

EFFECTS OF REDUCTION AND REOXIDATION OF STRUCTURAL IRON ON THE SURFACE CHARGE AND DISSOLUTION OF DIOCTAHEDRAL SMECTITES

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Abstract—The effect of Fe oxidation state on the surface charge (CEC) and solubility of smectites were studied using the <2- μm , Na⁺-saturated fraction of an Upton, Wyoming; a Czechoslovakian; and a New Zealand montmorillonite; and a Garfield, Washington, nontronite. The reduction of structural Fe³⁺ in the octahedral sheet of each clay produced a net increase in the negative surface charge of the clay. The observed cation-exchange capacities deviated from the linear relationship predicted by charge-deficit calculations, assuming changes only in the Fe²⁺/Fe³⁺ ratio, and reversibly followed Fe reduction according to a 2nd-degree polynomial function. The deviations suggest reversible changes in mineral structure and composition during Fe reduction.

These clays were susceptible to partial dissolution in citrate bicarbonate (CB) and citrate-bicarbonate-dithionite (CBD) solutions. Small amounts of Fe and Si dissolved as a result of Fe reduction in CBD, but affected <1% of the total clay mass except for the Czechoslovakian clay in which 2% of the clay dissolved. Although slightly more Fe dissolved than Si, no change in surface charge was noted. Almost no dissolution of these elements was detected in CB solution. In contrast, significant Al was detected in the CB solution, suggesting a heterogeneous dissolution mechanism. The CEC, however, was unchanged by the CB treatment. These results may be explained by the adsorption of hydrogen ions into the vacated Al³⁺ sites in the mineral structure. Dissolution seems to have been independent of the effects of Fe oxidation state on surface charge.

Key Words—Dissolution, Iron, Nontronite, Oxidation, Reduction, Smectite, Surface area.

INTRODUCTION

If Fe³⁺ in the octahedral layer of a clay mineral is reduced to Fe²⁺, the negative surface charge of the clay should increase linearly with the concentration of Fe²⁺ in the structure. This predicted relationship has important consequences relevant to the macroscopic properties of the mineral. According to double-layer theory, the swelling of clay in water is largely osmotic and should increase with surface charge density (Verwey and Overbeek, 1948). Low and co-workers (Odom and Low, 1978; Low and Margheim, 1979; Low, 1980, 1981; Viani *et al.*, 1983) on the other hand, reported that swelling is largely independent of surface charge, asserting that surface area is the determining factor. A knowledge of the precise effects of Fe oxidation state on surface charge would be useful to evaluate these apparently conflicting theories of clay swelling. Also, increasing the layer charge of a smectite mineral may cause its layers to collapse like a vermiculite, and thus alter the effective surface area and other mineral properties. These alterations could provide more complete information about the mechanisms for mineral weathering and the oxidation and reduction of Fe in clay minerals.

Experimental verification of the effect of Fe oxidation state on surface charge is difficult because conventional methods for determining cation-exchange

capacity (CEC) require numerous washings that can cause reoxidation. For example, Roth *et al.* (1969) reported that the CEC of Garfield, Washington, nontronite remained constant with the reduction of structural Fe³⁺. After careful examination of their procedure, however, it is evident that the precautions taken were insufficient to prevent reoxidation. When reduced suspensions of the same clay were washed with degassed solution, using serum stoppers to isolate the samples from the atmosphere, Stucki and Roth (1977) observed a reversible increase in CEC.

Readsorption of Fe, Si, or Al dissolved from the mineral structure during chemical reduction may also affect the results. These ions could block some cation-exchange sites and render the CEC an inaccurate measure of the layer charge. Clays containing tetrahedral Fe are particularly susceptible to irreversible alteration when reduced with dithionite (Russell *et al.*, 1979), but even clays with very little tetrahedral Fe, such as the Garfield nontronite, can suffer some dissolution (Stucki *et al.*, 1984). It appears, however, that the dissolution of clays containing little or no tetrahedral Fe is minimal if pH is maintained near neutral, as evidenced by the reversibility of the CEC in the Garfield nontronite.

The study by Stucki and Roth (1977) included only three reduction ratios of one clay (Garfield nontronite) which illustrated an increased CEC upon reduction of

Table 1. Unit-cell formula, cation-exchange capacity, and partial chemical composition of smectites used in the study.

Smectite ¹	Unit-cell formula	CEC (meq/g)	Si	Al	Fe ²⁺	Total Fe
			(mmole/g clay)			
UPM	Na _{0.70} (Si _{7.97} Al _{0.03})(Al _{2.99} Mg _{0.52} Fe ³⁺ _{0.42} Fe ²⁺ _{0.012})O ₂₀ (OH) ₄	0.876	10.518	4.358	0.015	0.539
CZM	Na _{0.44} (Si _{7.04} Al _{0.96})(Al _{2.69} Mg _{0.47} Fe ³⁺ _{1.10} Fe ²⁺ _{0.004})O ₂₀ (OH) ₄	0.496	9.090	4.714	0.004	1.257
NZM	Na _{0.70} (Si _{7.37} Al _{0.63})(Al _{2.29} Mg _{0.51} Fe ³⁺ _{1.31} Fe ²⁺ _{0.006})O ₂₀ (OH) ₄	0.799	9.407	3.724	0.007	1.502
GAN	Na _{0.93} (Si _{7.12} Al _{0.88})(Al _{0.19} Mg _{0.11} Fe ³⁺ _{3.72} Fe ²⁺ _{0.008})O ₂₀ (OH) ₄	1.046	8.342	1.260	0.009	4.201

¹ UPM = Upton, Wyoming, montmorillonite (API #25); CZM = Czechoslovakia montmorillonite (described by Low, 1980); NZM = New Zealand, montmorillonite (described by Low, 1980); and GAN = Garfield, Washington, nontronite (API #33a).

Fe³⁺; more work is needed, however, to determine whether this phenomenon occurs generally in other smectites. The purpose of the present study was (1) to establish a more complete understanding of the relationship between the oxidation state of structural Fe and the surface charge by studying several different clays over a wide range of Fe²⁺/total Fe ratios, and (2) to evaluate the possible effects of clay dissolution on surface-charge determinations.

MATERIALS AND METHODS

The clays selected for this study were API #25 Upton, Wyoming, Czechoslovakia #650, and New Zealand montmorillonites, and API #33a Garfield, Washington, nontronite. Their unit-cell formulae, cation-exchange capacities (CEC), and compositions with respect to Si, Al, Fe²⁺, and total Fe are listed in Table 1. Each clay was Na⁺-saturated using a 1 N solution of NaCl, fractionated to <2 μm, dialyzed and freeze-dried. The unit-cell formulae reported in Table 1 were calculated using the same weight percentages for Si, Al, and Mg that were obtained in earlier studies (Low, 1980; Stucki *et al.*, 1976); but the values for exchangeable Na⁺, Fe²⁺, and total Fe were revised according to the results obtained from improved methods for Fe²⁺ and total Fe analysis (Stucki and Anderson, 1981; Stucki, 1981).

Using the methods and apparatus described by Stucki *et al.* (1984), 200 mg of clay was added to a preweighed reaction vessel, suspended in 40 ml of citrate-bicarbonate (CB) solution (Stucki *et al.*, 1984), and reduced with 200 mg of Na₂S₂O₄ at 70°C for 30 min. The sample was washed four times with a deoxygenated solution of 5 × 10⁻³ N NaCl. Supernatants were saved in 50-ml polymethylpentene (PMP) erlenmeyer flasks, then analyzed for Fe, Si, and Al. The supernatant from the fourth wash was also assayed for Na.

After decanting the final supernatant, the vessel was weighed again to determine the weight of the entrained solution, and the clay was redispersed in 10 ml of deoxygenated, deionized H₂O. A 2-ml portion of the suspension was transferred to a pressure cell under N₂ atmosphere using an air-tight syringe, and most of the water was extruded from the clay through a porous, membrane filter at the base of the cell. The resulting

gel was transferred to a 100-ml polypropylene centrifuge tube and analyzed immediately for Fe²⁺ and total Fe using the method described by Stucki (1981). The remainder of the suspension was frozen with liquid N₂ and lyophilized. An accurately weighed portion (~10 mg) of the resulting freeze-dried material was digested in a 100-ml polypropylene centrifuge tube using the method for Fe²⁺ and total Fe (Stucki, 1981). An aliquot from the diluted digestate was transferred from the digestion tube to a 50-ml PMP erlenmeyer flask and diluted 1:10 with H₂O using an automatic dilutor. The concentration of Na⁺ in this solution was determined by flame emission on a Perkin-Elmer Model 5000 spectrophotometer at 589 nm in an air-acetylene flame. A set of Na⁺ standards ranging from 0 to 0.174 mmole/liter were prepared by taking selected aliquots of a standard NaCl solution through the identical procedure. The standard curve was linear up to 0.087 mmole/liter, and with the dilution ratios used, all samples analyzed were well within the linear range. The supernatant solution saved from the fourth washing was analyzed for Na⁺ in like manner after diluting 1:100 into a 50-ml PMP erlenmeyer flask. A separate set of standard solutions was prepared to simulate the matrix solution of the supernatant.

The method for calculating surface charge from these measurements was based on the total Na⁺ in the digested sample, corrected for a small portion attributable to Na⁺ in the external solution. This calculation required correction terms in the mass of the freeze-dried gel and in the amount of total Na⁺ observed in the digested portion of the sample. The total mmoles of Na⁺, N_s, in the entrained solution of the gel is given by

$$N_s = c_s f_s V_{es} \quad (1)$$

where c_s = concentration of Na⁺ in the diluted supernatant solution (mmole/liter), f_s = dilution factor for the supernatant solution (~10), and V_{es} = volume of supernatant entrained in the clay gel prior to freeze-drying (liter). If $c_s \neq 0$, the total mass of the freeze-dried gel, w_t , will consist of two parts: the Na⁺-saturated clay and the NaCl from the external solution. The portion of w_t attributable to the clay is then given by:

$$w_c = w_t - 0.0584 c_s f_s V_{es} \quad (2)$$

Table 2. Coefficients for the predicted and observed functional relationships between the surface charge and Fe²⁺ content of smectites.¹

Smectite ²	Coefficient	Predicted ³	Observed	Predicted - Observed
UPM	c ₀	0.861	0.830	0.031
	c ₁	1.000	1.648	-0.648
	c ₂	0	-1.979	1.979
CZM	c ₀	0.492	0.493	-0.001
	c ₁	1.000	0.802	0.198
	c ₂	0	-0.903	0.903
NZM	c ₀	0.792	0.797	-0.005
	c ₁	1.000	0.544	0.456
	c ₂	0	-0.403	0.403
GAN	c ₀	1.037	1.042	-0.005
	c ₁	1.000	0.703	0.297
	c ₂	0	-0.242	0.242

¹ Assuming a polynomial having the form $\omega = c_2(\text{Fe}^{2+})^2 + c_1(\text{Fe}^{2+}) + c_0$. (Fe²⁺ = mmole/g; ω = meq/g).

² See Table 1 for description of clays.

³ Based on charge deficit calculations (Gast, 1977) assuming no changes in composition except in the ratio Fe²⁺/Fe³⁺. This relationship is always linear.

where the numerical coefficient converts the units of the second term on the right from mmole to g. The clay fraction of the dried gel, then, is:

$$x_c = (w_t - 0.0584c_s f_s V_{cs})/w_t = w_c/w_t \quad (3)$$

The NaCl fraction is:

$$x_n = (0.0584c_s f_s V_{cs}) = (w_t - w_c)/w_t \quad (4)$$

The mass of clay digested, m_c, and the amount of excess NaCl in the digestate, m_n, are then obtained from the relations:

$$m_c = m_t x_c \quad (5)$$

and

$$m_n = m_t x_n \quad (6)$$

where m_t is the mass of dried gel transferred to the digestion tube. The expression for calculating the surface charge, ω , is:

$$\omega = (V_t c_d f_d - 17.11 m_n)/m_c \quad (7)$$

where V_t = volume of the diluted digestate (~0.080 liter), c_d = concentration of Na⁺ in the final dilution of the digestate solution (mmole/liter), and f_d = dilution factor for the final dilution of the digestate solution (~10). The numerical coefficient simply converts units from g back to mmole. After substituting for m_n and m_c, Eq. (7) can also be expressed in terms of the measured variables, viz.,

$$\omega = (w_t V_t c_d f_d - c_s f_s V_{cs} m_t)/(m_t w_t - 0.0584 c_s f_s V_{cs}) \quad (8)$$

This method assumes that the layer charge is neutralized completely and solely by Na⁺.

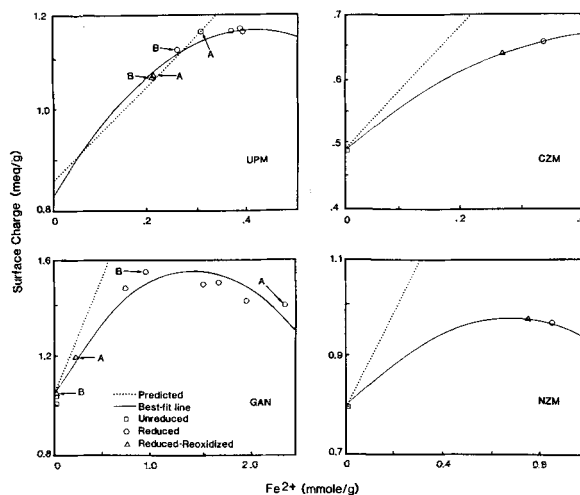


Figure 1. Effects of Fe²⁺ content on the surface charge, ω , of Upton, Wyoming; Czechoslovakian; New Zealand; and Garfield, Washington, smectites. (—) = predicted relationship assuming changes only in Fe²⁺/Fe³⁺; (---) = best-fit curve of the form $\omega = c_2(\text{Fe}^{2+})^2 + c_1(\text{Fe}^{2+}) + c_0$ (values of the coefficients are reported in Table 2). Pairs labeled either A or B represent separate sets of samples of which the more oxidized member was initially reduced to the level of its more reduced companion with the same letter.

Variations in the reduction ratios were achieved either by reoxidizing a reduced sample or by varying the amount of Na₂S₂O₄ added (Stucki *et al.*, 1984). The layer charge of the original clay was determined by submitting the sample to the same treatment as the reduced samples, except dithionite was omitted.

RESULTS AND DISCUSSION

Effects of Fe reduction and reoxidation on CEC

Results showing the effect of Fe oxidation state on the surface charge of the four clays are presented in Figure 1. The plotted values were obtained from clays in CB solution (pH = 8) that were either unreduced, reduced to various reduction ratios, or reduced and reoxidized. For each clay, the reduction of Fe³⁺ to Fe²⁺ in the octahedral sheet increased the surface charge of the clay. The history of a reoxidized sample was traced by preparing a set of two samples reduced under identical conditions to determine the reversibility of the Fe reduction effect on surface charge. One sample was reoxidized by passing H₂O-saturated O₂ through the partially washed suspension, and then determining the surface charge and reduction ratio in each sample. This experiment was performed with two sets of samples of the Garfield and Upton clays, and the results are superimposed on the plots (Figure 1) of surface charge vs. Fe²⁺ composition of samples of the same clays which were reduced to different levels by varying the amount of reducing agent. The results for each set of reduced and reoxidized samples are labeled in Figure 1 with

Table 3. The dissolution of Fe, Si, and Al during treatment with citrate-bicarbonate buffer (CB) and citrate-bicarbonate-dithionite (CBD).

Supernatant solution	UPM ¹		CZM ¹		NZM ¹		GAN ¹	
	CB	CBD	CB	CBD	CB	CBD	CB	CBD
	Fe							
Extract	3.16	13.35	—	53.07	0.62	38.33	2.72	75.02
1	0.30	1.95	—	45.73	4.80	5.10	1.19	3.27
2	0.29	0.00	—	48.17	2.11	14.68	1.27	1.35
3	0.00	0.00	—	39.63	1.05	10.74	0.82	1.34
4	2.01	0.00	—	20.84	1.50	8.01	0.82	1.29
Total	5.76	15.30	—	307.74	10.08	76.86	6.82	82.27
	Si							
Extract	30.42	40.57	—	87.76	30.47	41.16	18.95	61.36
1	11.62	9.82	—	9.02	8.84	0.00	6.62	9.91
2	3.04	3.44	—	9.04	0.88	10.91	3.86	9.19
3	3.33	2.25	—	3.92	6.96	3.38	3.40	26.76
4	3.27	2.49	—	3.75	2.48	2.49	2.47	8.79
Total	51.68	58.59	—	113.49	49.63	57.94	35.30	116.01
	Al							
Extract	24.2	14.8	—	25.1	18.8	23.0	13.1	13.2
1	299.5	243.2	—	21.4	474.9	66.6	35.1	11.3
2	187.3	188.7	—	266.2	303.7	389.1	34.1	10.8
3	210.6	161.3	—	271.1	88.5	168.6	16.4	18.0
4	189.7	155.4	—	111.5	99.4	165.1	7.0	7.4
Total	911.3	763.4	—	695.3	985.3	812.4	105.7	60.7

¹ See Table 1 for sample descriptions.

² Approximate detection errors are: Fe, $\pm 0.04 \mu\text{mole/g}$; Si, $\pm 0.03 \mu\text{mole/g}$; and Al, $\pm 0.6 \mu\text{mole/g}$. — = not determined.

either A or B. The points for the reoxidized samples are close to the best-fit curves through the points obtained by reduction, regardless of the level of reduction to which the sample was first taken. Thus, the original characteristics of the reoxidized sample were identical to its more reduced companion. Following oxidation with oxygen, these characteristics were altered to resemble those of samples that had reached that state of oxidation by the alternate path of reduction without reoxidation. In other words, the process was reversible.

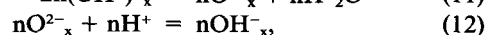
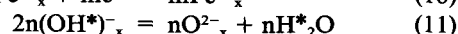
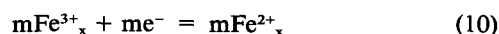
In the range 0 to $\sim 0.3 \text{ mmole Fe}^{2+}/\text{g clay}$, the surface charge seemed to follow the linear relationships predicted from charge deficit calculations (column 3, Table 2), assuming that the relative proportion of Fe^{3+} and Fe^{2+} in the octahedral sheet was altered but the total composition was otherwise constant. Above this range, deviations from the predicted lines were observed for all four clays and an apparent maximum value was observed for each clay. For the Garfield clay, where the attainable level of reduction was greatest, the surface charge actually decreased after reaching a maximum. For this clay, sufficient data were available to determine that the functional relationship between the CEC (ω) and Fe^{2+} content is best described by the second-degree polynomial:

$$\omega = c_2(\text{Fe}^{2+})^2 + c_1(\text{Fe}^{2+}) + c_0, \quad (9)$$

where the units of ω and Fe^{2+} are meq/g and mmole/

g of clay , respectively, and the values of the coefficients c_2 , c_1 , and c_0 are as reported in column 4 of Table 2. This equation was then used to construct the best-fit curve through the data for the Garfield sample in Figure 1. Assuming all four clays behaved uniformly, Eq. (9) was used also to determine the best-fit curves through the data (Figure 1) for the other three clays; the corresponding values for c_2 , c_1 , and c_0 for these clays are also reported in column 4 of Table 2.

The difference between the observed and predicted CEC values indicates that other changes in the mineral composition took place, which apparently compensated for at least part of the increased negative charge due to Fe^{2+} reduction. One physical model that could explain these results was proposed by Stucki and Roth (1977) which included the loss of structural hydroxyls during reduction. A modified version of their proposed mechanism is given by Eqs. (10) to (12):



where m and n are stoichiometry coefficients, * indicates the proton initially present as part of the structural hydroxyl ion, and x denotes the species in the clay structure. If Eqs. (11) and (12) account fully for the observed deviations from the predicted CEC, the corresponding dependence of n on Fe^{2+} content is given

Table 4. The total quantities of Fe, Si, and Al dissolved from smectites in 0.25 N citrate-bicarbonate buffer.

Smectite ¹	Treatment ²	Amount of element dissolved								Fe/Si ³		Al/Si ³	
		% of total element			Weight % of clay					Solution	Unit cell	Solution	Unit cell
		Fe	Si	Al	Fe	Si	Al	Total	Total as oxides				
UPM	CB	1.34	0.49	20.91	0.03	0.14	2.46	2.63	5.15	0.11	0.05	17.63	0.41
	CBD	3.56	0.56	17.51	0.08	0.16	2.06	3.20	4.53	0.26		13.03	
CZM	CB	— ⁴	—	—	—	—	—	—	—	—	0.14	—	0.52
	CBD	20.27	1.25	14.75	1.72	0.32	1.88	3.92	7.06	2.71		6.13	
NZM	CB	0.55	0.53	26.46	0.06	0.14	2.66	2.86	5.57	0.20	0.16	19.86	0.40
	CBD	4.21	0.62	25.23	0.43	0.16	2.54	3.13	5.94	1.33		16.22	
GAN	CB	0.15	0.42	8.39	0.04	0.10	0.28	0.42	0.91	0.19	0.50	2.99	0.15
	CBD	1.83	1.39	4.81	0.46	0.33	0.16	0.95	2.04	0.71		0.52	

¹ See Table 1 for description of clays.

² CB = citrate-bicarbonate only; CBD = citrate-bicarbonate-dithionite.

³ Mole ratio.

⁴ Not determined.

by the difference between the observed and predicted lines (column 5, Table 2). No experimental evidence, however, is presently available to test this hypothesis.

Dissolution of Fe, Si, and Al

All of the clays studied were susceptible to partial dissolution in the presence of CB or CBD, but the effects of dissolution and Fe oxidation state on the surface charge seem to be independent. Measurable quantities of Fe, Si, and Al were released from the clay into the supernatant solution during CBD treatment and subsequent NaCl washings. The CB buffer without dithionite also invoked some dissolution, especially of Al. Most of the soluble Fe and Si was recovered in the initial extract (Table 3), diminishing sharply in subsequent washings. The total quantities recovered were greater from the CBD than from the CB solutions, but amounted to only a small fraction (0.4–4%) of the total Fe and Si initially present in the mineral (Table 4). This value translates into the loss of only a fraction of a percent of the clay mass, except for the Czechoslovakian clay where the amount of Fe and Si recovered in solution summed to about 2% of the original clay weight. The higher mole ratios of Fe/Si in solution, as compared to the unit-cell mole ratios (Table 4), indicate that dissolution was moderately selective for Fe relative to Si. The selectivity for Fe was stronger in the Czechoslovakian clay than in the other clays.

The increased dissolution of Fe and Si following treatment with the reducing agent was likely the result of Fe²⁺ formation in the clay structure rather than of acid dissolution because the pH stayed near or above neutral. The replacement of Fe³⁺ with Fe²⁺ can create local instabilities in the crystal field energies of the Fe sites and thus provide the basis for structural rearrangements that include the dissolution of Fe and Si. These results clearly show that dissolution of Fe from the clay as a result of chemical reduction in CB buffer

was very small, and far below the 20% value suggested by Rozenson and Heller-Kallai (1976) for unbuffered solutions.

The dissolution data for Al (Tables 3 and 4) present quite a different picture than the data for Fe and Si. Dissolution was much more extensive, with as much as 26% of the Al being dissolved; the effects of the CB and CBD solution were reversed; and the concentration in the initial extract was much lower than in the NaCl wash solutions. Even the supernatant solutions from the fourth washings generally contained more Al than the extracts, raising the possibility that more Al would have been solubilized if more washing cycles had been used. The very large mole ratios of Al/Si in solution, as compared to the unit-cell Al/Si ratios, indicate a strong selectivity for Al dissolution in the CB medium. The addition of dithionite decreased slightly the Al concentration in solution. These observations contrast sharply with the dissolution of Fe and Si, which was enhanced by the addition of dithionite.

Comparison of the most oxidized points in Figure 1 with reported values for the same clays in non-CB environments (Low, 1980; Ross and Mortland, 1966; Lewis, 1950) reveals that the dissolution of Fe, Si, and Al from the unreduced clays had no apparent effect on their cation exchange capacities. Also, the reversibility of charge with Fe reduction and reoxidation suggests that dissolution had no permanent effect on CEC. This means that any loss of structural cations must have been exactly compensated either by the equivalent loss of structural anions or by the readsorption of cations without disturbing the surface exchange capacity. These observations eliminate many possible dissolution mechanisms.

One possible mechanism that is consistent with these observations is that the charge deficit created by the dissolution of Al³⁺ was balanced by the adsorption of three hydrogen ions into each site vacated by Al³⁺ in

the crystal structure of the clay (Paver and Marshall, 1934; Low, 1955; Shainberg *et al.*, 1975). The quantities of Fe and Si dissolved may have been insufficient to be reflected by the CEC. Whether or not this model can account for the continued release of Al^{3+} to subsequent wash solutions is unclear, but it is consistent with the other observations, including the reversibility of charge with reduction and reoxidation.

Another possible explanation is that the clay was dissolved homogeneously, i.e., no vacant sites or significant structural defects occurred, but Fe and Si subsequently precipitated as phases separate from the clay mineral. This reaction would have preserved the charge per unit mass of the remaining clay crystal and would have accounted for the greater mole fraction of Al relative to Fe and Si in the supernatant solution. Further experimentation will be required, however, before the correct reaction mechanism can be determined.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the U.S. Army Research Office (Contract No. DAAG 29-80-c-0004). They also acknowledge the work of Theresa L. Billing, High School Apprentice in Science and Engineering, 1980–1981, University of Illinois, whose preliminary laboratory results facilitated this study.

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(Received 22 April 1983; accepted 15 March 1984)

Резюме—Исследовался эффект состояния окисления Fe на поверхностный заряд и растворимость смектитов при использовании фракции размером $< 2 \mu\text{m}$ Na-насыщенных монтмориллонитов из Уптон, Вайоминг, из Чехословакии и из Новой Зеландии и нонтронита из Гарфельд, Вашингтон. Восстановление структурного Fe^{3+} в октаэдрическом пласте каждой глины вызывало результирующее увеличение отрицательного поверхностного заряда глины. Наблюдаемые значения катионообменной способности отклонялись от линейной зависимости, предсказанной по расчетам на основе недостатка заряда, предполагая изменения только в величине отношения $\text{Fe}^{2+}/\text{Fe}^{3+}$ и были обратно пропорциональны восстановлению Fe в соответствии с полиномом второй степени. Эти отклонения указывают на обратимые изменения в структуре и составе минерала во время восстановления Fe.

Эти глины легко подвергались частичному растворению в растворах бикарбоната цитрата (БКЦ) и бикарбоната цитрата-дитионита (БКЦД). Небольшие количества Fe и Si растворялись в результате восстановления Fe в БКЦД, но влияли только на $< 1\%$ всей массы глины, исключая глину из Чехословакии, для которой 2% массы растворялось. Хотя немного больше Fe, чем Si растворялось, то никаких изменений поверхностного заряда не наблюдалось. Почти никакого растворения этих элементов не обнаруживалось в растворе БКЦ. В противоположность, значительное количество Al обнаруживалось в растворе БКЦ, указывая на неоднородный механизм растворения. Катионообменная способность, однако, не изменялась в результате обработки в БКЦ. Эти результаты могут быть объяснены учитывая адсорбцию ионов водорода на пустых местах после Al^{3+} в структуре минерала. Растворение кажется быть независимым от эффектов состояния окисления Fe на поверхностный заряд. [E.G.]

Resümee—Die Auswirkung der Oxidationsstufe des Eisens auf die Oberflächenladung (CEC) und die Löslichkeit von Smektiten wurde untersucht, wozu die Na-gesättigte Fraktion eines Montmorillonits von Upton, Wyoming; eines Montmorillonits aus der Tschechoslowakei bzw. aus Neuseeland; und ein Nontronit von Garfield, Washington, verwendet wurden. Die Reduktion des strukturellen Fe^{3+} in der Oktaederschicht verursachte bei allen untersuchten Tonen eine Gesamtzunahme der negativen Oberflächenladung. Die beobachteten Kationenaustauschkapazitäten wichen von der linearen Beziehung ab, die durch Ladungsdefizitberechnungen vorhergesagt wurden unter der Annahme, daß sich nur das $\text{Fe}^{2+}/\text{Fe}^{3+}$ -Verhältnis ändert und folgten reversibel der Fe-Reduktion, die der 2. Ableitung einer polynomialen Funktion folgt. Die Abweichungen deuten auf reversibel Änderungen in der Mineralstruktur und in der Zusammensetzung während der Fe-Reduktion hin. Diese Tone waren teilweise in Citratbikarbonat (CB)- und Citrat-bikarbonatdithionit (CBD)-Lösungen löslich. Kleine Mengen an Fe und Si wurden infolge der Fe-Reduktion in CBD gelöst, was jedoch nur $< 1\%$ der gesamten Tonmenge betraf mit Ausnahme des tschechoslowakischen Tons, bei dem 2% der Gesamtmenge gelöst wurde. Obwohl etwas mehr Fe als Si gelöst wurde, wurde jedoch keine Veränderung der Oberflächenladung beobachtet. In CB-Lösungen fehlte eine Lösung dieser Elemente nahezu vollständig. Im Gegensatz dazu wurden beachtliche Mengen Al in der CB-Lösung gefunden, was auf einen heterogenen Lösungsmechanismus hindeutet. Die CEC wurde jedoch durch die Behandlung mit CB nicht beeinflusst. Diese Ergebnisse kann man durch die Adsorption von Wasserstoffionen an die leergewordenen Al-Plätze in der Mineralstruktur erklären. Die Auflösung scheint unabhängig von den Auswirkungen der Oxidationsstufe des Eisens auf die Oberflächenladung zu sein. [U.W.]

Résumé—On a étudié l'effet de l'état d'oxidation Fe sur la charge de surface (CEC) et la solubilité de smectites utilisant la fraction $< 2 \mu\text{m}$, saturée de Na^+ , d'une montmorillonite d'Upton, Wyoming, de Tchecoslovaquie, et de Nouvelle Zélande, et d'une nontronite de Garfield, Washington. La réduction de Fe^{3+} de structure dans la feuille octaédrale de chaque argile a produit une augmentation nette de la charge de surface négative de l'argile. Les capacités d'échange de cations observées ont dévié de la relation linéaire prédite par les calculs de déficit de charge, assumant des changements dans la proportion $\text{Fe}^{2+}/\text{Fe}^{3+}$ seulement, et elles ont réversiblement suivi la réduction Fe selon une fonction polynomiale du deuxième degré. Les déviations suggèrent des changements réversibles de la structure minérale et de la composition pendant la réduction Fe.

Ces argiles étaient susceptibles à la dissolution partielle dans des solutions de citrate bicarbonate (CB) et de citrate-bicarbonate-dithionite (CBD). De petites quantités de Fe et Si se sont dissoutes résultant de la réduction de Fe dans CBD, mais elle n'ont affecté que $< 1\%$ de la masse totale de l'argile, sauf dans le cas de l'argile tchecoslovaque dans laquelle 2% de l'argile s'est dissoute. Malgré qu'un peu plus de Fe s'est dissout que de Si, aucun changement n'a été remarqué dans la charge de surface. Pratiquement aucune dissolution de ces éléments n'a été détectée dans la solution CB. En contraste, des quantités significatives d'Al ont été détectées dans la solution CB, suggérant un mécanisme de dissolution hétérogène. Ces résultats peuvent être expliqués par l'adsorption d'ions hydrogène dans les sites Al^{3+} évacués dans la structure minérale. La dissolution semble avoir été indépendante des effets de l'état d'oxidation Fe sur la charge de surface. [D.J.]