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EXTRACTION OF IRON OXIDES FROM SEDIMENTS USING REDUCTIVE DISSOLUTION BY TITANIUM(III)

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Abstract—A new iron oxide dissolution method designed to measure the abundance of "free" Fe oxide phases and associated elements in soils and sediments has been tested. The method employs a ternary complex of Ti(III), citrate, and ethylenediaminetetraacetate (EDTA) as a reductant and bicarbonate as a proton acceptor. The Ti(III)-citrate-EDTA-HCO_3 method dissolved more synthetic amorphous ferric oxide and goethite, but less synthetic hematite, than the dithionite-citrate-HCO_3 method of Mehra and Jackson. The production of acidity by the dissolution indicated that Ti(IV) is hydrolyzed to TiO_2 during the extractions. The heated dithionite method dissolved 3–6 times more Al from kaolinite and nontronite standard clays than room temperature dithionite, and 4–6 times more Al than the Ti(III)-citrate-EDTA-HCO_3 method. Furthermore, the release of Fe from the clay mineral samples consistently and rapidly reached a plateau during multiple extractions by the Ti(III)-citrate-EDTA-HCO_3 method, indicating that a well-defined Fe oxide fraction was removed. Fe released by the dithionite method continued to increase with each extraction, suggesting that some release of structural Fe occurred. Tests on two natural sediments and one heavy mineral fraction from the Miocene Cohansey Sand in the New Jersey Coastal Plain suggested that the Ti(III)-citrate-EDTA-HCO_3 method removed Fe oxides more effectively and more selectively than the dithionite method. The selectivity of the Ti(III)-citrate-EDTA-HCO_3 method is enhanced by rapid extractions at room temperature and low free ligand concentrations.

Key Words—Dissolution, Dithionite, Extraction, Goethite, Hematite, Reduction, Titanium(III).

INTRODUCTION

Our interest in the dissolution of iron oxides from sediments stems from the need to evaluate the role of these oxides in the attachment of clay to framework grains in Atlantic Coastal Plain surficial aquifers (Ryan and Gschwend, 1990). We hypothesized that Fe oxides cemented the clays in oxic zones of the aquifers. We wanted to assess the correlation between the amount of secondary or "free" Fe (e.g., ferrihydrite, goethite, hematite), the concentration of colloidal clay, and the amount of clay attached to the aquifer grains. We turned to the many Fe oxide extraction techniques to quantify the amount of Fe oxide coatings in sediments.

Soil scientists, geologists, and oceanographers have developed a number of Fe oxide removal techniques to enhance clay mineral characterization, to disperse sediment grains for particle size analysis, and to extract trace metals scavenged by Fe oxide fractions. These techniques have also been used to examine the role of Fe oxides in clay illuviation (Harris *et al.*, 1987; Smith and Callahan, 1987), to assess the role of Fe oxides and associated Al and Si in soil stability (Ajmone Marsan and Torrent, 1989), and to identify the transport modes and weathering products of Fe-bearing minerals in sediments (Koehnken and Stallard, 1988; Rude and Aller, 1989). In these applications, and in ours, where the measurement of Fe and associated elements in the Fe oxide fraction is the goal, the selectivity of the Fe oxide extraction technique is critical. Since the removal techniques are not perfectly selective for Fe oxides, interpretations of the results are often confounded by uncertainty related to which mineral phases are actually dissolved.

Dissolution of Fe oxides and other reducible metal oxides (e.g., MnO_2) is facilitated by reductants, complexing ligands, and protons (Zinder *et al.*, 1986). Other oxide components of minerals (Al_2O_3, SiO_2, TiO_2) are dissolved only by ligand- and proton-promoted reactions (Furrer and Stumm, 1986). The most selective Fe oxide extraction techniques take advantage of the unique sensitivity of Fe oxides to reductive dissolution. These techniques also utilize complexing ligands to bind Fe^{2+} following the reduction to prevent reoxidation of Fe^{2+}, and a buffer to avoid drastic changes in pH. Low pH results in increased aluminosilicate dissolution by proton-promoted reaction, and high pH results in decreasing Fe oxide solubility.

We needed an extraction method capable of dissolving crystalline Fe oxides because X-ray diffraction revealed goethite in our soils and sediments. We also desired a highly selective method to minimize ambiguity concerning the source of Fe and other elements dissolved. Some methods are not designed to dissolve crystalline Fe oxides: acidified NH_4^+-oxalate (McKeague and Day, 1966; Schwertmann, 1973), alkaline ethylenediaminetetraacetate (EDTA) (Borggaard, 1979). We tested $NH_2OH \cdot HCl$-acetic acid (Chester and Hughes, 1967) and $NH_2OH \cdot HCl$-citrate (Robbins *et al.*, 1984) and found neither would dissolve crystalline Fe oxides in a reasonable number of short extractions.

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The only widely-used selective dissolution technique capable of rapidly dissolving crystalline Fe oxides was the sodium dithionite-citrate-HCO_3 method, as described by Mehra and Jackson (1960). They reported that this reductant-ligand-buffer, augmented by heating to 80°C, dissolved 1.25 mmole of hematite in one 2-minute extraction, and 2.25 mmole of goethite in three 15-minute extractions (the source of the Fe oxides was not mentioned). Dithionite is also capable of dissolving crystalline Fe oxides at room temperature in overnight extractions (Holmgren, 1967).

The strong reducing capability of dithionite methods comes at the expense of diminished selectivity, particularly when sediments contain Fe^{3+}-bearing smectite clays. Rozenson and Heller-Kallai (1976) found that dithionite readily reduced Fe^{3+} in nontronite and montmorillonite. Heath and Dymond (1977) observed that three successive dithionite extractions of a smectite-bearing ocean sediment removed all of the Fe in the sample. Stucki *et al.* (1984) and Ericsson *et al.* (1984) observed that dithionite-citrate-HCO_3 solutions reduced structural Fe in various smectites, resulting in increased cation exchange capacities due to the higher Fe^{2+}/Fe^{3+} ratio. Citrate-HCO_3 solutions also dissolved large quantities of Al from montmorillonite and nontronite (Stucki *et al.*, 1984). Multiple extractions are often necessary to completely remove crystalline Fe oxides from some sediments, so unintended removal of structural elements may be increased. Mendelovici *et al.* (1979) extracted Fe oxides from a kaolinite separated from lateritic soils 8–15 times before reaching a plateau in dissolved Fe.

In preliminary tests on our samples, dithionite (Mehra and Jackson, 1960) required multiple extractions to remove completely the free Fe oxides. In the process, Fe, Al, and Si must have been repeatedly dissolved from layer silicates and heavy minerals. We suspected that 80°C heating and the high citrate concentration (0.27 M) contributed to nonselective, ligand-promoted dissolution. We could have used dithionite in overnight room temperature extractions recommended by Holmgren (1967), but that method employs even higher citrate concentrations (0.66 M). We feared this would offset the advantage of the temperature reduction. In general, we desired short extractions because: (1) at least two extractions are necessary to prove that a well-defined Fe fraction has been removed in the first extraction, and (2) short extractions favor rapid Fe oxide reduction over relatively slow ligand-promoted dissolution.

These concerns led us to formulate a new treatment for the extraction of Fe oxides based upon a technique used to distinguish between extra- and intracellular Fe in marine phytoplankton (Hudson and Morel, 1989). They used the ternary complex of Ti(III)-citrate-EDTA (in a molar ratio of 1:1:1) reported by Fujiwara *et al.* (1964) as a reducing agent. Amorphous ferric oxides and particulate Fe associated with cells were dissolved in 2-minute extractions in a 0.05 M Ti(III) solution. Our new treatment for soils and sediments utilized the Ti(III)-citrate-EDTA ternary complex as the reducing agent and HCO_3^- as the pH buffer. We expected that lowering the free ligand concentration and eliminating the heating step, while keeping the extraction time short, would reduce dissolution of untargeted oxide components relative to the dithionite methods, but we were uncertain whether the Ti(III)-citrate-EDTA complex would be able to reduce crystalline Fe oxides. This communication reports a series of tests designed to compare the effectiveness and selectivity of the dithionite-citrate-HCO_3 method (Mehra and Jackson, 1960) and the Ti(III)-citrate-EDTA-HCO_3 method proposed here.

MATERIALS AND METHODS

Minerals

The reductive dissolution treatments were tested on three synthetic Fe oxides: amorphous ferric oxide, goethite, and hematite. Amorphous ferric oxide was prepared by dropwise addition of $FeCl_3$ solution to KOH solution to achieve a molar ratio of OH/Fe = 3.0. The goethite was prepared by dropwise addition of $Fe(NO_3)_3 \cdot 9H_2O$ solution to KOH solution to reach a molar ratio of OH/Fe = 1.0 (Atkinson *et al.*, 1968). The resulting suspension was aged 50 hours at room temperature, then the pH was raised to 12.0 by titration with KOH. The pH-12.0 suspension was aged 72 hours at 60°C. The amorphous ferric oxide and goethite precipitates were washed with distilled deionized water (ddW) and centrifuged three times, then dried at room temperature and ground to pass through a 120-mesh sieve (<125 μm). Hematite was obtained as ferric oxide (Fe_2O_3, 99%) powder prepared by calcination of ferrous sulfate from EM Science and sieved through a 120-mesh sieve. The crystallinities of the Fe oxides were checked by X-ray powder diffraction (XRD) using a Diano XRD-5 diffractometer and Fe-filtered CoKα radiation (35 kV, 15 mA). The amorphous ferric oxide sample yielded no diffraction peaks. Weak, diffuse peaks were observed only at the d(110,130) positions for the goethite sample, indicating that the short aging period limited development of crystalline order. For the hematite sample, strong, sharp peaks appeared at all major hematite lines, indicating a high degree of crystallinity.

The standard clay minerals used in the dissolution tests included a kaolinite (API #9b, Mesa Alta, NM) and an Al-nontronite (Cheney, WA) obtained from Ward's Natural Science Establishment (Table 1). The clays were ground to pass through a 120-mesh sieve. The Fe and Ti contents of the kaolinite were also determined by HF/HNO_3/HCl digestion in Teflon-lined bombs at 110°C (Lim and Jackson, 1982). Crystallinity was assessed by XRD using Ni-filtered CuKα radiation (35 kV, 15 mA) on oriented samples of the <2-μm fractions separated by settling in ddW. The clay was mounted on Ag membrane filters (Poppe and Hathaway, 1979), and air-dried. XRD did not reveal any crystalline impurities for either sample, although Kerr (1950) measured a total of 4.7% impurities in the kaolinite sample, which Main (1950) identified as quartz, orthoclase, sphene, leucoxene, and Fe oxides (0.5–1.0%).

Natural sediments

Samples of sediments from the Miocene Cohansey Sand in the New Jersey Coastal Plain were collected using a split-tube

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Table 1. Composition of clay mineral standards and heavy mineral sample. Kaolinite data from Kerr (1950); supplementary kaolinite data from this study; nontronite data from supplier, obtained by electron microprobe analysis; heavy minerals data from this study.

Structural oxide	Kaolinite		Nontronite (wt %)	Heavy minerals sample U.11.1 (wt %)
	API (wt %)	This study (wt %)		
SiO_2	45.98		52.9	8.5
Al_2O_3	37.61		14.1	2.4
Fe_2O_3	0.76	0.83 ± 0.01	23.9	24.2
TiO_2	0.50	0.86 ± 0.01	1.2	64.9
CaO	0.35		2.6	
Na_2O	0.32		<0.5	
K_2O	0.44		<0.5	
H_2O	13.92		5.3	

Table 2. Characteristics of sediment samples used in extraction tests.

	Sediment samples	
	Oxic (S.8.2)	Anoxic (S.8.1)
Al (μmol g^{-1})	750	710
Fe (μmol g^{-1})	59	86
Ti (μmol g^{-1})	26	180
Clay (<2 μm) (wt %)	2.4	1.2
Clay (<2 μm) minerals	kaolinite goethite quartz	kaolinite quartz
Heavy minerals (wt %)	0.54	2.6
Color	10YR 8/6 yellow	5YR 8/1 white

sampler during hollow-stem auger drilling in August, 1989 (Table 2). Samples S.8.1 and S.8.2 were taken from above and below a sharp redox boundary at a depth of about 6 meters below a swamp. The anoxic sample (S.8.1) is a white sand that has been bleached by reducing porewaters from the swamp; the oxic sample (S.8.2) is a yellow sand apparently coated by Fe oxides. Total clay content was determined by suspension of the sample in ddW, 10-minute sonication in an 80 watt sonicator bath, settling to separate the <2-μm fraction, and measurement of the turbidity of the suspension. The turbidity was compared with turbidities of suspensions of known quantities of <2-μm kaolinite (EM Science). The heavy mineral content was determined after isolating the heavy minerals in bromoform. Color was described for dry sediments by comparison to Munsell soil color charts.

Sediment mineralogy was determined by XRD using Ni-filtered CuKα radiation (35 kV, 15 mA) on randomly-oriented samples of whole sediments and heavy mineral fractions ground to <63 μm, and oriented samples of the <2-μm fraction. Equivalent masses of the clay fractions were loaded onto Ag filters (10 mg cm^{-2}). Only quartz peaks were found in the whole sediments samples. The heavy mineral fractions of both samples revealed peaks for pseudorutile ($Fe_2O_3 \cdot 3TiO_2$), ilmenite, rutile, zircon, and augite. Hematite and goethite were not detected in the heavy mineral fraction. The clay-sized (<2 μm) fraction of the anoxic sediment revealed kaolinite and quartz peaks. In the <2-μm fraction of sample S.8.2, kaolinite, goethite, and quartz were detected (Figure 1a). Crystalline Al oxides were not detected.

Heavy minerals were also separated from sample U.11.1, obtained from an oxic zone of the aquifer at a depth of 10 meters below the surface. The heavy minerals of this sample were used because the amount of heavy minerals extracted from remaining stocks of samples S.8.1 and S.8.2 was not sufficient for the heavy mineral treatments. The overall composition of the heavy mineral suite of sample U.11.1 was determined by energy-dispersive X-ray analysis (EDX) on an Au-coated sample (Table 1). XRD analysis showed that the major mineral constituents of this sample were the same as those of samples S.8.1 and S.8.2.

Reagents

Sodium dithionite at 78% purity was obtained from Aldrich Chemical Company. The major contaminant (~10% sodium sulfite) and the minor contaminants identified by the supplier diminished the reducing capacity of the reagent, so the amount used in the treatments was increased by a factor of 1.28. Sodium dithionite tends to be contaminated with Zn, which interferes with trace element studies (Tessier *et al.*, 1979; Shuman, 1982). The sodium dithionite was stored in a desiccator. Titanium(III) chloride was obtained from Aldrich as 12 wt % $TiCl_3$ in a 21 wt % HCl solution. The $TiCl_3$ reagent was significantly contaminated by Fe, and perhaps other trace elements, but the supplier could not provide an analysis. Other reagents used in the experiments include sodium citrate dihydrate, tetrasodium ethylenediaminetetraacetate dihydrate (Na_4EDTA), sodium bicarbonate, and sodium hydroxide, all ≥98% purity.

Reductive dissolution treatments

We set up a series of treatments in which only single components of the methods (reductant, ligand, buffer, heat) were changed (Table 3). All experiments were carried out in polyethylene and polycarbonate labware, with the exception of some ground glass-stoppered reagent bottles and volumetric flasks. All labware was soaked in 4 N HNO_3 and rinsed with Fe- and Al-free 1 MΩ resistivity water produced with a reverse osmosis water purification system.

DCB Heat is a modification of the traditional Mehra and Jackson (1960) dithionite-citrate-HCO_3 method, altered to provide more complete separation of solids from the supernatant by high-speed centrifugation. There are 8 steps:

1. Mineral sample (0.1 g) or sediment sample (0.3 g) weighed in 40 ml polyethylene or polycarbonate centrifuge tube.
2. Thirty ml of 0.27 M citrate-0.11 M $NaHCO_3$ solution added to tube.
3. Suspension heated at 80°C in a water bath for 30 minutes.
4. Sodium dithionite (0.64 g at 78% purity) added to heated tube.
5. Suspension shaken for 15 minutes (sediment suspension sonicated for 5 minutes and shaken for 10 minutes).
6. Suspension centrifuged at 13,000 rpm (maximum 26,900 g) in Beckman J2-21 centrifuge with JS-13.1 tilting rotor for 60 minutes.
7. Supernatant (25 ml) carefully removed by syringe and stored for analysis.
8. Extraction repeated on reduced residue to insure complete Fe removal.

DCB and all of the following treatments omit the heating of the suspension (Step 3).

TiCB uses the Ti(III)-citrate complex as the reductant in place of dithionite. The preparation of the reagent is best accomplished in a deaerated solution to prevent the oxidation of Ti(III) by dissolved oxygen. The following steps substituted for Step 2:

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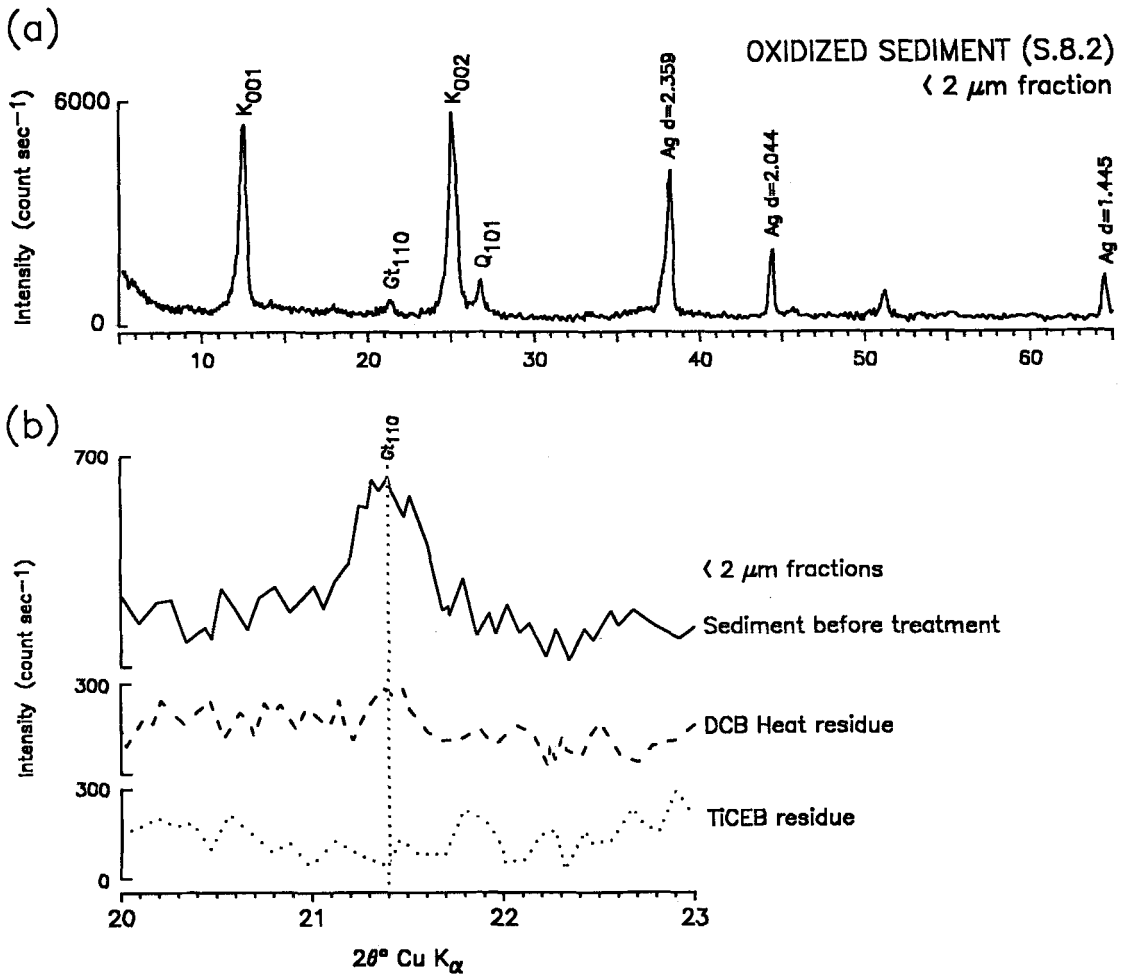


Figure 1. XRD results for (a) <2-μm fraction of the oxidized sediment (S.8.2) showing the goethite (Gt), kaolinite (K), quartz (Q), and Ag-calibration peaks, and (b) the major goethite peak (Gt_{110}) for <2-μm fraction of the untreated sediment, the *DCB Heat*-treated sediment, and the *TiCEB*-treated sediment.

2a. One liter of 0.27 M citrate solution bubbled with Ar for 60 minutes.

2b. Ti(III) chloride stock solution (64.28 g) diluted to 1 liter with the deaerated citrate solution, resulting in a dark brownish-purple solution.

2c. Ti(III)-citrate solution titrated to pH 7.0 with NaOH while bubbling with Ar and stirring magnetically.

2d. Neutral Ti(III)-citrate solution stored in ground glass-stoppered reagent bottles (no longer than 48 hours).

2e. Thirty ml of Ti(III)-citrate solution added to tube.

2f. $NaHCO_3$ solution (3.33 ml of 1.0 M $NaHCO_3$) added to tube.

The dithionite addition (Step 4) is omitted from this and all of the following treatments.

TiC omits the addition of the $NaHCO_3$ solution (Step 2f).

TiCE uses a combination of citrate and EDTA to form a ternary Ti(III) complex in solution. Steps 2a and 2b are changed to the following:

Table 3. Reductive dissolution treatment reagents and conditions.

Method	Complexing ligands	Buffer	Reducing agent	Temp (°C)	Argon purge
DCB Heat	0.27 M Na_3citrate	0.11 M $NaHCO_3$	0.096 M $S_2O_4^{2-}$	80	
DCB	0.27 M Na_3citrate	0.11 M $NaHCO_3$	0.096 M $S_2O_4^{2-}$	25	
TiCB	0.27 M Na_3citrate	0.11 M $NaHCO_3$	0.05 M Ti(III)	25	✓
TiC	0.27 M Na_3citrate		0.05 M Ti(III)	25	✓
TiCE	0.05 M Na_3citrate 0.05 M Na_4EDTA		0.05 M Ti(III)	25	✓
TiCEB	0.05 M Na_3citrate 0.05 M Na_4EDTA	0.11 M $NaHCO_3$	0.05 M Ti(III)	25	✓

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2a. One liter of 0.05 M citrate-0.05 M Na_4EDTA bubbled with Ar for 60 minutes.
2b. Ti(III) chloride stock solution (64.28 g) diluted to 1 liter with the deaerated citrate-EDTA solution, resulting in a transparent, deep-purple solution.

The $NaHCO_3$ addition (Step 2f) is omitted.

TiCEB includes the addition of the $NaHCO_3$ (Step 2f) to the Ti(III)-citrate-EDTA solution. Steps 2a and 2b from the *TiCE* treatment are used.

Reductive dissolution test procedures

We compared the Fe oxide reductive dissolution effectiveness of the six treatments by subjecting the three synthetic Fe oxides (0.1 g samples) to single extractions, and measuring Fe dissolved in triplicate analyses. Before and after each extraction, pH was measured in the supernatant following 1 minute without drift. The reported pH is a mean of the triplicate analyses (standard deviations were always <0.05 pH units). The Fe oxide dissolution results cannot readily be extrapolated to natural samples because these Fe oxides are synthesized under artificial conditions.

We tested the selectivity of the treatments by subjecting the clay minerals (0.1 g samples) to single extractions by the *DCB Heat, DCB, TiCE, TiCEB* treatments, and multiple extractions by the *DCB Heat* and *TiCEB* treatments. Dissolved Fe and Al were measured in tripicate analyses.

The overall effectiveness of the *DCB Heat* and *TiCEB* treatments for extracting Fe oxides from sediments was tested by subjecting the heavy minerals (0.05 g samples) and sediments (0.3 g samples) to multiple extractions. Dissolved Fe and Al were measured in the extracts in triplicate analyses.

Dissolved Fe and Al concentrations in the supernatant were measured by inductively-coupled plasma–atomic emission spectroscopy. Standards curves were prepared with blanks and standards made up in the treatment solutions. The overall results shown are means ± one standard deviation of triplicate analyses.

The removal of crystalline Fe oxides from the oxic sediment was monitored by XRD. The <2-μm fraction was separated from the reduced residues and equivalent masses were loaded onto Ag filters in the same manner as the clay fraction of the sediments. XRD peak positions were calibrated to the 2θ position of the sharp Ag peak (d = 2.044 Å), and peak intensities were normalized to the height of the same peak in all samples.

RESULTS AND DISCUSSION

Single extractions

Iron oxides. For all treatments except *DCB*, the amount of Fe dissolved from the Fe oxide corresponds to the relative solubilities of the oxides: amorphous ferric oxide > goethite > hematite (Table 4). *DCB* dissolved significantly more hematite than goethite in the 15 minute extraction period, consistent with the results of Mehra and Jackson (1960) for their heated dithionite treatment. Torrent *et al.* (1987) and Macedo and Bryant (1989) also observed that dithionite and microbial reduction dissolved hematite more rapidly than goethite from lateritic soils. The slower dissolution of goethite was attributed to Al substitution in goethite (up to 34 mol % AlOOH), which decreased the goethite solubility (Tardy and Nahon, 1985). The composition of the goethite dissolved by Mehra and Jackson (1960) was not specified, but the goethite synthesized for this study did not contain Al, so it is not clear why *DCB* dissolved hematite more rapidly than goethite. The crystal form and shape, aggregation, or the drying of the synthetic Fe oxides prepared for this study may have affected the dissolution kinetics.

The direction of pH change during the treatments suggests that dithionite reductions consume acidity and that Ti(III) reductions produce acidity. According to Jepson (1988) and thermodynamic equilibrium calculations using MINEQL (Westall *et al.*, 1976), the major species involved in Fe oxide reduction by dithionite at an initial pH 7.3 include:

$$S_2O_4^{2-} + Fe_2O_3 + 2\ cit^{3-} + 2\ H^+ \rightarrow 2\ SO_3^{2-} + 2\ Fe(II)\text{-}cit^- + H_2O.$$

The change in pH is caused by consumption of one proton for each Fe^{3+} reduced. The pH rose only slightly during the *DCB Heat* and *DCB* extractions because HCO_3^- donated protons. Initially, we expected that pH would increase in the Ti(III) reductions as well. Zehnder and Wuhrmann (1976) indicated that the Ti(III)-citrate complex is oxidized to Ti(IV)-citrate, resulting in the following reaction at neutral pH:

$$Ti(III)\text{-}cit + \tfrac{1}{2}\ Fe_2O_3 + cit^{3-} + 3\ H^+ \rightarrow Ti(IV)\text{-}cit^+ + Fe(II)\text{-}cit^- + \tfrac{3}{2}\ H_2O.$$

However, pH decreased during the Ti(III)-citrate reductions (by almost one pH unit in the unbuffered *TiC* treatment). We suspect that the oxidation of Ti(III) in Ti(III)-citrate destabilized the complex and Ti(IV) was hydrolyzed to TiO_2:

$$Ti(III)\text{-}cit + \tfrac{1}{2}\ Fe_2O_3 + \tfrac{1}{2}\ H_2O \rightarrow TiO_2 + Fe(II)\text{-}cit^- + H^+.$$

Stability constants for the Ti complexes are not available to evaluate the feasibility of this reaction. Ti concentrations remained high in the supernatants and the reduced residues, but crystalline TiO_2 was not detected in the latter by XRD. TiO_2 may remain in the supernatant as colloidal TiO_2 in the <50-nm range, or it may settle into the solid residue as amorphous TiO_2. Hudson and Morel (1989) observed that TiO_2 precipitation clogged filters used to separate phytoplankton cells from the reducing solution, but they did not investigate the nature of the TiO_2 solid. In either instance, investigations of Ti (or trace elements present as contaminants in the $TiCl_3$ reagent) in soils and sediments will encounter high background problems.

During the unbuffered *TiCE* treatment, pH decreased by nearly two pH units. In this instance, the hydrolysis of the resulting Ti(IV) liberates equimolar quantities of citrate and EDTA. EDTA outcompetes citrate for the Fe(II), forming Fe-EDTA complexes, and a proton is released:

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Table 4. Fe dissolved from three Fe oxides by six reductive dissolution methods. The amount of Fe dissolved (Fe Diss) is expressed as the fraction of Fe oxide dissolved. It was determined by normalizing the amount of dissolved Fe to the total amount of Fe dissolved in treatments where dissolution was complete.

Treatment	Initial pH	Amorphous ferric oxide		Goethite		Hematite	
		Fe Diss	Final pH	Fe Diss	Final pH	Fe Diss	Final pH
DCB Heat	7.3	0.94 ± 0.01	7.8	0.87 ± 0.02	7.8	0.62 ± 0.08	7.9
DCB	7.3	0.71 ± 0.04	7.7	0.39 ± 0.00	7.6	0.56 ± 0.03	7.4
TiCB	7.0	0.53 ± 0.03	7.3	0.19 ± 0.02	6.9	0.04 ± 0.00	7.3
TiC	7.0	0.53 ± 0.01	6.5	0.20 ± 0.00	6.1	0.03 ± 0.00	6.4
TiCE	7.0	1.00 ± 0.03	5.1	1.00 ± 0.01	5.4	0.38 ± 0.01	5.4
TiCEB	7.0	0.98 ± 0.05	6.7	0.98 ± 0.00	6.7	0.42 ± 0.01	6.6

$$\text{Ti(III)-cit-H}_2\text{EDTA}^{2-} + \tfrac{1}{2}\text{Fe}_2\text{O}_3 + \tfrac{1}{2}\text{H}_2\text{O} \rightarrow \text{TiO}_2 + \text{Fe(II)-H}_2\text{EDTA} + \text{cit}^{3-} + \text{H}^+.$$

Protons are accepted by HCO_3^- in *TiCEB* to maintain near-neutral pH.

The substitution of Ti(III)-citrate for dithionite as the reductant (*TiCB*) resulted in far less Fe dissolution from each Fe oxide. Based only on equilibrium redox potentials calculated from free energies and stability constants, we expected that the Ti(III)-citrate reduction would be nearly as effective as the dithionite reduction ($E_H = -480$ mV at pH 7 for Ti(III)-citrate → Ti(IV)-citrate [Zehnder and Wuhrmann, 1976]; $E_H = -459$ mV at pH 7.3 and $[S_2O_4^{2-}] = 0.096$ M for dithionite → sulfite). Incomplete complexation of Ti(III) probably caused the ineffectiveness of the Ti(III)-citrate solution. Titrating to neutral pH may destabilize the complex, as Hudson and Morel (1989) observed at pH 8, resulting in formation of $Ti(OH)_3$ ($K_{sp} \cong 10^{-40}$, Latimer (1956)).

Clay minerals. Single extractions of the clay minerals were designed to evaluate the selectivity of the *DCB Heat, DCB, TiCE,* and *TiCEB* treatments (Table 5). The *TiCB* and *TiC* treatments were not tested on the clay minerals because it was established that they were ineffective in Fe oxide dissolution.

In the single extractions of the kaolinite sample, the treatments removed between 2.5 and 7.4% of the total Fe, and between 0.027 and 0.15% of the total Al. This resulted in a molar ratio of Fe/Al removed that ranged from 0.6 to 3.3. Because Fe(III) substitution for Al^{3+} is usually limited to 3 mol % (Tardy and Nahon, 1985), it is apparent that much more Fe was dissolved from the samples than could have been present as structural Fe in the kaolinite. Thus, Fe dissolved from the sample must represent some portion of the 0.5–1.0% Fe oxide impurities reported by Main (1950). The single extraction of the kaolinite by *DCB Heat* dissolved about five times as much Al as the other three treatments, clearly showing the effect of heating to 80°C. The three room temperature treatments dissolved about the same amount of Al. We expected that *TiCE* and *TiCEB* would dissolve less Al than the room temperature *DCB* treatment because of lower free ligand activity. However, in the 15-minute reactions, no significant difference was observed.

The single extractions of the nontronite sample dissolved Fe and Al at a molar ratio of Fe/Al that ranged from 3 to 8. Because the molar ratio of Fe/Al is 1:1 in the nontronite sample, and Fe is dissolved much more extensively than Al from the sample, it is likely that reduction of structural Fe(III) in nontronite occurred. However, some of the Fe removed may have been present as Fe oxide impurities. Heating to 80°C in *DCB Heat* dissolved about 2.5 times as much Al from the nontronite sample as did the *DCB* and *TiCE* treatments. *TiCEB* dissolved the least Al, which we attribute to the combination of short, room temperature extractions, pH buffering, and low free ligand activity.

Multiple extractions

Clay minerals. The results of the kaolinite extractions show that the *TiCEB* extractions reached a plateau in dissolved Fe in the first extraction (Figure 2a). In contrast, the first *DCB Heat* extraction removed only half the total Fe ultimately dissolved, and successive ex-

Table 5. Selective reductive dissolution treatments on clay minerals.

Method	Initial pH	Kaolinite			Nontronite		
		Fe Diss (μmol g^{-1} clay)	Al Diss (μmol g^{-1} clay)	Final pH	Fe Diss (μmol g^{-1} clay)	Al Diss (μmol g^{-1} clay)	Final pH
DCB Heat	7.3	7.7 ± 1.2	12 ± 0.2	7.4	64 ± 3	24 ± 1	7.4
DCB	7.3	6.6 ± 2.6	2.0 ± 0.2	7.4	39 ± 8	9.1 ± 0.4	7.3
TiCE	7.0	2.7 ± 0.6	2.3 ± 0.7	6.0	55 ± 10	10 ± 0.5	5.8
TiCEB	7.0	4.1 ± 0.5	2.2 ± 0.2	6.8	47 ± 2	5.7 ± 0.2	6.8

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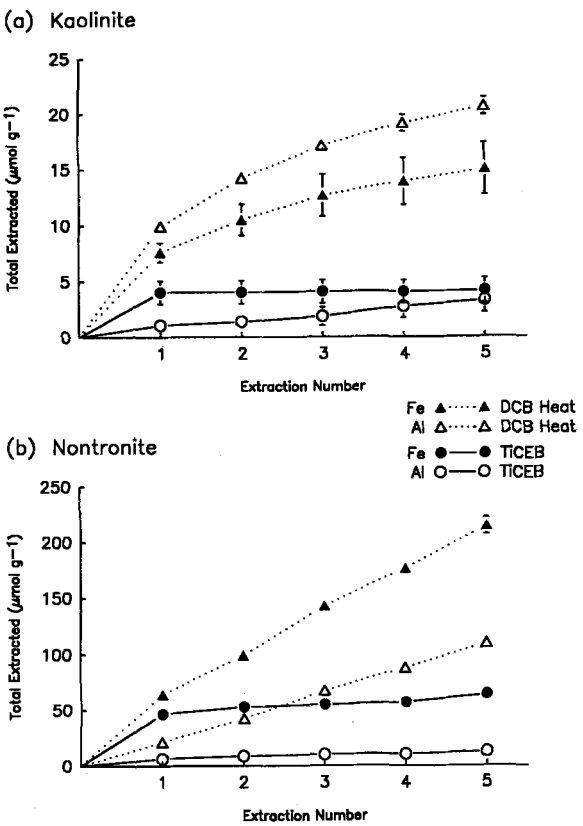


Figure 2. Comparison of Fe and Al dissolved from (a) kaolinite and (b) nontronite in multiple extractions by *DCB Heat* and *TiCEB*.

tractions continued to remove Fe. The total amount of Al dissolved increased with each extraction by both treatments, but *DCB Heat* dissolved nearly four times as much Al per extraction as *TiCEB*.

Successive *TiCEB* extractions of the nontronite sample dissolved only slightly more Fe than the amount of Fe dissolved in the first extraction, while the *DCB Heat* extractions removed Fe in relatively constant amounts (Figure 2b). Al dissolved increased with each successive extraction by both treatments, but *DCB Heat* dissolved nearly nine times as much Al per extraction as *TiCEB*.

TiCEB reached a plateau in dissolved Fe in the first extraction of both clay mineral samples, while successive *DCB Heat* extractions continued to dissolve Fe. This suggests that the *TiCEB* treatment dissolved a well-defined portion of the Fe in the clays (probably a free Fe oxide phase), and that dissolution of structural Fe by *TiCEB* was minimal compared to *DCB Heat*. Al was dissolved from the clay mineral samples in nearly constant amounts in successive extractions, suggesting that structural Al was dissolved by both treatments. However, *TiCEB* extractions dissolved far less Al from each clay mineral than *DCB Heat* extractions.

Although trends in the amounts of Fe and Al dissolved in multiple extractions gave some indication whether the Fe and Al came from free oxide phases or from clay mineral structures, the origin of the Fe and Al could not be ascertained without the aid of some nondestructive analysis, such as differential XRD or Mössbauer spectroscopy. XRD could not be used to determine the source of the dissolved Fe because crystalline Fe oxides were not detected in the clay mineral samples.

Heavy minerals. The effects of multiple extractions by *DCB Heat* and *TiCEB* on the heavy mineral fraction (Figure 3) were compared to assess the contribution of this fraction to the Fe and Al dissolved from the natural sediment samples. The two treatments removed similar amounts of Fe in five extractions, but the *DCB Heat* extractions reached a plateau in dissolved Fe slightly more quickly than the *TiCEB* extractions. The plateau in dissolved Fe may represent a minor Fe-bearing fraction of the sample that is more susceptible to reductive dissolution.

DCB Heat extractions dissolved slightly more Al than *TiCEB* extractions. The source of the dissolved Al may be the small amounts of aluminosilicate heavy minerals (augite) detected by XRD and EDX.

Natural sediment extractions. The first *TiCEB* extraction of the oxic sediment (S.8.2) removed almost all of the Fe ultimately dissolved, while the first *DCB Heat* extraction removed only about half of the Fe ultimately dissolved (Figure 4a). The *DCB Heat* extractions appear to have reached a plateau in dissolved Fe at 80% of the total Fe dissolved by *TiCEB*. Both the *TiCEB* and *DCB Heat* extractions dissolved essentially all of the goethite in the <2-μm fraction of the oxic sediment (Figure 1b). As with the Fe, the *TiCEB* extractions dissolved slightly more Al, and reached a plateau in dissolved Al in fewer extractions than did the *DCB Heat* extractions.

The multiple extractions of the anoxic sediment (S.8.1) revealed that the first *TiCEB* extraction removed a larger portion of the Fe ultimately dissolved than did the first *DCB Heat* extraction (Figure 4b). Subsequent *TiCEB* extractions dissolved less Fe per extraction than the *DCB Heat* extractions. The *DCB Heat* extractions dissolved Al from the anoxic sediment much more extensively than the *TiCEB* extractions.

To demonstrate the usefulness of the *TiCEB* method, the results of its application to the oxic and anoxic sediments are compared with those obtained by *DCB Heat*. With some knowledge of the mineralogy, and reasonable assumptions, we have estimated the amounts of Fe oxide, or "free" Fe, in each sediment.

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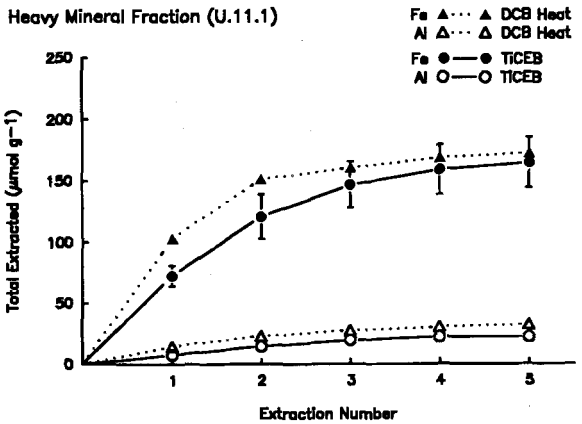


Figure 3. Comparison of Fe and Al dissolved from the heavy mineral fraction of sample U.11.1 in multiple extractions by *DCB Heat* and *TiCEB*.

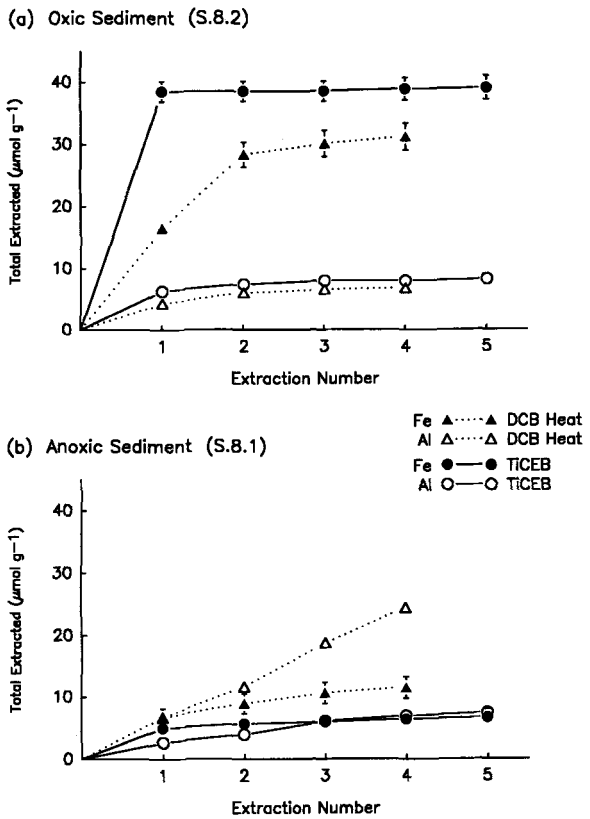


Figure 4. Comparison of Fe and Al dissolved from Pine Barrens (a) oxic sediment (S.8.2) and (b) anoxic sediment (S.8.1) in multiple extractions by *DCB Heat* and *TiCEB*.

The expected free Fe content was estimated by subtracting from the total Fe measured: (1) structural Fe in clay minerals, corresponding to a clay-sized fraction composed entirely of 1 mol % Fe-substituted kaolinite, and (2) structural Fe in the heavy mineral fraction, assuming the heavy mineral fractions have the same Fe content as that of sample U.11.1. Other sources of structural Fe in the sediments were considered negligible. The amount of Fe removed by the two methods was amended by subtracting Fe extracted from the heavy mineral fraction of sample U.11.1 (assuming that Fe is extracted from the heavy mineral fractions of the sediments at the same rate) from the total amount of Fe extracted from the sediments. The amount of structural Fe that may have been extracted from the clay minerals was considered negligible. The amount of Fe removed by *TiCEB* from the oxic sediment closely approximated the expected Fe oxide content, while the amount of Fe removed by *DCB Heat* fell short (Table 6). The small amounts of Fe removed from the anoxic sediment by both methods were reasonable, given the uncertainty in our estimated free Fe. However, the amount of Fe extracted by *DCB Heat* continued to increase slightly with each extraction.

The parallel behavior of Al and Fe dissolved from the oxic sediment suggests that most of the Al (the portion removed in the first extraction) was associated with a free Fe oxide phase. The Al removed by *TiCEB* was adjusted for the amount of structural Al expected from aluminosilicates in the heavy mineral fraction. The Al associated with the free Fe oxides may have been present as 15–20 mol % AlOOH substituting in the goethite detected by XRD. This assumes that all of the Fe removed by *TiCEB* was goethite, and that the amount of Al released by other aluminosilicates was negligible. Goethite d(110) peaks were shifted to smaller d-spacings in other clay fractions separated from oxic soil and sediment samples obtained in the same cores (Ryan and Gschwend, unpublished data), indi-

Table 6. Comparison of Fe dissolved in the multiple extractions of the sediment samples with expected concentrations of Fe in various fractions of the sediments. Estimated quantities followed by (est.).

	Sediment samples	
	Oxic (S.8.2) (μmol g^{-1})	Anoxic (S.8.1) (μmol g^{-1})
Total Fe	59	86
Fe in clay (est.)	−2.6	−0.9
Fe in hvy min (est.)	−16	−79
Expected free Fe	40	6.1
TiCEB		
Fe removed from sediment	39	6.7
Fe removed from hvy min	−0.9	−4.4
TiCEB-free Fe	38.1	2.3
DCB Heat		
Fe removed from sediment	31.2	11.5
Fe removed from hvy min	−0.9	−4.4
DCB Heat-free Fe	30.3	7.1

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cating Al substitution in goethite (Schulze, 1984). In contrast with the similarity between the behavior of the Fe and Al dissolved from the oxic sediment, the Al dissolved from the anoxic sediment continued to increase quite steadily for both treatments, suggesting that the dissolved Al came primarily from the clay and heavy mineral phases. *DCB Heat* extractions dissolved about four times as much Al from the anoxic sediment as did *TiCEB* extractions.

SUMMARY

Our attempts to characterize the abundance of the free Fe oxide phases led us to examine methods by which Fe oxides are extracted from soils and sediments. We tested the most widely-used version of the dithionite methods (Mehra and Jackson, 1960) on our samples and found that multiple extractions were required to remove a well-defined fraction of Fe from our samples. Furthermore, more Al was being dissolved in each extraction. We formulated a new Fe oxide dissolution method employing the Ti(III)-citrate-EDTA ternary complex (Fujiwara *et al.,* 1964) as the reductant and $NaHCO_3$ as a pH buffer.

The Ti(III)-citrate-EDTA-HCO_3 method dissolved synthetic amorphous ferric oxide and goethite slightly better than the dithionite method, but the hematite examined in this study was dissolved to a greater extent by dithionite. The change in pH during the experiments suggested that the Ti(III) reductions produced acidity, while the dithionite reductions consumed acidity. The heated dithionite method dissolved 3–6 times more Al from kaolinite and nontronite standard clays than the room temperature dithionite, and 4–6 times more Al than the Ti(III)-citrate-EDTA-HCO_3 method. Furthermore, the release of Fe from the clay mineral samples consistently and rapidly reached a plateau during multiple Ti(III)-citrate-EDTA-HCO_3 extractions, indicating that a well-defined fraction of Fe was removed, while Fe released by dithionite continued to increase with each extraction. Multiple extractions of natural sediments and heavy minerals from the Miocene Cohansey Sand revealed that: (1) the Ti(III)-citrate-EDTA-HCO_3 method extracted amounts of Fe that agreed well with the expected amount of free Fe oxides in the sediment, (2) both the Ti(III)-citrate-EDTA-HCO_3 and dithionite methods were effective at removing crystalline goethite from the oxic sample, and (3) the Ti(III)-citrate-EDTA-HCO_3 method dissolved much less Al from the sediments than the dithionite method. Application of the *TiCEB* method to 37 other soil and sediment samples collected from cores of the Cohansey Sand consistently indicated complete free Fe removal in single extractions.

Extraction at room temperature rather than at 80°C certainly enhanced the selectivity of Ti(III)-citrate-EDTA-HCO_3 relative to dithionite, but the lower free strong-ligand concentration in Ti(III)-citrate-EDTA-HCO_3 also discouraged ligand-promoted dissolution of oxide components not targeted for extraction. For our samples, the result was more complete dissolution of goethite in a small number of short extractions, and less dissolution of structural components of accompanying aluminosilicate minerals. Although the usefulness of the Ti(III)-citrate-EDTA-HCO_3 method may be limited by the presence of trace elements in the "off-the-shelf" $TiCl_3$ reagent and the high concentrations of Ti left in the extraction solution and residue, we suggest that researchers concerned with the amount of Fe and associated elements in free Fe oxide phases of soils and sediments compare the effectiveness and selectivity of the Ti(III)-citrate-EDTA-HCO_3 method with traditional methods.

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