the KHCO₃ system was 8.82 (Eberl *et al.* 1993). The pH of saturated KCl or KAc solutions was close to neutral. The IR spectra showed that the carbonate solutions were converted to bicarbonate in the early stages of WD cycles. K₂CO₃ treated samples were therefore exposed to a maximum pH of 13.68, similar to that of a N KOH solution, in the early WD cycles, but most of the subsequent cycles occurred at a much lower pH. Under these conditions, which are much milder than those encountered in WD cycles with KOH or even on heating with 3N KOH solutions, deprotonation, not dissolution, is the dominant reaction. Even after 120 WD cycles no recrystallization of a new phase was detected. Whether the deprotonated material is a metastable intermediate phase remains to be established.

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