

## STABILITY OF SOIL SMECTITE FROM A HOUSTON BLACK CLAY\*

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**Abstract**—The stability of smectite separated from a Houston Black clay soil was studied by solubility methods in an acid environment. High Silicon levels (supersaturated with respect to amorphous Si) probably were due to dissolution of the smectite and slow precipitation of amorphous Silicon. Also, mica and vermiculite impurities may have contributed to high solution Si values. Solubility data from equilibrium solutions of various treatments and chemical structural analyses permitted the formulation of a solubility equation. The  $\Delta G_f^\circ$  for the Houston Black smectite computed from pK values was  $-2433.9 \pm 0.8$  kcal/mole. The stability of this clay could then be determined by calculations for any desired solution environment. It was found that under some conditions this soil smectite could be more stable than Belle Fourche and Aberdeen montmorillonites. Therefore, it appears that this soil clay has the required stability area in which it can form in nature.

### INTRODUCTION

An understanding of mineral weathering requires that there be information on the stability of various minerals under different chemical conditions. The reaction of mineral assemblages with an aqueous phase of its common components is the fundamental basis of clay mineral formation and dissolution.

The early work of Garrels (1957) in estimating thermodynamic values of important soil minerals from geological relationships was followed by actual experimental determination of such values. Most of the experimental thermodynamic data on clay minerals to date have been obtained from pure mineral materials from geologic formations. Weaver *et al.* (1971) obtained stability information indirectly on a soil montmorillonite by analysis of solutions contacting whole soil and mixed clay fractions. The objective of this investigation was to measure the stability by solubility methods of a soil smectite that was separated from a Houston Black soil.

### MATERIALS AND METHODS

A relatively pure Houston Black (HB) smectite was concentrated in  $<0.08 \mu\text{m}$  clay from a Houston Black soil clay of Bell County, Texas. The soil sample was treated for removal of carbonates with pH 5 1N NaOAc and destruction of organic matter with  $\text{H}_2\text{O}_2$  in pH 5 1N NaOAc and removal of free-iron oxides with dithionite–citrate–bicarbonate solutions (Jackson, 1956, pp. 33–36, 47). Dispersion was done in

dilute pH 10  $\text{Na}_2\text{CO}_3$  solution (without boiling in 2%  $\text{Na}_2\text{CO}_3$ ). The HB smectite was washed three times with 0.1 M  $\text{MgCl}_2$  and washed salt-free with water.

Hematite was added to control the pH-1/3  $p \text{Fe}^{3+}$  as described by Kittrick (1971a). The hematite was Mapico Red No. 347 from Columbian Carbon Company. Kaolinite was added to some samples in an effort to control the  $p \text{H}_4\text{SiO}_4$  level. This kaolinite was from England and designated as No. 3 by Hamill and Gillespie, Incorporated.

### Sample treatments

To attain equilibrium, samples were placed in 250 ml plastic centrifuge bottles and shaken continuously at a slow speed on an Eberbach shaker. Two samples, Id and IIB, were unshaken for several weeks before final analysis, instead of the usual shaking procedure. All samples were initially adjusted to a pH near 3 by slowly adding 0.1 N HCl. Final pH adjustment often required several hours. Detailed descriptions are given for the various treatments. Mineral combinations are indicated by Roman numerals. The numeral I indicates the combination of 3 g HB smectite, 3 g English kaolinite and 3 g Mapico hematite; while numeral II indicates only the smectite and hematite at 3 g of each. Chemical treatments are indicated by lower case letters and OH for the 0.5 N NaOH treatment. All equilibria were carried out at  $25^\circ\text{C} \pm 1^\circ$ . The following includes detailed descriptions for all treatments:

(I) This treatment consisted of 3 g HB smectite, 3 g kaolinite, 3 g of hematite and 25 ml 0.01 M  $\text{MgCl}_2$ . The initial pH after acid adjustment was 2.9.

(Ia-OH) After completion of the first equilibration run, sample I was treated with boiling 0.5 N NaOH for 2.5 minutes (Hashimoto and Jackson, 1960) to remove amorphous material. The sample was then saturated with Mg as described previously and 25 ml

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of 0.01 M MgCl<sub>2</sub> was added and reacidified to an initial pH of 3.3.

(Ib) This treatment was a duplicate of I above; containing 3 g HB smectite, 3 g kaolinite, 3 g hematite and 25 ml 0.01 M MgCl<sub>2</sub>. The initial pH of this sample was 2.9 after acid adjustment.

(Ic) After the first equilibration run, sample Ib was reacidified to a pH of 2.6 and fresh 0.01 M MgCl<sub>2</sub> was added.

(Id) After the second equilibration run, sample Ic was given 5 centrifuge washes with 0.01 M MgCl<sub>2</sub> at pH 2.0. The material was resuspended in 25 ml of 0.01 M MgCl<sub>2</sub> resulting in an initial pH of 2.5.

(II-OH) To check the effects of sodium hydroxide treatment without added kaolinite on a fresh sample (not yet equilibrated), 3 g of HB smectite and 3 g hematite were treated with NaOH as for Ia-OH. This sample was then Mg-saturated, acidified with HCl, 25 ml of 0.01 M MgCl<sub>2</sub> added, resulting in an initial pH of 3.1.

(IIa) This sample was the same as II-OH except that no NaOH treatment was given. It differs from samples I and Ib because it contains no kaolinite. The HB smectite-hematite mixture was Mg-saturated, acidified, 25 ml of 0.01 M MgCl<sub>2</sub> added, resulting in an initial pH of 2.8.

(IIb) After equilibrium, sample IIa was resaturated with Mg, and suspended in 0.01 M MgCl<sub>2</sub> of pH 2.0 to give an initial pH of 2.5.

#### Chemical analyses

For pH measurements and ultimately to take solution samples, the suspension aliquots were transferred to 40 ml plastic tubes for high speed centrifugation. Solution aliquots were taken using a Shaw pipette rack with a 5 ml capacity pipette. The samples were stored for future analysis in small plastic bottles. The presence of suspended matter in the solutions was checked in a colorimeter against a blank of distilled water at a wavelength of 4000 Å. Previous testing showed that less smectite could be detected by this procedure than was visible as suspended particles. All supernatant solutions checked gave the same value as water.

A Corning Model 12 pH meter with a combination electrode was used with a recorder to indicate when equilibrium occurred (usually 2–3 hr). The pH meter was calibrated with several buffers to ensure accuracy. The course of equilibration was followed by monitoring sample pH as a function of time. The pH increase was rapid initially, but became very slow after about a month. Some samples required several months to reach a constant pH.

Total chemical analysis of the minerals was performed using the method of Bernas (1968) as modified by Carson and Dixon (1972). Solution magnesium was determined by atomic absorption nitrous oxide flame to avoid interferences after diluting 1 ml aliquots to 200 ml with a fluoboric acid solution (Bernas, 1968). Silica in equilibrium solution was

measured colorimetrically with molybdate, (American Public Health Association, 1960). Aluminum in the equilibrium solution was determined by the method of Hsu (1963). By starting the samples at a pH below 3.4, it was assumed that Al in solution could be determined. Ion activities for Mg and Al were computed from the Debye-Hückel equation (Klotz, 1964).

Samples previously Mg-saturated, acidified, and equilibrated were employed for cation exchange determinations. Cation exchange capacity was determined by saturating 100 mg samples with sodium and displacing it with ammonium. The samples were washed salt-free and then saturated with sodium using 1 N NaCl and washed free of Cl<sup>-</sup> with small amounts of methanol to avoid dispersion. Displacement of Na<sup>+</sup> was obtained with pH 7 N NH<sub>4</sub>OAc for a total of 3 washes of approx. 30 ml each. Exchangeable magnesium, aluminum and iron were replaced from initially salt-free samples by using 3 washes of 0.5 N BaCl<sub>2</sub> solution with each involving a 15 min shaking time and centrifugation.

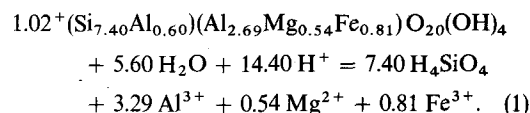
## RESULTS AND DISCUSSION

### Equilibration data

The slope of the solubility line of minerals depends upon their chemical composition. The unit cell formula calculated for HB smectite was:



The solubility line was derived from the following equation showing dissolution into the various components:



An equilibrium constant (*K*) was written in terms of the activities of the different components assuming the activities of the smectite and water to be unity:

$$K = \frac{(\text{H}_4\text{SiO}_4)^{7.40} + (\text{Al}^{3+})^{3.29} + (\text{Mg}^{2+})^{0.54} + (\text{Fe}^{3+})^{0.81}}{(\text{H}^+)^{14.40}} \quad (2)$$

Taking negative logarithms:

$$\begin{aligned} \text{p}K = 7.40 \text{p} \text{H}_4\text{SiO}_4 + 3.29 \text{p} \text{Al}^{3+} + 0.54 \text{p} \text{Mg}^{2+} \\ + 0.81 \text{p} \text{Fe}^{3+} - 14.40 \text{p} \text{H}^+. \end{aligned} \quad (3)$$

By rearranging and dividing by 9.87:

$$\begin{aligned} \text{pH} - 1/3 \text{p} \text{Al}^{3+} = 0.75 \text{p} \text{H}_4\text{SiO}_4 \\ - [0.11(\text{pH} - 1/2 \text{p} \text{Mg}^{2+}) \\ + 0.25 (\text{pH} - 1/3 \text{p} \text{Fe}^{3+}) \\ + 0.10 \text{pH}^+ + 0.10 \text{p}K]. \end{aligned} \quad (4)$$

The arrangement of the data follows the pattern of Kittrick (1969) where it is assumed the solubility of smectite depends upon ions common to its structure and the total ion exchange capacity. By plotting

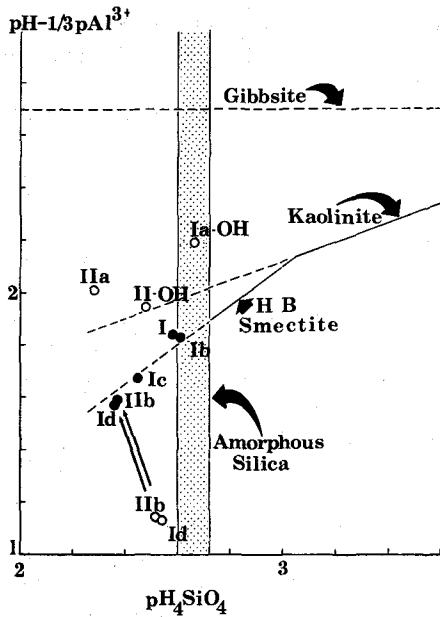


Fig. 1. Analyses of solutions equilibrated with Houston Black smectite. The size of each circle is based upon an analysis precision of  $pH^+ \pm 0.01$ ,  $pH_4SiO_4 \pm 0.02$ ,  $pAl^{3+} \pm 0.04$  and  $pMg^{2+} \pm 0.02$ . Open circles are sample analyses that are not at or near equilibrium. Closed circles are data points that are near equilibrium (listed in Table 2). Solubility lines are solid where they represent the most stable mineral of the group and are dashed where metastable.

$pH - 1/3 pAl^{3+}$  (aluminum hydroxide potential) as the dependent variable and  $pH_4SiO_4$  as the independent variable, equation (4) indicates that the solubility line of HB smectite will have a slope of 0.75 whereas the intercept is the negative quantity inside the brackets of equation (4). The intercept depends upon  $(pH - 1/2 pMg^{2+})$ ,  $(pH - 1/3 pFe^{3+})$ , and  $pH^+$ , as well as the  $pK$  computed from equation (3). Dashed lines in Fig. 1 indicate a metastable condition while solid lines denote where a mineral is the most stable. The mineral that supports the lowest aluminum hydroxide potential is considered the most stable (Kittrick, 1969). Another approach to equation (3) employs the exchangeable cations in the equilibrium expression (Garrels, 1967). If the data are interpreted in this way, it is necessary to know the ions on the exchange sites of the smectite. Therefore, samples Id and IId were analyzed for exchangeable cations fol-

lowing the equilibration (Table 1), so that this method could be used.

Samples I, Ia-OH, Ib, Ic and Id contained English kaolinite, but it is evident in Fig. 1 that none of these samples were in equilibrium with the kaolinite stability line established in an earlier report (Kittrick, 1966). Sample Ia-OH which was treated for amorphous Si removal was supersaturated with respect to both kaolinite and HB smectite. The NaOH treatment appears to have made sample Ia-OH more soluble (less stable) than before. Sample Ic displayed a greater stability, indicating some soluble materials may have been removed by the acidification treatment that were not removed by sodium hydroxide. Sample II-OH was a fresh soil smectite and hematite mixture without previous equilibration history, treated with 0.5 N NaOH to remove amorphous material. The position of sample II-OH in Fig. 1 indicates an increase in solubility caused by the NaOH treatment as was observed for Ia-OH. The causes of NaOH treatment increasing solubility of the smectite sample are not known but increased particle dispersion to monolayers of smectite and removal of hydroxy-Al from interlayer and external exchange sites are likely possibilities.

Initially it was unclear whether or not sample Ic was actually on the metastable extension of the HB smectite solubility line so sample Ic and sample IIa (which appeared unusually soluble) were further acidified. This was done in hopes of dissolving traces of labile material and revealing the true stability of the samples. After reacidification, samples Id and IId (lower set) eventually both returned (upper set) to the HB smectite solubility line where sample Ic was originally.

*Establishment of the solubility line*

Of the 8 different treatments in Fig. 1, only 5 appear to be in equilibrium with HB smectite. These five sample treatments with 10 different sample dates (Table 2) are indicated by the solid circles in Fig. 1. Their positions are in reasonable agreement with a line of slope 0.75 as calculated with equation (4). The sample points deviate slightly from the calculated slope which may be slightly in error due to the effect of impurity minerals on the correct analysis of soil smectite. However, substantial agreement with a solubility line of the correct slope is a good indicator

Table 1. Cation exchange properties of Houston Black smectite\*

Treatment, sampling date	Cation exchange capacity $Na^+/NH_4^+$	Exchangeable cations		
		$Mg^{2+}/Ba^{2+}$	$Al^{3+}/Ba^{2+}$	$Fe^{3+}/Ba^{2+}$
		(m-equiv./100 g)		
Id-19-6-74	34.3	19.4	2.9	1.5
IId-20-6-74	50.3	28.8	3.9	2.6

\* Each value represented the average of 2 determinations.

Table 2. Solution compositions near equilibrium with Houston Black smectite\*

Sample	Equilibration time (days)	pH <sup>+</sup>	p H <sub>4</sub> SiO <sub>4</sub>	p Al <sup>3+</sup>	pH - 1/3 p Al <sup>3+</sup>	p Mg <sup>2+</sup>	pH - 1/2 p Mg <sup>2+</sup>	pK	Intercept
I-6-7-72	21	3.26	2.59	4.31	1.83	2.06	2.23	-3.75	-0.12
I-13-7-72	28	3.27	2.58	4.30	1.84	2.03	2.26	-3.97	-0.10
I-20-7-72	35	3.28	2.58	4.32	1.84	2.04	2.26	-3.97	-0.10
Ib-6-7-72	21	3.33	2.62	4.48	1.82	2.06	2.29	-3.62	-0.14
Ib-13-7-72	28	3.33	2.61	4.51	1.82	2.07	2.29	-3.65	-0.14
Ic-25-10-72	104	3.10	2.45	4.29	1.67	2.12	2.04	-2.85	-0.17
Ic-1-11-72	111	3.11	2.45	4.32	1.67	2.20	2.01	-2.87	-0.17
Ic-7-11-72	117	3.12	2.45	4.34	1.67	2.20	2.02	-2.87	-0.17
Id-19-6-74	355	2.95	2.36	4.14	1.57	2.01	1.95	-2.20	-0.21
IIf-20-6-74	356	2.98	2.37	4.18	1.59	2.16	1.90	-2.33	-0.19

Ave. pK -3.21

Ave. deviation ±0.6

$\Delta G_f^0 = -2433.9 \pm 0.8$  kcal/mole

\* The Fe<sup>3+</sup> activity was assumed controlled by hematite at a pH-1/3 p Fe<sup>3+</sup> = -0.32.

of sample equilibrium. As a further indicator of equilibrium, the various treatments gave solution analyses that were initially both supersaturated and undersaturated with respect to the solubility line.

Sample points establishing the HB smectite line are all near or above the saturation with respect to amorphous silica; thus, they are on a metastable extension (dashed in Fig. 1) of the HB smectite solubility line. Silica levels where HB smectite is the most stable mineral of the group in Fig. 1 range from p H<sub>4</sub>SiO<sub>4</sub> = 2.72-3.30, at which point kaolinite becomes more stable. Most of the solution Si in this study probably came from dissolution of the smectite. Elemental analysis of sample IIf after equilibration showed the same ratio of elements as prior to the experiment, suggesting that dissolution or precipitation of smectite was congruent. X-ray powder diffraction of the samples before and after equilibrium showed no evidence of additional impurities. A previous study (Carson and Dixon, 1972) showed small amounts of vermiculite, mica and kaolinite present in a similar Houston Black <0.08 μm clay.

Potassium data for sample IIf after equilibrium showed 4.8% mica present while before it was 6.7%. Some of the solution Si may thus be from mica and vermiculite impurities. Presumably the slow rate of amorphous Si precipitation relative to sample dissolution contributed to the solution levels of Si exceeding the equilibrium level of amorphous Si.

Measurements at the end of equilibration showed the sample IIf to be over 8% aluminum saturated (Table 1), as opposed to being 100% magnesium saturated at the start of the experiment. Exchange capacity data in Table 1 represent mixed mineralogies for both Id and IIf. The initial Id sample was approximately one-third smectite (3 g smectite, 3 g kaolinite and 3 g hematite all air dry weights). Assuming the exchange to come mostly from the smectite (CEC ca. 110 m-equiv./100 g) then it appears little exchange capacity was lost during the experiment. Sample IIf was approximately one-half smectite (3 g smectite and

3 g hematite) which once again is in general agreement with the original exchange capacity of the smectite. Following equilibration, both of these samples (Id and IIf) were X-rayed with Mg and K-saturation. The K-saturated samples upon heating (550°C) contracted to 10 Å, indicating little or no stable interlayer of hydroxy-aluminum was present.

#### Standard free energy of formation

The average pK value for HB smectite is -3.21 ± 0.6 (Table 2). The Gibbs free energy of reaction value is derived from the equation:

$$\Delta G_r^0 = RT \ln K = 1.36 \text{ pK} \\ = -4.4 \pm 0.8.$$

Further,

$$\Delta G_r^0 = 3.29 \Delta G_{f\text{Al}^{3+}}^0 + 0.54 \Delta G_{f\text{Mg}^{2+}}^0 \\ + 0.81 \Delta G_{f\text{Fe}^{3+}}^0 + 7.40 \Delta G_{f\text{H}_4\text{SiO}_4}^0 \\ - 5.60 \Delta G_{f\text{H}_2\text{O}}^0 - \Delta G_{f\text{HB smectite}}^0 \\ \Delta G_{f\text{HB smectite}}^0 = -\Delta G_r^0 - 2438.3 = 4.4 \pm 0.8 - \\ 2438.3 \\ = -2433.9 \pm 0.8 \text{ kcal/mole.}$$

The  $\Delta G_f^0$  values for Al<sup>3+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup> and H<sub>2</sub>O were taken from (Robie and Waldbaum, 1968). The  $\Delta G_{f\text{H}_4\text{SiO}_4}^0$  value of -312.6 was from data of Mackenzie and Gees (1971). The  $\Delta G_f^0$  values used for Al<sup>3+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup> and H<sub>2</sub>O were -116, -108.9, -2.52 and -56.69 respectively. It must be recognized that accuracy of  $\Delta G_f^0$  values for Mg<sup>2+</sup>, Fe<sup>3+</sup>, H<sub>4</sub>SiO<sub>4</sub>, H<sub>2</sub>O and Al<sup>3+</sup> will directly influence the  $\Delta G_f^0$  values for smectite. The least accurate may be  $\Delta G_f^0$  Al<sup>3+</sup>. Because of their different chemical compositions, the HB smectite  $\Delta G_f^0$  value can not be directly compared with  $\Delta G_f^0$  values previously determined for specimen montmorillonites such as Aberdeen montmorillonite, which was -2450.3 (1971c), and Belle Fourche and Clay Spur montmorillonites which were -2468.5 (1971b). However, it can be calculated for example

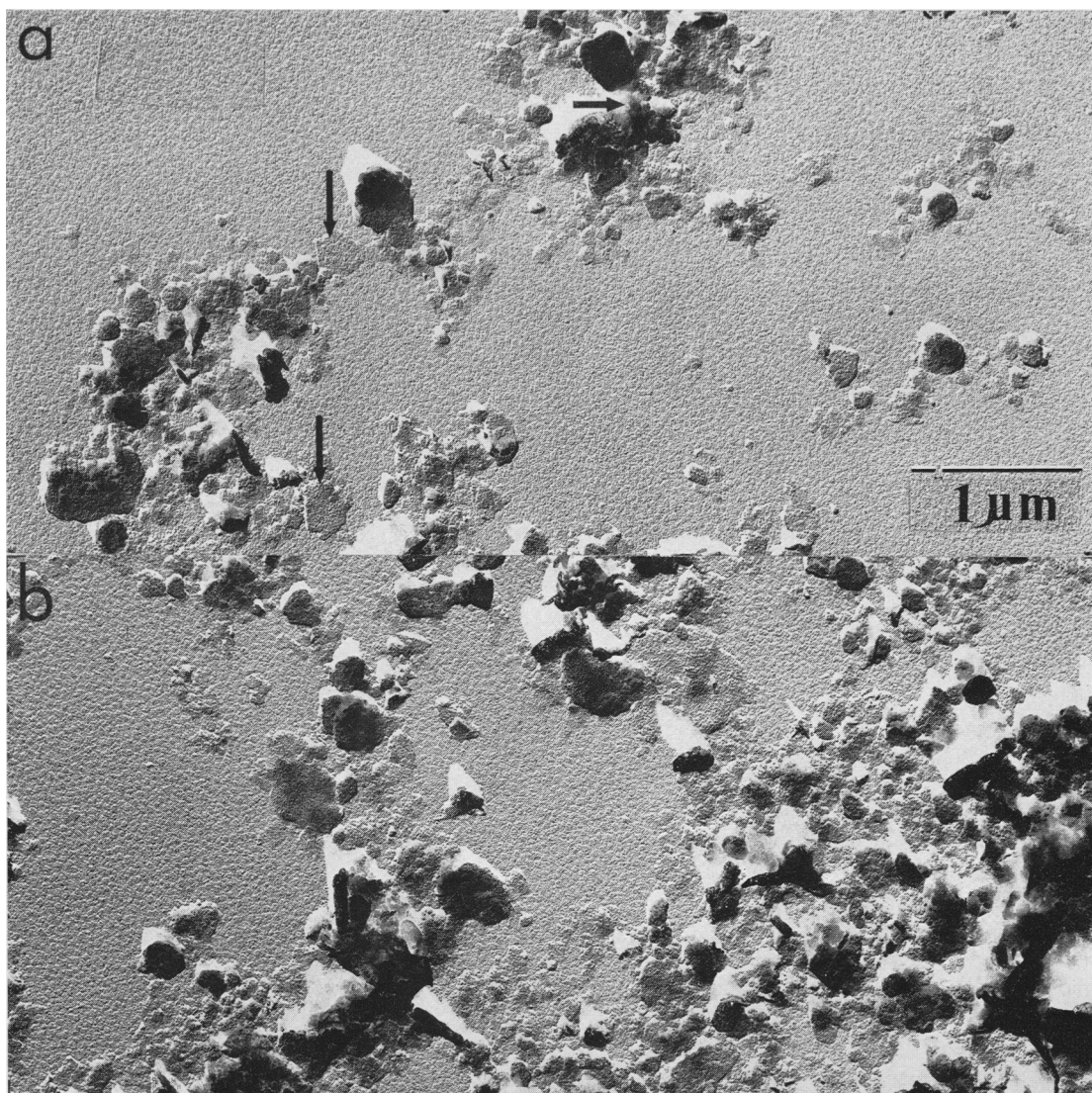


Fig. 2. Electron micrographs of Houston Black smectitic clay (non-equilibrated): (a) thin flakes and fluffy masses (arrows thought to be smectite; and (b) hexagons assumed to be kaolinite (a and b same scale). [Sample drop mounted on carbon film and shadowed with Pt-Pd at arc tan 1/3. Micrographs taken with Hitachi HUIIE at 50 kV.] Appreciation is expressed to Dr. E. L. Thurston for use of facilities in the Electron Microscopy Center of Texas A&M University.

at a  $\text{pH}^+ = 8$ ,  $p\text{H}_4\text{SiO}_4 = 3$  and  $\text{pH} - 1/2 p\text{Mg}^{2+} = 4.15$ , the HB smectite is more stable than either the Belle Fourche or Aberdeen montmorillonites. Under other conditions the reverse is true. The stability of HB smectite appears to be compatible with both Belle Fourche and Aberdeen montmorillonites in that there are reasonable solution conditions under which each is stable. The formation at near surface conditions of a montmorillonite such as the one of this study could occur. Magnesium and Si contents of displaced soil solution from two acid Wisconsin soils (Weaver *et al.*, 1971) that contain significant amounts of montmorillonite represent a stability area similar to equilibrium solutions of this experiment suggesting that approximately the equilibrium conditions of our experiment exist in natural soil in the field.

#### Particle morphology and size

The electron micrographs of Fig. 2 depict the smectite used in this study. The photomicrographs were made of the HB smectite prior to equilibration. They show the clay to be mostly very thin packets of what appears to be smectite (Fig. 2a, arrows). Many of the thinnest plates are about 100 Å thick and the smallest ones are only about 1000 Å across. Such fine particles probably contributed to the smectite dissolution rate and indirectly to the high  $\text{H}_4\text{SiO}_4$  concentrations reported at equilibrium. Appreciable scrolling of the thin, presumably smectite plates is shown in several places in Fig. 2b, especially in the lower right corner. Such conical rolls were thicker and more heavily shadowed than most horizontal plates. Consequently, they are dark in the micrograph. There are some euhedral hexagonal particles that are assumed to be kaolinite (Fig. 2b).

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