

PREPARATION AND HANDLING OF DITHIONITE-REDUCED SMECTITE SUSPENSIONS

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Abstract—Using Garfield, Washington, nontronite as the model mineral system, methods and apparatus were developed to prepare reduced suspensions in citrate-bicarbonate-dithionite (CBD) solution. These techniques were effective in removing excess, undesired solutes from reduced suspensions while maintaining a high Fe²⁺ content. They also enabled the preparation of dried, reduced films preferentially oriented with respect to the crystallographic *c*-axis. Supernatant solutions were collected and analyzed for Fe, Al, and Si, from which the extent of dissolution of the clay as a result of CBD treatment was assessed. Results indicated that very little Fe and Si were released to solution, but as much as about 8% of the total Al was solubilized. The highest levels of Al in solution were observed in CB treatments without dithionite.

Key Words—Dithionite, Iron, Nontronite, Reduction, Reoxidation, Smectite.

INTRODUCTION

Interest in the reduced (Fe²⁺) form of Fe-bearing smectites has increased markedly during recent years, but the characterization of such materials has been severely limited by the high susceptibility of reduced suspensions to reoxidation and by uncertainties surrounding the effects of reducing agents on the integrity of mineral structures (Rozenon and Heller-Kallai, 1976; Russell *et al.*, 1979). The presence of excess salts in the reduced product as a result of using sodium dithionite (Na₂S₂O₄) as the reducing agent largely precludes the quantitative analysis of reduced samples for Fe²⁺ and Fe³⁺, the determination of surface charge, and the measurement of other properties, such as water tension or swelling pressure, that require a low concentration of solutes in the solution external to the clay particles. Other reducing agents have been investigated, but Na₂S₂O₄ is by far the most effective and the easiest to remove. Conventional methods for removing excess salts, however, require washing by either centrifugation, filtration, or dialysis usually in air with no provision for an inert atmosphere.

In addition, many measurements require a dried powder or oriented film, but the reduced state of the clay suspension changes readily upon drying if oxygen is present, even if excess Na₂S₂O₄ remains. Oriented films prepared by drying a clay suspension containing even modest levels of solutes are commonly brittle, and the solutes coat the surfaces rendering them unsatisfactory for some measurements.

The possible irreversible alteration of the mineral during reduction due to the dissolution of metals from the clay crystal structure is also of concern. Russell *et al.* (1979) and Rozenon and Heller-Kallai (1976) ob-

served that the Mössbauer spectrum of reduced-reoxidized nontronite (reduced with Na₂S₂O₄) has a much larger quadrupole splitting than does the spectrum of the unaltered material, suggesting a major alteration in the electronic environment of the iron. The effect of Na₂S₂O₄, however, may depend on other properties of the system such as pH, amount of tetrahedral Fe present in the clay, and the presence of chelating agents. In the two studies mentioned above, the pH of the system was unbuffered and probably deviated markedly from neutral because Na₂S₂O₄ in H₂O forms an acidic solution. The clay studied by Russell *et al.* (1979) contained a considerable amount of tetrahedral Fe. Rozenon and Heller-Kallai (1976) studied the SWa-1 ferruginous smectite and reported that the originally yellow clay (oxidized) turned black upon reduction, then reoxidized to a rust color. They attributed this change to the release of as much as 20% of the structural Fe. Stucki and Roth (1977), on the other hand, observed a blue-green color for Garfield nontronite when it was reduced with Na₂S₂O₄ in a near-neutral, citrate-bicarbonate medium. Upon reoxidation with O₂ or H₂O₂, the color returned to yellow. Other measurements also suggested that the process was largely reversible. None of these studies, however, included direct measurements of the amount of Fe, Al, and Si released to the external solution during reduction. Techniques available for handling reduced systems were incapable of decreasing the ionic concentration of the supernatant solution to levels suitable for the determination of metal ions dissolved from the clay crystal.

Studies in our laboratories have focused on characterizing smectites in various states of oxidation, and have required measurements of swelling pressure, water

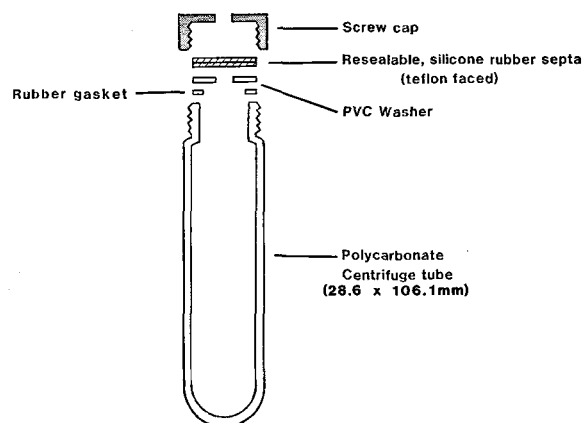


Figure 1. Schematic illustration of the reaction vessel used to prepare reduced smectite suspensions.

content, surface charge, Fe^{2+} and Fe^{3+} composition, magnetic susceptibility, and X-ray powder diffraction, infrared, UV-visible, and Mössbauer spectra. We found that conventional methods of sample preparation for these analyses were inadequate to preserve the reduced state, so special methods and apparatus were developed. The purpose of this publication is to describe these methods and apparatus and to illustrate their use in addressing the problems outlined above.

MATERIALS AND METHODS

Materials

The clay used in this study was nontronite from Garfield, Washington (API No. 33-a). Its composition with respect to Fe^{2+} and total Fe is 0.009 and 4.201 mmole/g clay, respectively. The clay was Na^+ -saturated using a 1 N solution of NaCl, fractionated to $<2 \mu\text{m}$, dialyzed, and freeze-dried.

Reduction of clay suspensions

A special reaction vessel was designed and constructed for the preparation of reduced suspensions. The vessel (Figure 1) consists of a 50-ml, round-bottom, polycarbonate centrifuge tube for which a special screw cap containing an imbedded septum was manufactured. The cap is aluminum and has a 7.6-mm diameter hole drilled through the top. The resealable septum inside the cap consists of two wafers 25 mm in diameter cut from a sheet stock (from LC Company, Schaumburg, Illinois) of silicone rubber bonded to Teflon on one side using polyimide. The septum is supported by a washer made of polyvinyl chloride plastic. A rubber gasket fits between the washer and the rim of the tube to form an air-tight seal.

Using this reaction vessel, reduced clays were prepared by suspending 100–200 mg of freeze-dried clay in 10 ml of citrate-bicarbonate (CB) buffer solution,

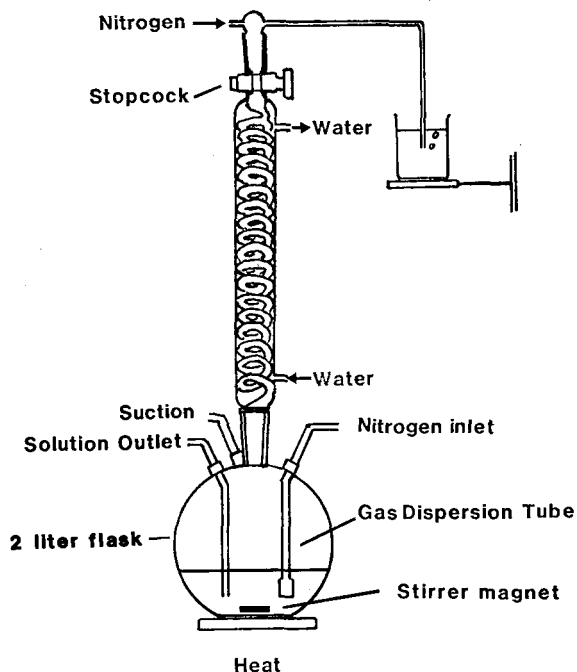


Figure 2. Schematic drawing of the glass apparatus for deoxygenating solutions.

and diluting the solution to 40 ml with purified water having a resistivity of 18 megohm/cm. The buffer solution was prepared by combining 8 parts of 1 N sodium bicarbonate (NaHCO_3) with 1 part of 0.3 M sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$). Amounts of $\text{Na}_2\text{S}_2\text{O}_4$ salt ranging from 0 to 600 mg were then added to the suspension, and the vessel was sealed and placed in a constant-temperature bath at either room temperature or 70°C for a specified length of time ranging from 5 min to 168 hr. The state of oxidation was determined using the method described by Stucki (1981) after removing the excess solutes from the sample.

Removal of undesired solutes

Undesired solutes were removed from the reduced suspensions by washing four times with a deoxygenated solution of 5×10^{-3} N NaCl, followed by one wash with deoxygenated water (18 megohm/cm resistivity). Solutions were deoxygenated according to the following procedure, using the apparatus illustrated in Figure 2. The solution to be deoxygenated was siphoned into the flask through the condenser by applying a vacuum to the suction port; or, alternatively, the solution was added through the neck of the flask with the condenser removed. O_2 -free N_2 was then passed through the solution via a gas dispersion tube, and the solution was boiled vigorously with stirring for about 1 hr. The stopcock was opened and a steady flow of N_2 was maintained across the top of the condenser column to prevent pressure build-up in the flask. After the solution

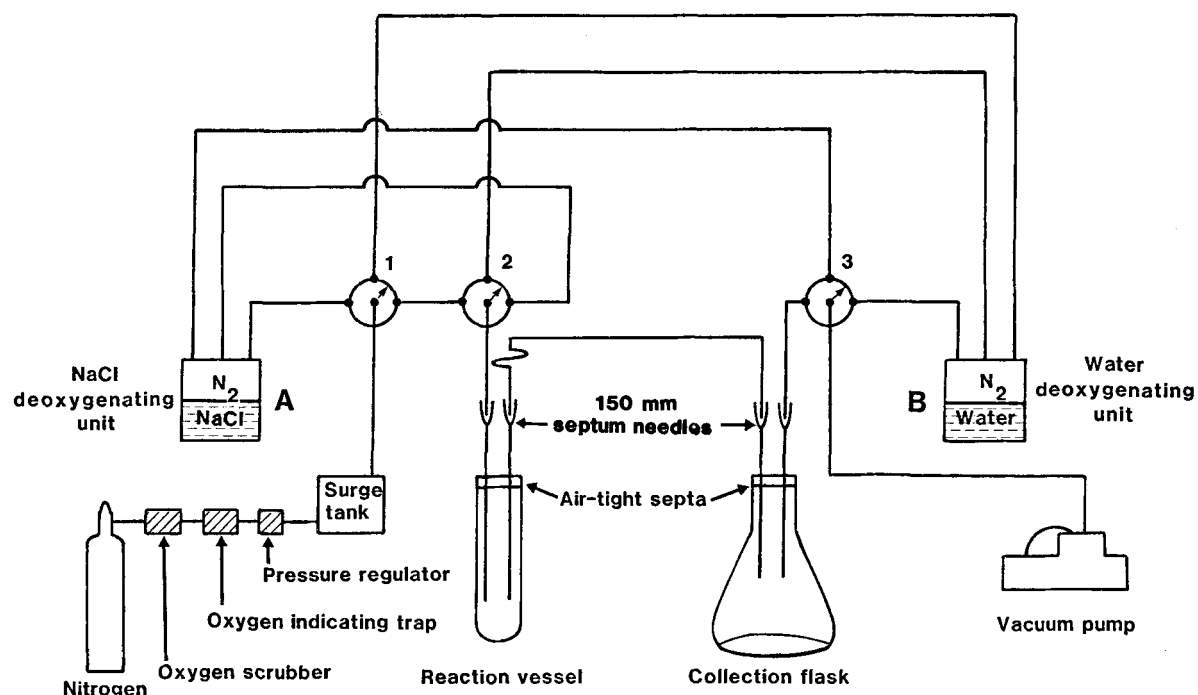


Figure 3. Schematic drawing of the apparatus for exchanging and collecting supernatant solutions under an inert atmosphere. (For a more detailed view of the deoxygenating units, see Figure 2.)

had cooled, the stopcock was closed, the flow of N_2 halted, and portions of the solution removed as needed through the solution outlet port. Safety shields were placed around the deoxygenating units in case of accidental over-pressurization of the system.

Clay suspensions were washed by centrifuging (IEC Model B-20A centrifuge, slant head no. 870) with a force of about $35,000 \times g$, and exchanging the supernatant with the desired wash solution using the apparatus illustrated in Figure 3. Access to the tube contents without opening the reaction vessel was achieved using 150-mm, 22-gauge, septum penetration needles made on special order by Popper & Sons, New Hyde Park, New York. The tip of these needles was designed with the orifice in the side wall rather than in the bevelled end, thus allowing the needle to penetrate the septum without coring a hole. Two needles were inserted into the reaction vessel, and two into the collection flask. By proper positioning of valves 1–3, the collection flask was evacuated and the reaction vessel was pressurized with O_2 -free N_2 . The decanting needle, connected to the flexible tubing leading to the collection flask, was lowered into the clear supernatant solution of the sample to a point just above the sediment in the bottom, and the supernatant was decanted in response to the pressure gradient. The liquid volume in the reaction vessel was replaced with N_2 . When the supernatant transfer was complete, the decanting needle was

raised, and valve 2 was adjusted to connect the sample to the desired deoxygenated solution, i.e., either H_2O or $5 \times 10^{-3} N$ NaCl. Valve 1 was positioned so that the atmosphere above the solution selected by valve 2 was pressurized (~ 2 atm) with N_2 . This facilitated the transfer of fresh solution to the sample and helped maintain the integrity of the deoxygenated liquid.

When the reaction vessel was filled with about 40 ml of fresh wash solution, it was removed from the apparatus and the clay sediment was resuspended using a vortex mixer. The more compacted sediments (as a result of longer centrifugation times) were resuspended by placing the vessel directly on a vortex mixer immediately as fresh solution began to enter. Sediments from the highest centrifugation times (~ 30 – 60 min) required, in addition, a short (30–60 sec) sonic treatment with a 76.3-mm cup horn (Branson Model 314-012-020) filled with water. Each sample was taken through this procedure four times using $5 \times 10^{-3} N$ NaCl as the wash solution. Some samples received one additional wash using deoxygenated water to achieve a 1:10 dilution of the solute concentration in the final suspension.

The principal limitations of this method of dialysis are: (1) a maximum of about 500 mg of clay can be treated in a single reaction vessel due to the volume capacity of the vessel and to the possibility of gel formation when the mass ratio of clay to water exceeds

10 mg/g; (2) the reaction vessel must consist of clear material to allow the operator to insert the decanting needle into the supernatant solution without disturbing the sediment in the bottom of the vessel; and (3) the reaction vessel as designed can withstand a maximum force of $40,000 \times g$, which is insufficient to produce a clear supernatant upon centrifugation when clay-size particles less than $0.02 \mu\text{m}$ (e.s.d.) are present. Inasmuch as none of the supernatants of the clays used in these experiments was clear after centrifuging for 60 min at $35,000 \times g$, it was necessary to induce some flocculation by adding NaCl ($5 \times 10^{-3} \text{N}$) to the wash solution.

Valves 1, 2, and 3 of the apparatus in Figure 3 are brass, multiport ball valves manufactured by the Whitney Company, Highland Heights, Ohio. The various components of the apparatus were connected with 3.18-mm (o.d.) polyethylene tubing, except the needles which were connected by Luer-Lok fittings.

Assay of solutions for Fe, Al, Si, and Na

Using the decanting apparatus (Figure 3), the supernatant solution from each washing was collected into a separate, 50-ml, polymethylpentene Erlenmeyer flask with a threaded top. The contents of each flask were subsequently analyzed for Si using the vanado-molybdate method described by Weaver *et al.* (1968), and for Al and Fe by atomic absorption spectrometry. Al was determined in a nitrous oxide-acetylene flame at 309.3 nm, and Fe in an air-acetylene flame at 248.3 nm using a Perkin-Elmer Model 5000 spectrometer. Total Fe was also determined colorimetrically using the method of Stucki (1981) after oxidizing the dithionite with air. The extent of dissolution of these elements from the clay was evaluated by summing the amounts detected in all solutions collected from each sample. The concentration of Na in the final supernatant solution of selected samples was determined by atomic emission spectrometry at 589 nm.

Reoxidation

Following the third wash with $5 \times 10^{-3} \text{N}$ NaCl , samples to be reoxidized were uncapped and O_2 was passed through the clay suspension using a 150-mm needle. The O_2 flow rate was adjusted to prevent sample loss, and evaporation of the suspension was minimized by first passing the gas through a water bath using a side-arm flask and gas dispersion tube. Thirty minutes of reoxidation in this manner was sufficient to produce extensive, although incomplete, reoxidation. Some clays were reoxidized for as long as 24 hr to increase reoxidation.

Preparation of dry films

Clay suspensions were dried in a closed, cylindrical Plexiglas chamber (Figure 4) containing a 15-bar, porous ceramic plate imbedded in the top of a No. 13

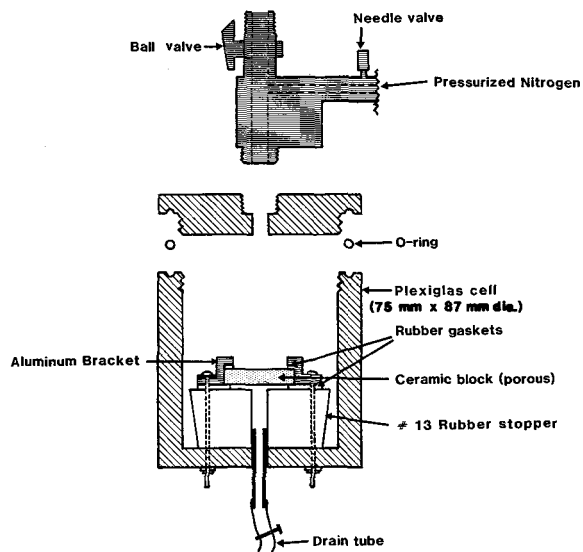


Figure 4. Schematic drawing of the chamber used to prepare oriented films of reduced smectites.

rubber stopper. A 3.18 mm-thick aluminum bracket with an underlying rubber gasket was clamped onto the ceramic plate with two bolts penetrating the rubber stopper and the bottom bulkhead of the chamber to form an air-tight seal around the top edge of the plate and at the bottom of the chamber. The side walls of the plate were unsealed. A drain leading to the outside of the chamber was established by drilling a hole vertically through the center of the stopper and the bottom of the chamber and inserting a glass tube connected to a short extension of flexible tubing. The top of the chamber was threaded onto a brass adaptor block connected to a ball valve on the top and a pressurized (~ 3 atm) N_2 manifold on one side.

The chamber was purged with O_2 -free N_2 for 2 min, then about 3 ml of washed clay suspension was delivered through the open ball valve onto the ceramic plate using an air-tight syringe with a 150-mm long needle. The ball valve was closed and the pressure in the chamber increased to the level previously established in the manifold. Once the excess water was expressed from the clay, the supply pressure was reduced and drying was completed by evaporation into the slowly flowing gas stream. The resulting film was oriented with the *c*-axis normal to the ceramic plate.

Self-supporting films were prepared in a similar manner except that a membrane filter ($0.025\text{-}\mu\text{m}$ pore size) was placed between the clay suspension and the surface of the ceramic plate. Because of the very small pore size of the membrane filter most clays will not penetrate it and thus can be removed easily as a self-supporting film. When the clays adhered to the membrane filter, a Mylar sheet was substituted for the

membrane filter, and the sample was dried entirely by evaporation into the flow stream of N_2 flowing through the system.

Powdered samples were prepared by freeze-drying in a N_2 atmosphere.

RESULTS

The procedures and apparatus described above were effective in decreasing the solute concentration in the clay suspension while maintaining a high level of reduction. The concentration of Na^+ in the supernatant solutions from four washings was determined by atomic emission spectroscopy to be 5.02×10^{-3} mole/liter, which corresponds to the initial concentration of the wash solution and indicates that washing is complete after four cycles. The maintenance of a high level of reduction during washing is illustrated by comparing the $Fe^{2+}/total\ Fe$ ratios of three identical samples of the Garfield nontronite reduced for 15 min at $70^\circ C$ using 200 mg of $Na_2S_2O_4$ to 100 mg of clay in a CB-buffered medium: one sample was washed four times with the deoxygenated, 5×10^{-3} N NaCl solution as described above; the second was washed similarly except that the cap was removed from the reaction vessel momentarily to expose the contents to atmospheric O_2 ; the third was washed four times with a NaCl solution which had not been deoxygenated, and during each wash the cap was removed to exchange supernatant solutions. The respective ratios of $Fe^{2+}/total\ Fe$ were 0.343, 0.324, and 0.026. During one trial, the sample washed with non-deoxygenated solution was otherwise kept under an inert atmosphere by using the decanting apparatus to exchange supernatant solutions rather than removing the cap from the reaction vessel. The extent of reoxidation was significantly less than when the cap was removed.

The method and apparatus described above clearly yield a much more reduced product than conventional techniques, and are superior to those used by Stucki and Roth (1977) who reported much greater reoxidation after one brief exposure to the atmosphere. O_2 in the air space above the reduced suspension has greater influence on reoxidation than does O_2 dissolved in the wash solution, which obviously is the result of the relative amounts of O_2 in the respective phases. One cannot conclude with certainty, however, that these techniques prevent reoxidation completely because the Fe^{2+} composition of the reduced, unwashed suspension is unknown.

The level of reduction that can be achieved in any given sample depends on the concentration of $Na_2S_2O_4$ in the suspension, the mass ratio of $Na_2S_2O_4$ to clay (D_c), the reaction time, and the temperature. Table 1 summarizes the $Fe^{2+}/total\ Fe$ ratios measured in Garfield nontronite following treatments in which all of these factors were varied systematically. The values for Fe^{2+} and total Fe were determined on the wet gel re-

Table 1. Effect of time, temperature, and dithionite on the ratio of $Fe^{2+}/total\ Fe$ in CB-buffered Garfield nontronite suspensions.

Sample	Clay (mg)	Dithionite (mg)	Time (hr)	$Fe^{2+}/total\ Fe$
$25^\circ C$				
1	100	200	0.25	0.008
2	100	200	168.0	0.514
3	200	200	0.083	0.008
4	100	600	0.25	0.073
5	100	600	168.0	0.611
$70^\circ C$				
6	100	200	0.25	0.326
7	100	200	168.0	0.702
8	200	200	0.50	0.472
9	200	200	0.083	0.038
10	200	200	0.50	0.306
11	200	200	1.00	0.360
12	200	200	3.00	0.477
13	100	600	0.25	0.554
14	100	600	168.0	0.779

maining after the fourth washing cycle. At room temperature the rate of reduction was relatively slow, and the reduction ratio exceeded 0.5 only after about 168 hr of reaction time. A six-fold increase in D_c increased the initial rate of the reaction almost nine-fold, but produced only about a 20% increase in the overall reduction ratio after 168 hr.

The rate of reduction increased markedly by raising the temperature to $70^\circ C$, but apparently had only a modest effect on the ultimate, attainable Fe^{2+} composition of the clay. Even with the increased initial rate, reaction times of several hours were still required for the reduction ratio to exceed 0.5, and the maximum ratio observed in the Garfield nontronite was approximately 0.80.

The Fe^{2+} content was varied from one sample to

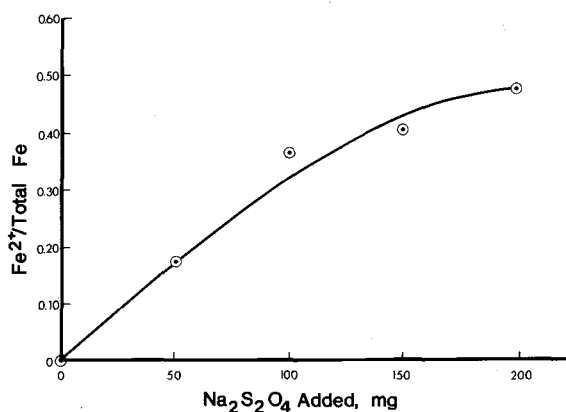


Figure 5. $Fe^{2+}/total\ Fe$ ratios for 100 mg of Garfield nontronite suspended in 40 ml of 0.25 N CB buffer, then treated with varying amounts of $Na_2S_2O_4$ for 30 min at $70^\circ C$.

Table 2. The release of Fe, Si, and Al from 100 mg of Garfield nontronite in 40 ml of 0.25 N CB buffer as affected by time, temperature, and $\text{Na}_2\text{S}_2\text{O}_4$.

Treatment				Amount of element released					
Time (hr)	Temp (°C)	$\text{Na}_2\text{S}_2\text{O}_4$ (mg)	$\text{Fe}^{2+}/$ total Fe	As % of total element			As mass ratio ¹ to Si released		
				Fe	Si	Al	Fe	Al	
0.25	25	0	0.003	0.15	0.42	8.38	0.38	2.87	
0.25	25	200	0.008	0.63	0.63	8.28	1.07	1.91	
0.25	25	600	0.073	1.69	0.81	10.15	2.23	1.82	
0.25	70	200	0.326	1.84	1.39	4.81	1.41	0.50	
0.25	70	600	0.554	2.08	0.80	4.55	2.80	0.83	
168	25	0	0.004	0.14	0.50	7.77	0.28	2.10	
168	25	200	0.514	2.42	1.80	4.49	1.44	0.36	
168	25	600	0.611	3.89	3.17	6.04	1.31	0.28	
168	70	20	0.702	1.69	3.34	2.99	0.54	0.13	
168	70	600	0.779	2.72	7.80	5.39	0.37	0.10	

¹ Based on the unit-cell formula of Garfield nontronite (Stucki *et al.*, 1976), the mass ratios in the structure are: Fe/Si = 1.068; Al/Si = 0.145.

another either by adjusting the amount of $\text{Na}_2\text{S}_2\text{O}_4$ added to the suspension, and thus altering the initial level of reduction, or by reducing all samples under identical conditions, then reoxidizing to different levels by passing H_2O -saturated O_2 through the reduced suspensions for different lengths of time. The effect of varying the amount of $\text{Na}_2\text{S}_2\text{O}_4$ is illustrated in Figure 5 and shows a general trend toward increased Fe^{2+} content. These relationships should be regarded as qualitative rather than quantitative because the curve could shift depending on the air volume above the suspension, the efficiency of oxygen traps, the purity of N_2 , and the seal of the reaction vessel.

Treatment of the clay with $\text{Na}_2\text{S}_2\text{O}_4$ in 0.25 N CB buffer released Fe, Si, and Al to the solution external to the clay particles (Table 2). The amount of element in solution depended on time of exposure to the CBD medium, temperature, and amount of $\text{Na}_2\text{S}_2\text{O}_4$ added relative to the amount of clay. The total amount of Fe and Si released was small, but increased gradually as the condition variables increased. But even after the most severe treatments with $\text{Na}_2\text{S}_2\text{O}_4$, only 2–3% of the total Fe was in solution, much less than the 20% reported by Rozenson and Heller-Kallai (1976), indicating that the reducing conditions greatly affect the extent of Fe in solution. Furthermore, the Fe/Si ratios in solution indicate a slight selectivity for Fe as the amount of $\text{Na}_2\text{S}_2\text{O}_4$ increases, but the range varies from less than half to almost triple the elemental mass ratio derived from the structural formula. Selectivity for Si is favored if $\text{Na}_2\text{S}_2\text{O}_4$ is omitted or if the clay is treated with $\text{Na}_2\text{S}_2\text{O}_4$ at 70°C for 168 hr.

The amount of Al in solution was much greater than Fe or Si, and the effect of CB was greater than CBD. Thus, the loss of Al is the result of reaction with CB rather than with $\text{Na}_2\text{S}_2\text{O}_4$, and is independent of Fe

reduction. The Al/Si ratio in CB solution exceeds the structural ratio by 20-fold, indicating that either Al is selectively dissolved from the mineral or is present in a separate phase, or Si and Fe dissolve simultaneously with Al but reprecipitate. Based on the present data it is unclear which of these interpretations is correct. The simultaneous increase in Si and decrease in Al solubilities as $\text{Na}_2\text{S}_2\text{O}_4$, temperature, and reaction time are increased suggest, however, that insoluble phases external to the clay mineral may exist at some stage of the reaction.

ACKNOWLEDGMENT

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REFERENCES

- Rozenson, I. and Heller-Kallai, L. (1976) Reduction and oxidation of Fe^{3+} in dioctahedral smectite. I: Reduction with hydrazine and dithionite: *Clays & Clay Minerals* **24**, 271–282.
- Russell, J. D., Goodman, B. A., and Fraser, A. R. (1979) Infrared and Mössbauer studies of reduced nontronites: *Clays & Clay Minerals* **27**, 63–71.
- Stucki, J. W. (1981) The quantitative assay of minerals for Fe^{2+} and Fe^{3+} using 1,10-phenanthroline. II. A photochemical method: *Soil Sci. Soc. Amer. J.* **45**, 638–641.
- Stucki, J. W. and Roth, C. B. (1977) Oxidation-reduction mechanism for structural iron in nontronite: *Soil Sci. Soc. Amer. J.* **41**, 808–814.
- Stucki, J. W., Roth, C. B., and Baitinger, W. E. (1976) Analysis of iron-bearing clay minerals by electron spectroscopy for chemical analysis (ESCA): *Clays & Clay Minerals* **24**, 289–292.
- Weaver, R. M., Syers, J. K., and Jackson, M. L. (1968) Determination of silica in citrate-bicarbonate-dithionite extracts of soils: *Soil Sci. Soc. Amer. Proc.* **32**, 497–501.

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Резюме—Используя нонтронит из Гарфильд в Вашингтоне, разработаны методы и аппараты для подготовки редуцированных суспензий в растворе цитрата-бикарбоната-дитионита (ЦБД). Эти техники были эффективны для удаления избытков нежелательных растворенных веществ из редуцированных суспензий, тогда как сохранялось высокое содержание Fe^{2+} . Они также облегчали подготовку сухих, редуцированных фильмов предпочтительно ориентированных по отношению к кристаллографической оси *c*. Всплывающие растворы собирались и анализировались по содержанию Fe, Al, и Si; из этих данных оценивалась степень растворения глины в результате обработки ЦБД. Результаты показали, что очень малые количества Fe и Si освобождались в растворе, тогда как растворялось почти 8% всего Al. Наиболее высокое содержание Al в растворе наблюдалось при обработке ЦБ без дитионита. [E.G.]

Résumé—Nonttronit von Garfield, Washington, wurde als Beispiel für ein Mineralsystem verwendet, um Methoden und Apparaturen zu entwickeln, um reduzierte Suspensionen in Citrat-Bicarbonat-Dithionit (CBD)-Lösung herzustellen. Diese Techniken waren bei der Entfernung überschüssiger, unerwünschter gelöster Stoffe aus reduzierten Suspensionen wirksam, während ein hoher Fe^{2+} -Gehalt erhalten blieb. Außerdem ermöglichten sie die Präparation von getrockneten, reduzierten Filmen, die im Hinblick auf die kristallographische *c*-Achse bevorzugt orientiert sind. Überstehende Lösungen wurden gesammelt und auf Fe, Al, und Si analysiert, woraus das Ausmaß der Unlöslichkeit des Tons in Abhängigkeit von der CBD-Behandlung erhalten wurde. Die Ergebnisse deuteten darauf hin, daß sehr wenig Fe und Si in Lösung ging, daß aber bis zu 8% des gesamten Al gelöst wurden. Der höchste Al-Gehalt in der Lösung wurde bei CB-Behandlungen ohne Dithionit beobachtet. [U.W.]

Résumé—En employant de la nonttronite de Garfield, Washington, comme système minéral modèle, des méthodes et appareils ont été développés pour préparer des suspensions réduites dans une solution dithionite-bicarbonate-citrate (CBD). Ces techniques étaient efficaces pour enlever des produits dissolus en excès, non-désirables des suspensions réduites, tout en maintenant un contenu élevé en Fe^{2+} . Elles ont aussi permis la préparation de films secs, réduits, orientés préférentiellement par rapport à l'axe cristallographique *c*. Des solutions supernatantes ont été collectées et analysées pour Fe, Al, et Si, à partir desquelles on a déterminé l'étendue de la dissolution de l'argile résultant du traitement CBD. Les résultats ont indiqué que très peu de Fe et de Si ont été relâchés en solution, mais que jusqu'à à peu près 8% de l'Al total a été solubilisé. Les niveaux d'Al en solution les plus élevés ont été observés dans les traitements CB sans dithionite. [D.J.]