

## EFFECTS OF OXIDATION STATE OF OCTAHEDRAL IRON ON CLAY SWELLING

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**Abstract**—Three montmorillonites and a nontronite were reduced by sodium dithionite to obtain different amounts of Fe<sup>2+</sup> in their octahedral sites. The mass ratio of water to clay,  $m_w/m_c$ , was determined as a function of Fe<sup>2+</sup> at several values of the swelling pressure,  $\Pi$ . The value  $m_w/m_c$  decreased markedly with increasing Fe<sup>2+</sup> at each value of  $\Pi$  for each clay. Moreover, curves of  $\Pi$  vs.  $m_w/m_c$  for the different clays were displaced downwards as Fe<sup>2+</sup> increased. A straight line was obtained when  $\ln(\Pi + 1)$  was plotted against  $1/(m_w/m_c)$ ; however, at some oxidation states of three of the samples this line exhibited a sharp break at a specific value of  $1/(m_w/m_c)$ . The slope of the line decreased for each clay as Fe<sup>2+</sup> increased, and an increase in Fe<sup>2+</sup> was accompanied by an increase in the cation exchange capacity. These observations are thought to be due to a collapse or partial collapse of the superimposed clay layers resulting from the increase in cation-exchange capacity.

**Key Words**—Iron, Nontronite, Oxidation, Reduction, Smectite, Swelling.

### INTRODUCTION

The presence of swelling clays in soils and sediments is of great importance. If a dry clay comes in contact with water, it swells to many times its original volume and, if confined, develops a high swelling pressure. Clay swelling markedly diminishes the permeability of a soil to water and, therefore, controls drainage and seepage through soil profiles, earth dams, and canal banks. It also has a significant influence on the trafficability of wet soils. The pressure produced by clay swelling can disrupt building foundations, highways, and airport runways. Ideally, sites for agricultural or engineering projects should be chosen where the soils and sediments have the appropriate swelling characteristics; but sometimes other requirements preclude these sites. Thus, an *in situ* method of modifying the swelling behavior of the existing soils and sediments would be advantageous.

Clay swelling may be controlled by altering the oxidation state of the Fe in the octahedral layer of the clay. Using freshly mined bentonite from Bell Fourche, South Dakota, Foster (1953) observed that the swelling volume of the blue-grey (reduced) fraction, measured in a graduated cylinder, was about two-thirds that of the olive-green (oxidized) fraction. Also, Ravina and Low (1972, 1977) observed an empirical, inverse relationship between *b*-dimension and swelling, and Kohyama *et al.* (1973) provided evidence that the *b*-dimension of a phyllosilicate is increased by the reduction of its structural Fe. Hence, the reduction of octahedral Fe<sup>3+</sup> should decrease swelling.

The purpose of the present study was to investigate the effect of the state of oxidation of the octahedral Fe in a clay on its swellability; and to see if this effect is generally valid for all dioctahedral smectites.

### MATERIALS AND METHODS

The clays used in this study were the <2- $\mu$ m, Na<sup>+</sup>-saturated forms of the API #25 montmorillonite from Upton, Wyoming, and montmorillonites from Czechoslovakia #650 and New Zealand; and API #33a nontronite from Garfield, Washington. Their chemical compositions were described by Low (1980) and Stucki *et al.* (1984b).

The clays were suspended in 0.25 N citrate-bicarbonate (CB) solution in a special reaction vessel having a septum cap and then brought to various states of Fe reduction using sodium dithionite. Some samples were subsequently reoxidized with O<sub>2</sub>. Details of the methods and apparatus have been reported elsewhere (Stucki *et al.*, 1984a). The solute concentration in the final suspension was  $\sim 5 \times 10^{-4}$  mole/liter Na<sup>+</sup>.

To measure the swelling pressure of the clays, an apparatus similar to the one described by Low (1980) was used, except two modifications were made. The first modification was in the pressure cell itself (Figure 1). Whereas Low's cells were constructed of plastic, those used in the present study were constructed of stainless steel and were coated internally with Teflon. The second modification was the introduction of a ball valve and adapter block between the pressure cell and needle valve leading to the manifold. This modification was adopted to permit sample injection directly into the pressure cell without exposing it to atmospheric oxygen.

Prior to each experiment, the cell base and barrel were disassembled, washed in deionized water (18 megohm/cm resistivity), and allowed to drain for several hours. The barrel was fitted with a Teflon gasket and screwed onto the adapter block, and the porous stainless steel filter in the cell base was covered with a

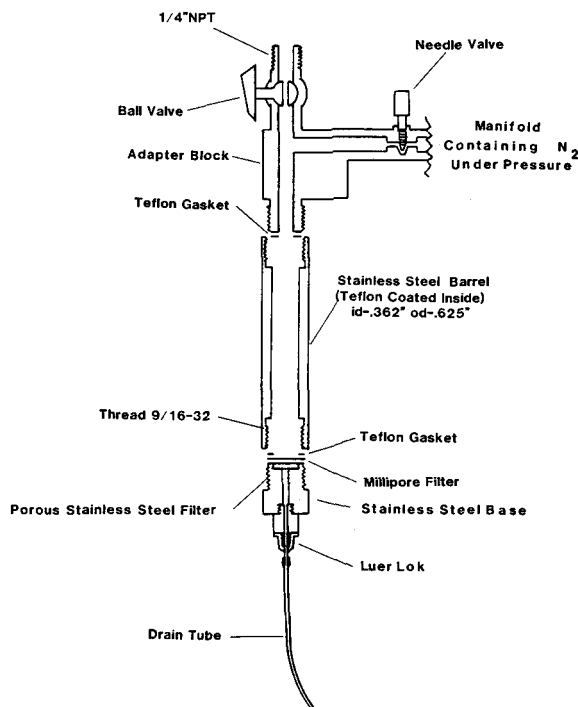


Figure 1. Diagram of the pressure cell and adapter block.

Millipore filter (pore diameter =  $0.025 \mu\text{m}$ ). The entire cell base was saturated with degassed water by forcing the water upwards through the drain tube with a syringe. After removing the syringe, a Teflon gasket was placed on the cell base, and the base was screwed into the barrel. While this connection was being made, the ball valve was held open to maintain atmospheric pressure above the water-saturated filter and base.

Once the manifold was pressurized to the desired pressure (i.e., 1, 3, 5, or 7 atm) and the cell was assembled and in place, the needle valve was opened and the cell was flushed with  $\text{N}_2$  from the manifold. While the cell was being flushed in this way, a 2.5-ml aliquot of the clay suspension was transferred from the reaction vessel to the pressure cell by means of a gas-tight syringe with a six-inch long needle that extended through the open ball valve and into the barrel of the cell. Immediately following the transfer, the ball valve was closed and the pressure in the cell increased until it became equal to the pressure previously established in the manifold. The same procedure was followed for each of the nine cells used for each run, i.e., three cells for each of three samples.

After the water was expressed from each suspension and equilibrium had been attained, the mass ratio of water to clay,  $m_w/m_c$ , in two of the three replicates of each sample was determined by closing the needle valve, removing the cell base, transferring the filter cake quickly to a weighing bottle, and determining the weight

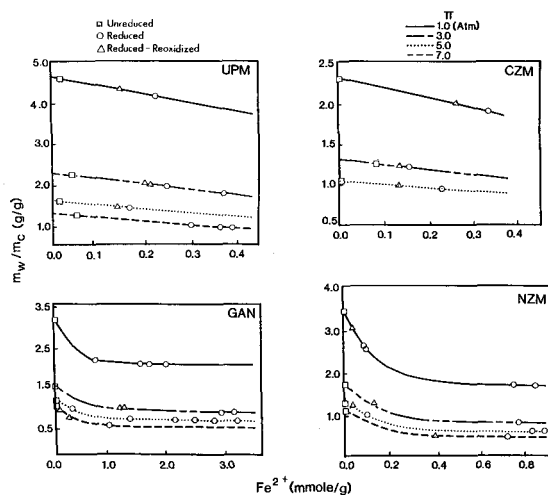


Figure 2. The mass ratio of water to clay,  $m_w/m_c$ , as a function of octahedral  $\text{Fe}^{2+}$  content at specific values of the swelling pressure,  $\Pi$ , for clays from Upton, Wyoming (UPM), Czechoslovakia (CZM), New Zealand (NZM), and Garfield, Washington (GAN) (external solution =  $5 \times 10^{-4}$  N NaCl).

before and after drying. The dried samples were subsequently digested and analyzed for total Fe by the method of Stucki (1981).

The filter cake from the third cell was removed in like manner but was transferred to a previously prepared digesting solution in a 100-ml polypropylene centrifuge tube for the determination of the ratio of  $\text{Fe}^{2+}$  to total Fe (Stucki, 1981). This ratio was subsequently converted to mmole  $\text{Fe}^{2+}$  per gram of clay by multiplying it by the total Fe content of the dried filter cake.

## RESULTS AND DISCUSSION

The values of  $m_w/m_c$  for the four clays were determined at four different swelling pressures,  $\Pi$ , for various ratios of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in the octahedral sheet. The results are reported in Table 1 and Figure 2. Note that in Figure 2 the relation between  $m_w/m_c$  and  $\text{Fe}^{2+}$  is linear in the  $\text{Fe}^{2+}$  composition range between 0 and 0.4 mmole/g, for the Upton and Czechoslovakian clays. In these clays, the maximum  $\text{Fe}^{2+}$  content did not exceed 0.4 mmole/g. Insufficient data were obtained to determine whether or not the relation between  $m_w/m_c$  and  $\text{Fe}^{2+}$  was linear below  $\sim 0.4$  mmole/g of  $\text{Fe}^{2+}$  for the New Zealand and Garfield clays; however, this relation was linear (with a slope near zero) at higher contents of  $\text{Fe}^{2+}$ . In general, all clays appear to have behaved uniformly, and the relation between  $m_w/m_c$  and  $\text{Fe}^{2+}$  can be described by two straight lines intersecting at an  $\text{Fe}^{2+}$  content of  $\sim 0.4$  mmole/g. Hence, the curvilinearity in the plots of  $m_w/m_c$  vs.  $\text{Fe}^{2+}$  for the New Zealand and Garfield clays may not be real. In any event, it is obvious that  $m_w/m_c$  decreased significantly

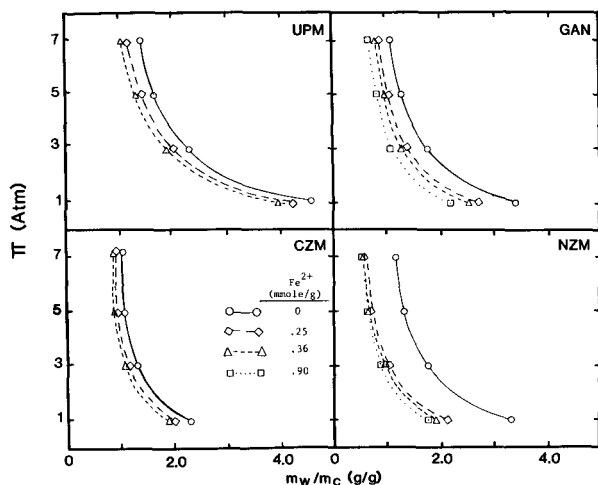


Figure 3. The relation between the swelling pressure,  $\Pi$ , and the mass ratio of water to clay,  $m_w/m_c$ , at selected values of the octahedral  $\text{Fe}^{2+}$  content for clays from Upton, Wyoming (UPM), Czechoslovakia (CZM), New Zealand (NZM), and Garfield, Washington (GAN) (external solution =  $5 \times 10^{-4}$  N NaCl).

with increasing  $\text{Fe}^{2+}$  up to an  $\text{Fe}^{2+}$  content of  $\sim 0.4$  mmole/g.

The results reported in Table 1 and Figure 2 represent clays in CB buffer solution that were reduced,

Table 2. Initial values (i) and final values (f) for  $\alpha$  and  $\ln B$  in Eq. (4).

Smectite <sup>1</sup>	$\text{Fe}^{2+}$ (mmole/g)	$\alpha_i$	$\ln B_i$	$\alpha_f$	$\ln B_f$
UPM	0.00	3.25	-0.01	2.56 <sup>2</sup>	0.28 <sup>2</sup>
	0.25	2.74	0.04	1.93	0.44
	0.36	2.51	0.06	1.67	0.52
CZM	0.00	2.28	-0.30		
	0.25	2.00	-0.30		
	0.36	1.87	-0.30		
NZM	0.00	2.46	-0.04		
	0.25	1.42	0.02	1.05	0.37
	0.36	1.32	0.02	0.96	0.39
	0.90	1.13	0.06		
GAN	0.00	2.53	-0.04	2.02	0.24
	0.25	1.89	0.00	1.43	0.43
	0.36	1.76	0.01	1.39	0.38
	0.90	1.52	0.00	1.00	0.62

<sup>1</sup> Localities listed in footnote to Table 1.

<sup>2</sup> When no value is reported in this column, no break in the plot of  $\ln(\Pi + 1)$  vs.  $1/(m_w/m_c)$  was observed.

reduced then reoxidized, or not reduced. One set of Garfield samples was treated for seven days to gauge the effect of time in the reaction medium (including CB buffer without dithionite) on the relationship between  $\text{Fe}^{2+}$  and  $m_w/m_c$ . Inasmuch as all points for a

Table 1. The effect of octahedral  $\text{Fe}^{2+}$  on the mass ratio of water to clay ( $m_w/m_c$ ) at various swelling pressures ( $\Pi$ ).

Smectite <sup>1</sup>	Total Fe (mmole/g)	$\Pi = 1.0$ atm		$\Pi = 3.0$ atm		$\Pi = 5.0$ atm		$\Pi = 7.0$ atm	
		$\text{Fe}^{2+}$ (mmole/g)	$m_w/m_c$ (g/g) <sup>2</sup>	$\text{Fe}^{2+}$ (mmole/g)	$m_w/m_c$ (g/g) <sup>2</sup>	$\text{Fe}^{2+}$ (mmole/g) <sup>3</sup>	$m_w/m_c$ (g/g) <sup>2</sup>	$\text{Fe}^{2+}$ (mmole/g)	$m_w/m_c$ (g/g) <sup>2</sup>
UPM	0.539	0.016	4.591*	0.042	2.273	0.014	1.636*	0.053	1.379*
		0.150	4.337+	0.204	2.086+	0.147	1.532+	0.304	1.125
		0.224	4.233	0.207	2.083+	0.165	1.492	0.367	1.049
				0.250	2.033			0.391	1.025
CZM	1.257	0.004	2.300*	0.084	1.290*	0.004	1.091*	not determined	
		0.262	2.009+	0.123	1.260+	0.133	1.020+		
		0.329	1.951	0.157	1.240	0.224	0.975		
NZM	1.502	0.036	3.073+	0.005	1.743*	0.010	1.291*	0.007	1.162*
		0.097	2.660	0.136	1.202+	0.030	1.205+	0.385	0.581+
		0.108	2.600	0.759	0.893	0.102	0.995	0.721	0.563
		0.755	1.810			0.821	0.680		
GAN	4.201	0.020	3.400	0.008	1.712*	0.014	1.327*	0.007	1.144*
		0.737	2.275	1.128	1.128+	0.018†	1.256*	0.019	1.125+
		1.540	2.191	1.228	1.126+	0.035	1.245	0.216	0.975+
		1.697	2.175	3.109	1.026	0.308	1.021	0.948	0.770
		1.983	2.145	3.188	1.025	1.367	0.875	2.376	0.751
						2.161†	0.869		
						2.328	0.836		
						2.566†	0.854		
				2.950†	0.846				
				3.274†	0.850				

<sup>1</sup> UPM = Upton, Wyoming, montmorillonite (API #25); CZM = Czechoslovakia #650 montmorillonite (see Low, 1980); NZM = New Zealand montmorillonite (see Low, 1980); GAN = Garfield, Washington, nontronite (API #33a).

<sup>2</sup> \* = Unreduced; + = reduced and reoxidized; no symbol = reduced.

<sup>3</sup> † = Reduced for 7 days; otherwise reduced for 30 min.

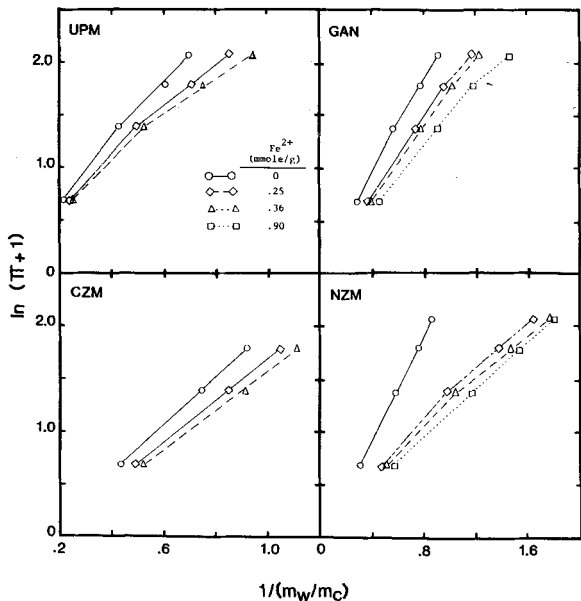


Figure 4. The relation between  $\ln(\Pi + 1)$  and the reciprocal mass ratio of water to clay,  $1/(m_w/m_c)$ , at selected values of the octahedral  $Fe^{2+}$  content for clays from Upton, Wyoming (UPM), Czechoslovakia (CZM), New Zealand (NZM), and Garfield, Washington (GAN) (external solution =  $5 \times 10^{-4}$  N NaCl).

given clay at the same pressure fit nicely on the same line (or lines if two linear regions exist) regardless of the sample history, the effect of the oxidation state of octahedral Fe on  $m_w/m_c$  was reversible. It depended only on the state of oxidation, and not on the path by which that state was reached. Treatment of this clay with citrate-bicarbonate and with dithionite dissolves some Fe, Si, and Al (Stucki *et al.*, 1984b) and raises the possibility that changes in  $m_w/m_c$  might be attributable to mineralogical alterations other than the reduction of structural  $Fe^{3+}$ . The aforementioned reversibility, however, precludes this possibility.

Curves of  $\Pi$  vs.  $m_w/m_c$  at selected values of  $Fe^{2+}$  (Figure 3) were constructed from the data in Figure 2. Note that the shifts in position of these curves with  $Fe^{2+}$  content are distinct and substantial, especially in the range 0–0.4 mmole  $Fe^{2+}$ /g, and demonstrate that the reduction of structural Fe markedly decreased  $\Pi$ . To be specific, an increase in  $Fe^{2+}$  from 0 to 0.36 mmole/g decreased  $\Pi$  for the Upton, Czechoslovakian, Garfield, and New Zealand clays at  $m_w/m_c = 1.5$  g/g by 26%, 34%, 42%, and 63%, respectively. For such a relatively small change in the oxidation state of octahedral Fe, these changes in  $\Pi$  are profound.

To explain these results, it is useful to consider the work of Low (1980). Using methods on which those of the present study are based, Low studied the swelling of 35 Na-saturated, natural (oxidized) montmorillon-

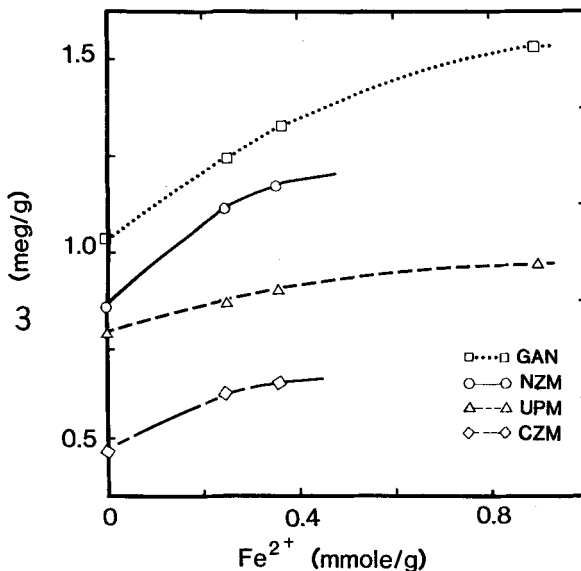


Figure 5. The relation between the cation-exchange capacity,  $\omega$ , and the octahedral  $Fe^{2+}$  content for clays from Upton, Wyoming (UPM), Czechoslovakia (CZM), New Zealand (NZM), and Garfield, Washington (GAN) (from Stucki *et al.*, 1984b).

ites and found that: (1)  $\Pi$  is described by the following empirical equation

$$(\Pi + 1) = B \exp(\alpha/(m_w/m_c)) \quad (1)$$

where  $\alpha$  and  $B$  are constants; (2) the values of  $\alpha$  and  $B$  may change abruptly at a specific value of  $1/(m_w/m_c)$ ; and (3) the value of  $\alpha$  is given by

$$\alpha_i = 3.75 \times 10^{-7}S + 1.15\omega, \quad (2)$$

or

$$\alpha_f = 3.31 \times 10^{-7}S + 0.30\omega, \quad (3)$$

where  $S$  is the specific surface area of the montmorillonite in  $cm^2/g$ ,  $\omega$  is the cation-exchange capacity in meq/g, the subscript  $i$  denotes the initial value (before any abrupt change), and the subscript  $f$  denotes the final value. Alternatively, Eq. (1) can be written

$$\ln(\Pi + 1) = \alpha/(m_w/m_c) + \ln B. \quad (4)$$

In discussing Eqs. (2) and (3), Low expressed doubts about the significance of the terms involving  $\omega$ . Later, the omission of these terms was justified by the work of Viani *et al.* (1983) who, using Low's clays, measured  $\Pi$  as a function of the interplanar spacing of the fully expanded layers, i.e., layers that continued expanding when the interplanar spacing reached  $\sim 20 \text{ \AA}$ . They found that the relation between  $\Pi$  and the interplanar spacing of these expanded layers was independent of the surface charge density,  $\omega/S$ . In other words, they found that  $\omega/S$  had no effect on the swelling of the fully expanded layers within the clay crystals. This means

that, if  $\omega/S$  affects the swelling of these crystals, it must do so by affecting the proportion of layers that fully expand and, thereby, the effective value of  $S$ . From data on  $S$  reported by Low (1980) and data on interplanar spacings reported by Norrish (1954), Foster *et al.* (1955), Rhoades *et al.* (1969), and Viani *et al.* (1983), it is evident that unexpanded, partially expanded (interplanar spacing  $\sim 20 \text{ \AA}$ ), and fully expanded layers can co-exist in the same crystal. Figure 4 shows that our data obey Eq. (4), Table 2 shows that  $\alpha$  decreased as  $\text{Fe}^{2+}$  increased, and Figure 5 shows that  $\omega$  increased as  $\text{Fe}^{2+}$  increased. On the basis of these observations and the foregoing discussion, we conclude that the increase in  $\omega$  accompanying the increase in  $\text{Fe}^{2+}$  enhanced the relative stability of the unexpanded and/or partially expanded layers and, consequently, increased the proportion of these layers. As the proportion of unexpanded and/or partially expanded layers increased, the effective value of  $S$  decreased and, in keeping with Eqs. (2) and (3), the value of  $\alpha$  also decreased. According to Eq. (1), a decrease in  $\alpha$  will produce a decrease in  $\Pi$  at any value of  $m_w/m_c$ , and vice versa. Thus, swelling was reduced. This conclusion is supported by a preliminary experiment with the Garfield clay which showed that the interplanar spacing of some layers collapsed to  $\sim 20 \text{ \AA}$  when its octahedral  $\text{Fe}^{3+}$  was reduced to  $\text{Fe}^{2+}$ .

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#### REFERENCES

- Foster, M. D. (1953) Geochemical studies of clay minerals: II. Relation between ionic substitution and swelling in montmorillonites: *Amer. Mineral.* **38**, 994–1006.
- Foster, W. R., Savins, J. G., and Waite, J. M. (1955) Lattice expansion and rheological behavior of relationships in water-montmorillonite systems: in *Clays and Clay Minerals, Proc. 3rd Natl. Conf., Houston, Texas, 1954*, Ada Swineford, ed., *Natl. Acad. Sci. Natl. Res. Coun. Publ.* **395**, 296–316.
- Kohyama, N., Shimoda, S., and Sudo, T. (1973) Iron-rich saponite (ferrous and ferric forms): *Clays & Clay Minerals* **21**, 229–237.
- Low, P. F. (1980) The swelling of clay. II. Montmorillonite: *Soil Sci. Soc. Amer. J.* **44**, 667–676.
- Norrish, K. (1954) The swelling of montmorillonite: *Disc. Faraday Soc.* **18**, 120–134.
- Ravina, I. and Low, P. F. (1972) Relation between swelling, water properties, and  $b$ -dimension in montmorillonite-water systems: *Clays & Clay Minerals* **20**, 109–123.
- Ravina, I. and Low, P. F. (1977) Change of  $b$ -dimension with swelling of montmorillonite: *Clays & Clay Minerals* **25**, 196–200.
- Rhoades, J. D., Ingvalson, R. D., and Stumpf, H. T. (1969) Interlayer spacing of expanded clay minerals at various swelling pressures: an X-ray diffraction technique for direct determination: *Soil Sci. Soc. Amer. Proc.* **33**, 473–475.
- Stucki, J. W. (1981) The quantitative assay of minerals for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  using 1,10-phenanthroline. II. A photochemical method: *Soil Sci. Soc. Amer. J.* **45**, 638–641.
- Stucki, J. W., Golden, D. C., and Roth, C. B. (1984a) Preparation and handling of dithionite-reduced smectite suspensions: *Clays & Clay Minerals* **32**, 191–197.
- Stucki, J. W., Golden, D. C., and Roth, C. B. (1984b) Effects of reduction and reoxidation of structural iron on the surface charge and dissolution of dioctahedral smectites: *Clays & Clay Minerals* **32**, 349–355.
- Viani, B. E., Low, P. F., and Roth, C. B. (1983) Direct measurement of the relation between interlayer force and interlayer distance in the swelling of montmorillonite. *J. Colloid Interface Sci.* **96**, 229–244.

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**Резюме**—Три монтмориллониты и нонтронит восстанавливались при помощи дитионита натрия, чтобы получить различные количества  $\text{Fe}^{2+}$  в их октаэдрических местах. Отношение массы воды до массы глины,  $m_w/m_c$ , определялось как функция  $\text{Fe}^{2+}$  при нескольких величинах давления набухания,  $\Pi$ . Значение  $m_w/m_c$  уменьшалось значительно с увеличением  $\text{Fe}^{2+}$  при всех величинах  $\Pi$  для каждой глины. Кроме того, кривые  $\Pi$  как функции  $m_w/m_c$  для различных глин перемещались вниз, когда  $\text{Fe}^{2+}$  увеличивалось. Прямая линия получалась для функции  $\ln(\Pi + 1)$  в зависимости от  $1/(m_w/m_c)$ ; однако, при некоторых состояниях окисления трех образцов эта линия имела острый перелом при определенном значении  $1/(m_w/m_c)$ . Наклон линии уменьшался для каждой глины, тогда как  $\text{Fe}^{2+}$  увеличивалось, и увеличению  $\text{Fe}^{2+}$  сопутствовало увеличение катионообменной способности. Предполагается, что эти наблюдения были в результате полного или частичного разрушения наложенных глинистых слоев, получающихся в следствие увеличения катионообменной способности. [E.G.]

**Resümee**—Drei Montmorillonite und ein Nontronit wurden mittels Na-Dithionit reduziert, um verschiedene  $\text{Fe}^{2+}$ -Gehalte auf den Oktaederplätzen zu erhalten. Das Mengenverhältnis von Wasser zu Ton,  $m_w/m_c$ , wurde als eine Funktion von  $\text{Fe}^{2+}$  bei verschiedenen Werten des Quelldruckes,  $\Pi$ , bestimmt. Der  $m_w/m_c$ -Wert nahm mit zunehmendem  $\text{Fe}^{2+}$  bei jedem  $\Pi$ -Wert für jeden Ton beachtlich ab. Darüberhinaus verlagerten sich die Kurven, bei denen  $\Pi$  gegen  $m_w/m_c$  für die verschiedenen Tone aufgetragen sind, mit zunehmendem  $\text{Fe}^{2+}$  nach unten. Eine gerade Linie wurde erhalten, wenn  $\ln(\Pi + 1)$  gegen  $1/(m_w/m_c)$  aufgetragen wurde; jedoch zeigte diese Linie bei einigen Oxidationszuständen bei 3 der Proben einen scharfen Knick bei einem spezifischen Wert von  $1/(m_w/m_c)$ . Die Neigung der Linie nahm für jeden Ton ab, wenn  $\text{Fe}^{2+}$  zunahm, und eine Zunahme des  $\text{Fe}^{2+}$  wurde von einer Zunahme der Kationenaustauschkapazität begleitet. Man nimmt an, daß diese Beobachtungen mit einem Zusammenbruch oder einem teilweisen Zusammenbruch der überlagerten Tonlagen zusammenhängen, der von der Zunahme der Kationenaustauschkapazität herrührt. [U.W.]



**Résumé**—Trois montmorillonites et une nontronite ont été réduites par une dithionite de sodium pour obtenir différentes quantités de  $\text{Fe}^{2+}$  dans leurs sites octaédriques. La proportion de masse d'eau à argile  $m_w/m_c$  a été déterminée en fonction de  $\text{Fe}^{2+}$  à plusieurs valeurs de la pression de gonflement  $\Pi$ . La valeur  $m_w/m_c$  a diminué de manière marquée au fur et à mesure de l'augmentation de  $\text{Fe}^{2+}$  à chaque valeur de  $\Pi$  pour chaque argile. De plus, les courbes de  $\Pi$  vs.  $m_w/m_c$  pour différentes argiles ont été déplacées vers le bas au fur et à mesure de l'augmentation de  $\text{Fe}^{2+}$ . On a obtenu une ligne droite lorsqu'on a relevé  $\ln(\Pi + 1)$  vs.  $1/(m_w/m_c)$ ; cette droite a cependant exhibé une cassure nette à une valeur spécifique de  $1/(m_w/m_c)$  à certains états d'oxydation des trois échantillons. L'inclinaison de la droite a diminué pour chaque argile au fur et à mesure de l'augmentation de  $\text{Fe}^{2+}$ , et une augmentation de  $\text{Fe}^{2+}$  a été accompagnée d'une augmentation de la capacité d'échange de cations. On croit que ces observations sont dues à l'affaissement ou l'affaissement partiel des couches d'argile superimposées résultant de l'augmentation de la capacité d'échange de cations. [D.J.]