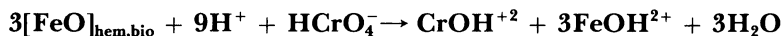


# KINETICS OF CHROMATE REDUCTION BY FERROUS IONS DERIVED FROM HEMATITE AND BIOTITE AT 25°C

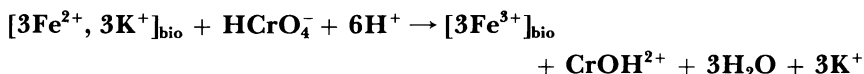
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**ABSTRACT.** Experimental results on the kinetics of chromate reduction indicate that residual amounts of ferrous iron in weathering minerals can act as reductants for oxidized aqueous species. Chromate reduction solely by ferrous ions is nearly instantaneous, but when the only source of ferrous ion is the amount contained in hematite or biotite, the initial rate of chromate reduction is dependent on the dissolution rates of the ferrous iron contents of these minerals, increased at low pH or by high concentrations of anions that complex ferrous ions. Reduction of chromate by the ferrous ions produced by dissolution of the ferrous iron components of hematite and biotite in acidic media is described by the reaction



After dissolution produces an initial amount of dissolved iron, spontaneous reduction of  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$  occurs at the biotite surface by coupled electron-cation transfer reactions but not at the hematite surface. Transfer reactions at the biotite surface rapidly create ferrous ions even in oxygenated solutions, resulting in additional chromate reduction according to



where the release of  $\text{K}^+$  is required to maintain the internal charge balance in the biotite structure.

Chromate reduction occurs in the solution phase rather than at the mineral surfaces by reaction with the ferrous ions produced by both the dissolution and transfer reactions. Thus, the effective oxidation potential exerted by the residual ferrous iron in minerals is defined by the  $\text{Fe}^{+2}/\text{Fe}(\text{OH})_{3(s)}$  redox couple. The reduction of chromate results in the precipitation of  $(\text{Cr}, \text{Fe})(\text{OH})_{3(s)}$ , which limits the concentrations of dissolved chromium to less than  $10^{-6}$  M between pH 4 and 12. Chromate reduction was evident even in oxygenated solutions, implying that the ferrous ions derived from the residual amounts in oxide and silicate minerals can cause transient periods of apparent redox disequilibrium between major and minor redox couples in weathering environments.

## INTRODUCTION

Commonly, redox conditions in aqueous environments are defined by the dominant electron donors or acceptors that can be expected to react quickly with other aqueous species to maintain the redox state of a solution. For example, the ferrous and ferric ion concentrations can provide a reliable measure of the prevailing redox conditions in acidic

mine drainage waters (Nordstrom, Jenne, and Ball, 1979). However, many dilute surface waters are not well poised, making it difficult to predict aqueous speciation for all redox sensitive trace elements based on the "system" redox potentials that are defined by analytical determinations of major redox species or electrochemical measurements (Lindberg and Runnells, 1984). Also, many redox reactions are slow, especially those involving dissolved oxygen, resulting in redox disequilibrium. Disequilibrium negates the use of system redox potentials to describe redox speciation. An alternative approach involves describing the kinetic processes that control the redox speciation of individual couples. Although it may be impractical to obtain absolute rates of changes in oxidation states for all aqueous redox couples for all possible conditions, knowledge of the important kinetic factors affecting such changes can lead to a better understanding of the tendency of specific couples to evolve to predominantly one oxidation state or another for a given set of conditions.

Recently, White and Yee (1985) have shown that coupled electron-cation transfer reactions that occur at the surfaces of ferrous iron-containing silicates are important for controlling the redox speciation of dissolved iron. Numerous primary silicates and oxides, such as hornblende, augite, biotite, and magnetite contain ferrous iron, and weathering products such as maghemite, hematite, and some clay minerals also may contain residual amounts of ferrous iron. These minerals are often present in groundwater environments and represent a reservoir of reductant for the oxidized species of other aqueous redox species whose equilibria exist at higher potentials than that defined by the ferrous/ferric couple. We expect that the basic factors affecting the reduction kinetics of each reducible species may be similar in type but are likely to be different in magnitude depending on solution chemistry, surface properties of the involved ferrous iron minerals, structural coordination of the ferrous iron in those minerals, and physical conditions. This paper discusses experimental investigations of the factors that affect the kinetics of chromate reduction (Cr(VI) to Cr(III)) caused by reactions with the ferrous ions that are derived from hematite and biotite. These experimental studies provide insight on how residual amounts of ferrous iron in minerals can affect the redox speciation of aqueous chromium and, by analogy, other redox-sensitive trace species in aqueous environments.

Chromate species are known to be toxic to plants and organisms (Towill and others, 1978) and the EPA drinking water limit is set at  $50 \mu\text{g} \cdot \text{liter}^{-1}$  (Förstner and Wittman, 1981). Chromate may be introduced into the environment by the disposal of wastes from a number of industries including tanneries, electroplating, mining, and electric power generation. The mobility of chromate in the groundwater environment is dependent on adsorption reactions and the rate at which it is reduced to chromic and, subsequently, incorporated into sparingly soluble solids. Because ferrous iron is ubiquitous in many soils and rock

types and also is used effectively in various aqueous and solid forms for reducing and precipitating chromate in wastewater treatment processes (Eary and Rai, 1988), we expected that the ferrous iron contained in naturally occurring minerals would be an important inorganic reductant for chromate in groundwater environments.

#### PROCEDURES

*Materials.*—The hematite from Iron-ton, Minnesota and the biotite from Bancroft, Ontario were obtained from Ward's Scientific Establishment, Inc. The hematite was dark reddish-brown in appearance with streaks of steel-gray and had the slight iridescence that is characteristic of specular hematite. The biotite was olive-green, and plates that were judged by eye to be free of contaminants were used. Minerals were ground in ceramic mortars and sieved to separate the grain size of 53 to 106  $\mu\text{m}$ . The separated fractions were washed repeatedly with deionized water and air dried. Minerals were identified by powder X-ray diffraction (XRD), and the ground hematite was determined by combined XRD and chemical analyses to contain about 11.4 wt percent quartz (table 1). Specific crystalline impurities in the biotite were not detectable in the powder XRD patterns. The hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) was slightly magnetic, but diffraction peaks characteristic of maghemite, magnetite, or ilmenite were not found even for subsamples potentially enriched in these minerals by magnetic separation. The hematite did contain 3.0 wt percent ferrous iron (table 1), but it is unlikely that this amount was present as magnetite because it would require the presence of 11.5 wt percent magnetite within the hematite matrix. This amount would have provided clearly discernable diffraction peaks for magnetite in both the bulk hematite and the magnetically enriched hematite samples. We estimate that the hematite could contain at most about 1.0 wt percent magnetite. The very low titanium content of the hematite (table 1) eliminates ilmenite as the source of the ferrous iron. The absence of iron minerals other than hematite indicates that the ferrous iron exists in the hematite structure or as amorphous material and is probably a residual amount derived from the weathering of an original magnetite-bearing rock.

TABLE 1

*Elemental compositions by wet chemical analyses and BET surface areas for the hematite and biotite (b.d. means below detection limit)*

	Weight %							
	Fe(II)	Fe <sub>total</sub>	Si	Al	Mg	K	Ca	Ti
Hematite ( $1.05 \pm 0.09 \text{ m}^2 \cdot \text{g}^{-1}$ )	$3.0 \pm 0.4$	$61.7 \pm 2.5$	5.3	0.14	b.d.	b.d.	0.32	b.d.
Biotite ( $2.84 \pm 0.08 \text{ m}^2 \cdot \text{g}^{-1}$ )	$11.7 \pm 0.4$	$14.6 \pm 1.0$	17.1	5.6	8.1	6.3	0.3	1.3

The ferrous and total iron contents (ferric iron by difference) of the unreacted biotite samples (table 1) and experimental products (table 2) were determined according to the method of Begheijn (1979) with a precision of  $\pm 5$  percent on replicate determinations. The ferrous and total iron contents of the hematite samples were determined by a method that was a slightly modified version of Begheijn (1979) in which the volume of concentrated sulfuric acid in the digesting solution was increased from 1 to 10 ml and the time of digestion was increased from 2 to 60 min. Reagent-grade ferrous salts were subjected to the same treatment, but no oxidation of their ferrous contents was found, and 100 percent of the total iron was recovered. The precision of the ferrous and total iron determinations for the hematite samples was  $\pm 10$  percent. The concentrations of other major elements and the specific surface areas of the prepared minerals, which were determined by nitrogen gas adsorption and Brunauer-Emmett-Teller (BET) calculation, are also given in table 1.

*Experimental.*—Experiments were conducted at  $25^{\circ} \pm 2^{\circ}\text{C}$  in 1.0-liter polyethylene bottles placed on magnetic stirrers. Teflon stir bars were used to mix solutions, and most experiments were stirred continuously at a constant rate that was sufficient to keep the majority of the particles suspended. A few unstirred experiments were conducted with the hematite in which the suspensions were swirled for only 10 to 20 sec just before the samples were withdrawn.

Solutions were aerated continuously with water-saturated and  $\text{CO}_2$ -free air resulting in dissolved-oxygen concentrations of about 7.5 to 8.2 ppm, depending on the electrolyte concentration and small variations in temperature. Experiments were started by adding the hematite or biotite to a solution of known chromate and dissolved-oxygen concentrations, ionic composition, and pH. A stock solution of  $10^{-1.7}$  M  $\text{K}_2\text{Cr}_2\text{O}_7$  was the source of chromate in the experiments. The ionic compositions were adjusted with either  $\text{Na}_2\text{SO}_{4(s)}$ ,  $\text{NaCl}_{(s)}$ ,  $\text{NaClO}_4 \cdot \text{H}_2\text{O}_{(s)}$ , or  $\text{NaH}_2\text{PO}_{4(s)}$ . Most of the experiments were conducted in  $10^{-3}$  to  $10^{-1}$  M  $\text{Na}_2\text{SO}_4$  solutions, because sulfate is the dominant anion in many industrial waste waters (Summers, Rupp, and Gherini, 1983), where chromate mobility may be of concern. For a few experiments in which ferric ions were required, reagent grade  $\text{FeCl}_{3(s)}$  dissolved in  $10^{-3}$  M HCl was used. The pH was adjusted with NaOH or an acid with the same anion as that used for setting the ionic composition. The pH was manually readjusted to the initial value by adding acid at each sampling time. Variations in the pH during the experiments were within  $\pm 0.10$  pH units of the initial value. A summary of the chemical compositions of the experimental solutions and ferrous and total iron contents in the reacted hematite and biotite is given in table 2 for the chromate reduction experiments. These data are arranged in subsets to indicate the various rate effects investigated.

Reaction rates were measured by periodically removing solution samples and determining the concentrations of dissolved chromium and

TABLE 2

*Summary of experimental conditions and iron contents of the reacted solids. Letters H and B denote hematite and biotite experiments, respectively, b.d. means below detection, and error limits are estimated from the variance about the mean of duplicate analyses*

Exp. No.	hrs	pH	Anion		10 <sup>5</sup> mol·liter <sup>-1</sup>					Weight %	
			mol·l <sup>-1</sup>	(A/V) m <sup>2</sup> ·l <sup>-1</sup>	Cr(VI) initial	Cr(VI) final	Cr(III) final	Fe(II) final	Fe(III) final	Fe(II)	Fe(III)
(A/V)											
H4	504	10.0	0.01SO <sub>4</sub>	0.53	9.02	7.98	b.d.	b.d.	b.d.	2.41±0.05	61.43±1.92
H15	793	10.0	0.01SO <sub>4</sub>	1.05	9.58	7.94	0.14	b.d.	0.73	2.75±0.32	61.10±3.10
H2 <sup>a</sup>	671	10.0	0.01SO <sub>4</sub>	2.11	9.02	6.43	0.11	b.d.	b.d.	2.45±0.05	61.48±1.38
H14	783	10.0	0.01SO <sub>4</sub>	2.11	9.58	6.03	0.80	b.d.	1.31	2.65±0.23	61.18±1.42
H22	575	10.0	0.01SO <sub>4</sub>	3.69	9.79	2.00	0.79	b.d.	0.89	2.60±0.16	55.35±1.70
H3 <sup>a</sup>	671	10.0	0.01SO <sub>4</sub>	5.27	9.02	3.12	b.d.	b.d.	b.d.	2.24±0.17	62.38±0.70
H11	1146	10.0	0.01SO <sub>4</sub>	5.27	9.58	3.07	1.25	b.d.	1.31	2.65±0.18	59.47±0.35
H23	575	10.0	0.01SO <sub>4</sub>	7.37	9.79	0.10	0.29	b.d.	0.89	2.79±0.25	58.10±1.70
pH											
H16	646	12.0	0.01SO <sub>4</sub>	5.27	9.58	9.58	b.d.	b.d.	1.78	2.98±0.22	59.33±0.74
H35	555	11.5	0.01SO <sub>4</sub>	5.27	9.79	9.38	b.d.	b.d.	1.50	3.00±0.08	64.53±1.53
H18	670	11.0	0.01SO <sub>4</sub>	5.27	9.30	7.02	0.10	b.d.	1.20	2.95±0.42	60.71±2.23
H33	578	10.5	0.01SO <sub>4</sub>	5.27	9.79	6.15	0.68	b.d.	1.78	3.10±0.04	58.89±1.37
H11	1146	10.0	0.01SO <sub>4</sub>	5.27	9.58	3.07	1.25	b.d.	1.31	2.65±0.18	61.18±1.42
H19	625	9.5	0.01SO <sub>4</sub>	5.27	9.30	1.32	0.74	b.d.	1.49	2.87±0.16	58.03±1.36
H17	331	8.5	0.01SO <sub>4</sub>	5.27	9.58	0.04	0.45	b.d.	1.49	2.72±0.13	62.92±2.90
H39	557	8.5	0.01SO <sub>4</sub>	5.27	95.05	85.30	b.d.	b.d.	b.d.	2.83±0.05	63.34±0.62
H34	56 <sup>b</sup>	7.5	0.01SO <sub>4</sub>	5.27	9.79	b.d.	b.d.	b.d.	b.d.	2.73±0.18	61.88±1.24
H24	48 <sup>b</sup>	7.0	0.01SO <sub>4</sub>	5.27	9.79	b.d.	b.d.	b.d.	b.d.	2.41±0.20	60.35±4.29
H38	192	7.0	0.01SO <sub>4</sub>	5.27	95.05	80.97	1.45	b.d.	b.d.	2.75±0.10	63.68±2.18
H31	49 <sup>b</sup>	5.9	0.01SO <sub>4</sub>	5.27	9.65	b.d.	b.d.	b.d.	b.d.	2.92±0.18	64.80±1.07
H40	557	5.9	0.01SO <sub>4</sub>	5.27	95.05	80.97	b.d.	b.d.	b.d.	2.78±0.11	58.23±1.22
H36	24 <sup>b</sup>	5.0	0.01SO <sub>4</sub>	5.27	9.65	b.d.	b.d.	1.12	0.03	2.56±0.16	62.27±2.33
H32	2 <sup>b</sup>	4.0	0.01SO <sub>4</sub>	5.27	9.65	b.d.	0.45	83.32	b.d.	2.29±0.10	63.33±1.83
H37	1 <sup>b</sup>	3.5	0.01SO <sub>4</sub>	5.27	9.65	b.d.	2.61	18.34	19.51	2.64±0.58	60.08±4.91
anion											
H42	1105	10.0	0.01PO <sub>4</sub>	5.27	9.58	9.29	0.13	b.d.	b.d.	2.85±0.07	61.47±0.11
H26	576	10.0	0.01ClO <sub>4</sub>	5.27	9.79	8.38	0.54	b.d.	1.13	3.01±0.04	62.51±2.49
H30	622	10.0	0.01Cl	5.27	9.79	6.47	1.27	b.d.	1.64	2.85±0.15	61.31±0.11
H29	643	10.0	0.001SO <sub>4</sub>	5.27	9.79	6.26	1.08	b.d.	1.42	2.75±0.04	60.43±1.85
H11	1146	10.0	0.01SO <sub>4</sub>	5.27	9.58	3.07	1.25	b.d.	1.31	2.65±0.18	59.47±0.35
H25	504	10.0	0.10SO <sub>4</sub>	5.27	9.79	1.28	b.d.	b.d.	0.09	2.78±0.06	62.30±2.09

<sup>a</sup> Unstirred experiments.

<sup>b</sup> Time at which Cr(VI) decreased to below detection limit.

TABLE 2  
(continued)

Exp. No.	hrs	pH	10 <sup>5</sup> mol.liter <sup>-1</sup>								Weight %	
			Anion	(A/V)	Cr(VI)	Cr(VI)	Cr(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	
			mol.l-1	m <sup>2</sup> .l-1	initial	final	final	final	final			
<u>(A/V)</u>												
B15	668	4.0	0.01SO <sub>4</sub>	1.42	9.59	7.71	0.78	b.d.	0.17	10.69±0.12	14.28±0.11	
B12	527	4.0	0.01SO <sub>4</sub>	2.84	9.59	6.24	1.82	b.d.	0.09	10.84±0.13	14.00±0.17	
B2	1130	4.0	0.01SO <sub>4</sub>	5.68	9.79	2.54	2.71	b.d.	0.58	10.81±0.17	14.39±0.23	
<u>pH</u>												
B14	744	11.0	0.01SO <sub>4</sub>	5.68	9.74	9.56	b.d.	b.d.	b.d.	11.58±0.05	14.69±0.38	
B1	769	10.0	0.01SO <sub>4</sub>	7.11	9.30	8.22	b.d.	b.d.	b.d.	11.51±0.23	14.33±1.12	
B13	672	8.5	0.01SO <sub>4</sub>	5.68	9.74	9.29	b.d.	b.d.	b.d.	11.41±0.08	14.39±0.24	
B3	598	6.0	0.01SO <sub>4</sub>	5.68	9.79	8.64	b.d.	b.d.	0.09	11.37±0.45	14.18±0.34	
B5	673	5.0	0.01SO <sub>4</sub>	5.68	9.59	7.70	b.d.	b.d.	b.d.	11.28±0.19	14.83±0.21	
B8	649	4.5	0.01SO <sub>4</sub>	5.68	9.59	6.95	0.50	b.d.	b.d.	10.80±0.40	14.06±0.48	
B2	1130	4.0	0.01SO <sub>4</sub>	5.68	9.79	2.54	2.71	b.d.	0.58	10.81±0.17	14.39±0.23	
B10	481 <sup>b</sup>	3.5	0.01SO <sub>4</sub>	5.68	9.59	b.d.	7.49	0.50	1.09	10.26±0.21	14.16±0.04	
B7	12 <sup>b</sup>	3.0	0.01SO <sub>4</sub>	5.68	9.59	b.d.	8.59	4.93	b.d.	10.15±0.05	14.20±0.35	
<u>anion</u>												
B16	717	4.0	0.01PO <sub>4</sub>	5.68	9.56	6.19	0.82	b.d.	0.17	11.15±0.05	14.48±0.24	
B4	602	4.0	0.01ClO <sub>4</sub>	5.68	9.79	6.15	0.87	b.d.	0.09	11.63±0.06	14.57±0.41	
B11	601	4.0	0.01Cl	5.68	9.74	4.50	0.64	b.d.	b.d.	11.11±0.07	14.62±0.12	
B9	649	4.0	0.001SO <sub>4</sub>	5.68	9.59	4.39	0.60	b.d.	0.09	11.02±0.12	14.42±0.10	
B2	1130	4.0	0.01SO <sub>4</sub>	5.68	9.79	2.54	2.71	b.d.	0.58	10.81±0.17	14.39±0.23	
B6	553 <sup>b</sup>	4.0	0.10SO <sub>4</sub>	5.68	9.59	b.d.	7.70	0.76	b.d.	10.27±0.02	14.14±0.43	

a Unstirred experiments.

b Time at which Cr(VI) decreased to below detection limit.

iron. All solution samples were passed through 0.22- $\mu$ m filters before analyses, and the concentrations of chromate and ferrous ion were determined within 15 min after sample collection to minimize possible changes in concentrations caused by continued reactions.

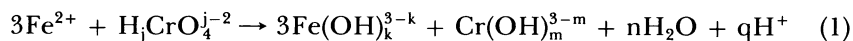
*Analytical.*—The concentrations of ferrous and total iron (ferric by difference) were determined with the ferrozine chromagen (Gibbs, 1979) to a detection level of 50 ppb. The concentrations of chromate and total chromium (chromic by difference) were determined by a colorimetric method that used a diphenylcarbazide chromagen (Skougstad and others, 1979) to a detection level of approx 50 ppb. These

analytical methods work well for determining the concentrations of different oxidation states when significant amounts of each oxidation state are present. However, when one oxidation state dominates, small errors in precision can lead to large apparent errors in the concentration of the species determined by difference. Difficulties in making precise determinations of chromic concentrations were encountered at total chromium concentrations of less than 100 to 200 ppb. The pH and dissolved oxygen-concentrations were measured with a combination glass-reference electrode and a dissolved-oxygen electrode, respectively.

*Adsorption versus reduction.*—Most experimental solutions contained 100 times more sulfate ( $\approx 10^{-2}$  M) than chromate to minimize adsorption of the anionic chromate species ( $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ ). To verify that the loss of chromate from the experimental solutions was caused by a reduction process rather than adsorption to the solids, two lines of evidence were used: (1) an increase in the chromic concentrations in solutions that initially contained only chromate, and (2) unsuccessful attempts to desorb any chromate from the reacted solids at the ends of the reduction experiments. For solutions with pH less than about 5.0 or greater than 10.0, chromic ions were consistently detected in the experimental solutions, providing clear evidence of reduction. The desorption tests were used for experiments at intermediate pH levels (5.0–10.0) because  $(\text{Cr, Fe})(\text{OH})_{3(s)}$  precipitation resulted in chromic concentrations below the detection limit of the colorimetric method used to determine the amounts of chromic and chromate ions in solution. For these tests, either the pH was raised to 12.0 or enough of a 1.0 M  $\text{NaH}_2\text{PO}_4$  solution was added to give a concentration of  $10^{-2}$  M  $\text{NaH}_2\text{PO}_4$ . At pH's greater than 11.5 to 12.0, Zachara and others (1987) have shown that chromate is not adsorbed onto iron oxides, and we assumed that chromate also is not adsorbed to biotite at high pH. Phosphate anions have been shown to displace chromate from soil minerals (Amacher and Baker, 1982). However, altering the solutions by increasing the pH or adding phosphate did not produce increases in chromate concentrations even after as long as one week. Some initial adsorption of chromate undoubtedly occurred, but the lack of desorption at the conclusions of experiments under conditions of pH greater than 12 or after the addition of phosphate was taken as evidence that the process removing chromate from the intermediate pH solutions was reduction and subsequent precipitation.

#### RESULTS

*Chromate reduction by ferrous ions.*—Chromate reduction by ferrous ions is described by the reaction

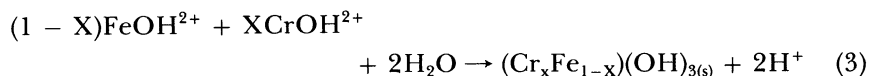


where  $\text{Fe}^{2+}$  is the primary reducing species, and the possible hydrolyzed species are defined by  $j = 0$  to 1,  $k = 0$  to 4,  $m = 0$  to 4,  $n = 4 - (3k + m)$ ,

and  $q = j - (3k + m + 2n)$ . Additionally, ferrous ions are oxidized by dissolved oxygen according to



where  $i = 0$  to  $3$ ,  $j = 0$  to  $4$ ,  $k = (1/2 + i) - j$ , and  $m = i - (j + 2k)$ . The oxidized products of reactions (1) and (2) may precipitate as separate hydroxide solids or as a chromic-ferric hydroxide solid solution (Sass and Rai, 1987), depending on the pH and the activities of the hydrolyzed species of dissolved iron and chromium, that is,



Chromate reduction by  $\text{Fe}^{2+}$  in the aqueous phase [reaction (1)] is expected to be very rapid for most conditions, but ferrous ion oxygensation [reaction (2)] also is rapid in neutral to alkaline solutions. The half-life for the ferrous ion is only a few seconds at pH greater than about 7.5 (Stumm and Morgan, 1981). Consequently, it was important to determine the conditions under which ferrous ions react dominantly with chromate rather than with dissolved oxygen. To determine these conditions, a series of reduction experiments were conducted in which an aliquot of a ferrous ion stock solution was added to a well-stirred and air-saturated chromate solution. The resulting reactions were found to be complete within the first one to two minutes, too rapid to make accurate rate measurements by the batch methods used here. However, the ratios of the moles of ferrous ion oxidized to moles of chromate reduced could be used to determine the reaction stoichiometry and, thus, the relative rates of reactions (1) and (2). Figure 1 shows these molar ratios for aerated sulfate, chloride, perchlorate, and phosphate solutions with pH between 2 and 12. If chromate reduction by the ferrous ions is significantly faster than ferrous ion oxygensation, then a ratio of 3.0 moles of  $\text{Fe}^{2+}$  oxidized to 1.0 mole of chromate reduced is predicted from reaction (1). A molar ratio of approx 3.0 was measured in the experiments for the pH range of 2.0 to 10.0 in sulfate, chloride, and perchlorate solutions (fig. 1), indicating that the ferrous ions had reacted with the chromate ions according to reaction (1) under these conditions. However, molar ratios were greater than 3.0 for pH greater than about 9.0 to 10.0 in the sulfate, chloride, and perchlorate solutions (fig. 1). Also, in the phosphate solutions, molar ratios were slightly greater than 3.0 for solutions with pH between 3.0 and 6.0 and much greater than 3.0 for solutions with pH greater than 6.0 (fig. 1). Chromate and dissolved oxygen were the only oxidants for the ferrous ions in the experimental solutions. Therefore, the increases in the molar ratios to values above 3.0 (fig. 1) show that ferrous ions are oxidized by dissolved oxygen at a rate competitive with oxidation by chromate under conditions of pH greater than 10.0 and at lower pH in phosphate solutions (Eary and Rai, 1988).



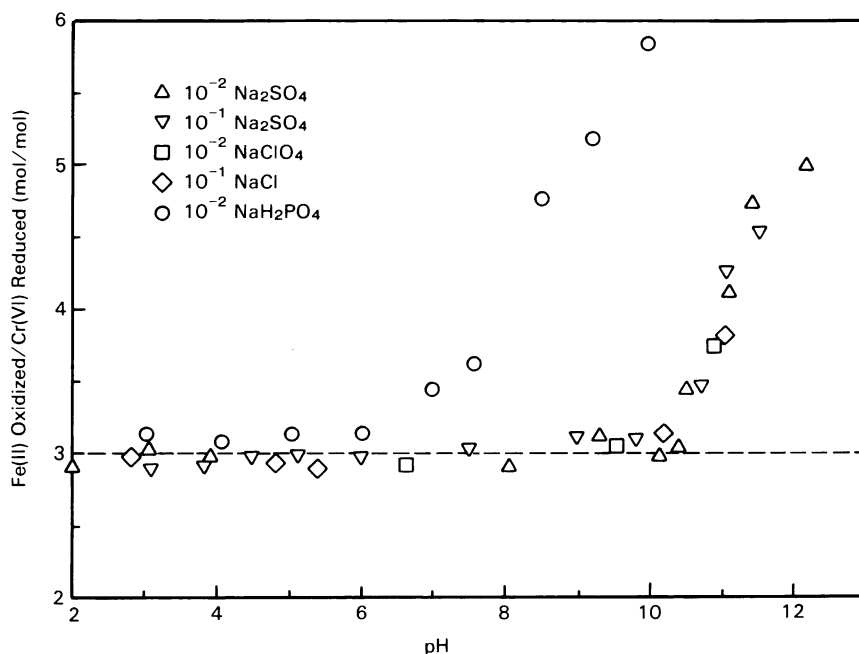
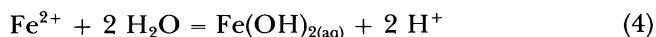


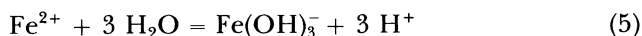
Fig. 1. Molar ratios of ferrous iron [Fe(II)] oxidized to chromate [Cr(VI)] reduced for aerated solutions of different ionic composition (molar). The initial concentrations of Fe(II) and Cr(VI) were  $19.2 \times 10^{-5}$  M and  $9.6 \times 10^{-5}$  M, respectively. The dashed line indicates an ideal ratio of 3.0.

The effects on the relative rates of reactions (1) and (2) caused by high pH and phosphate are consistent with the kinetics of ferrous ion oxidation by dissolved oxygen. The dependence of this reaction on the hydrogen ion activity changes transitionally from 0 to possibly inverse first order to inverse second order as the pH is increased from 2.0 to 7.0 in dilute solutions (Tamura, Goto, and Nagayama, 1976). This pH effect is caused by the more rapid oxidation of the hydrolyzed ferrous species, whose concentrations are increased with increase in pH, compared to the rate of oxidation of the free  $\text{Fe}^{2+}$  ions, which are dominant in more acidic solutions. Specifically, the second-order dependence on hydroxyl ion for ferrous ion oxidation in near-neutral solutions implies that the doubly hydrolyzed species, whose formation is described by



( $\log K = -20.5$  at  $25^\circ\text{C}$ , Baes and Mesmer, 1976), is oxidized more rapidly than  $\text{Fe}^{2+}$  or  $\text{FeOH}^+$  (Millero, 1985). For solutions with pH greater than about 8.0, less rate information is available because the oxidation rate is extremely rapid and is catalyzed by ferric hydroxide

precipitates (Sung and Morgan, 1980). However, the third hydrolysis species,



( $\log K = -29.4$  to  $-31.9$  at  $25^\circ\text{C}$ , Baes and Mesmer, 1976) may be oxidized even more rapidly by dissolved oxygen than the second hydrolysis species. The increase in the rate of ferrous ion oxygenation at pH greater than 10.0 relative to oxidation by chromate, for sulfate, chloride, and perchlorate solutions (fig. 1), coincides with the pH above which  $\text{Fe}(\text{OH})_3^-$  becomes the dominant ferrous species.

The rate of ferrous ion oxidation by dissolved oxygen also is known to be more rapid in phosphate and fluoride solutions compared to most other common anions (Tamura, Goto, and Nagayama, 1976). These authors reasoned that phosphate and fluoride ions must take part in the oxygenation reaction, perhaps as ferrous complexes, which are more reactive to oxidation by dissolved oxygen than the free and hydrolyzed ferrous species. The important conclusion here is that ferrous ions reduce chromate less efficiently in solutions containing high phosphate concentrations and/or pH higher than 10.0 (fig. 1).

*Chromate reduction by hematite and biotite.*—Chromate concentrations were stable indefinitely in blank solutions but were totally or partially reduced to chromic in aerated solutions that contained suspensions of hematite or biotite. The processes causing chromate reduction are complicated in slightly acidic to alkaline solutions, because the reaction products are precipitated as hydroxide solids but are well illustrated in acidic solutions. For example, approx  $10^{-4}$  moles of chromate were reduced to chromic in less than 1 hr in a hematite suspension with a pH of 3.5 (fig. 2A) and within 12 hrs in a biotite suspension with a pH of 3.0 (fig. 3A). In response, the chromic concentrations increased initially before decreasing to steady-state concentrations (figs. 2A and 3A) because of the formation of  $(\text{Cr}, \text{Fe})(\text{OH})_{3(s)}$  (discussed below). In every instance, as long as chromate remained in solution all dissolved iron existed as ferric. After the chromate was reduced completely to chromic, the ferric concentration decreased while ferrous increased (figs. 2B and 3B). The correspondence between the disappearance of chromate and the appearance of ferrous ions (figs. 2 and 3) indicates that it is the ferrous ions, which were derived from the hematite and biotite, that reduced chromate to chromic.

The continued reduction of ferric to ferrous that appears to have occurred after the complete reduction of the chromate (figs. 2B and 3B) was unexpected, because the dissolved-oxygen concentrations in the experimental solutions were maintained at saturation by continuous aeration [ $0.2 \text{ atm O}_{2(g)}$ ]. Also, the molar quantities of dissolved iron measured in the experiments shown in figures 2 and 3 do not represent amounts that could have been sufficient to cause the complete reduction of the chromate according to reaction (1). For the hematite experiment shown in figure 2, this insufficiency may be explained by the precipita-

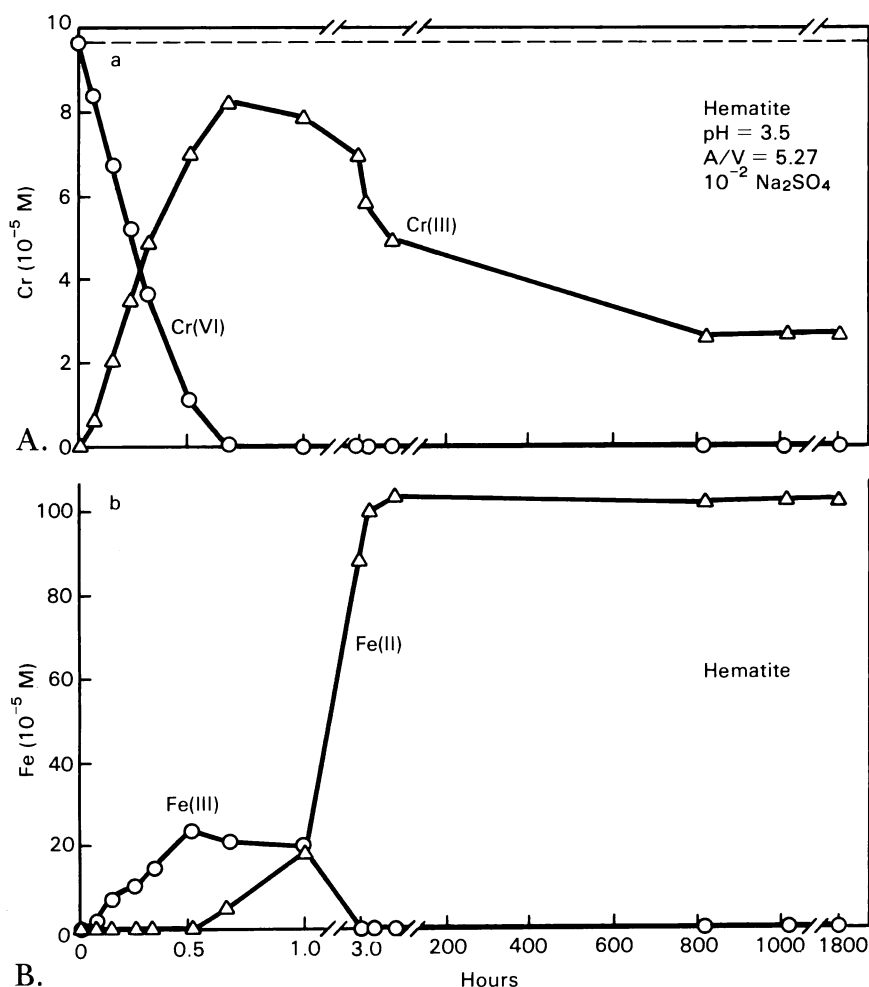


Fig. 2. Changes in (A) chromium and (B) iron concentrations with time for a hematite experiment with a surface area to solution volume ratio,  $(A/V) = 5.27 \text{ m}^2 \cdot \text{liter}^{-1}$ , at a pH of 3.5 in  $10^{-2}$  M  $\text{Na}_2\text{SO}_4$ . The dashed line in (A) indicates the initial chromate concentration.

tion of the produced ferric species, because the solubility of  $\text{Fe(OH)}_{3(s)}$  for a  $10^{-2}$  M sulfate solution with a pH of 3.5 (about  $10^{-5}$  M  $\text{Fe(III)}_t$ , Baes and Mesmer, 1976) was rapidly exceeded. Thus, the apparent conversion of ferric to ferrous was not caused by a redox reaction but resulted from the loss of ferric ions from solution by  $\text{Fe(OH)}_{3(s)}$  precipitation while the more soluble ferrous component of the hematite

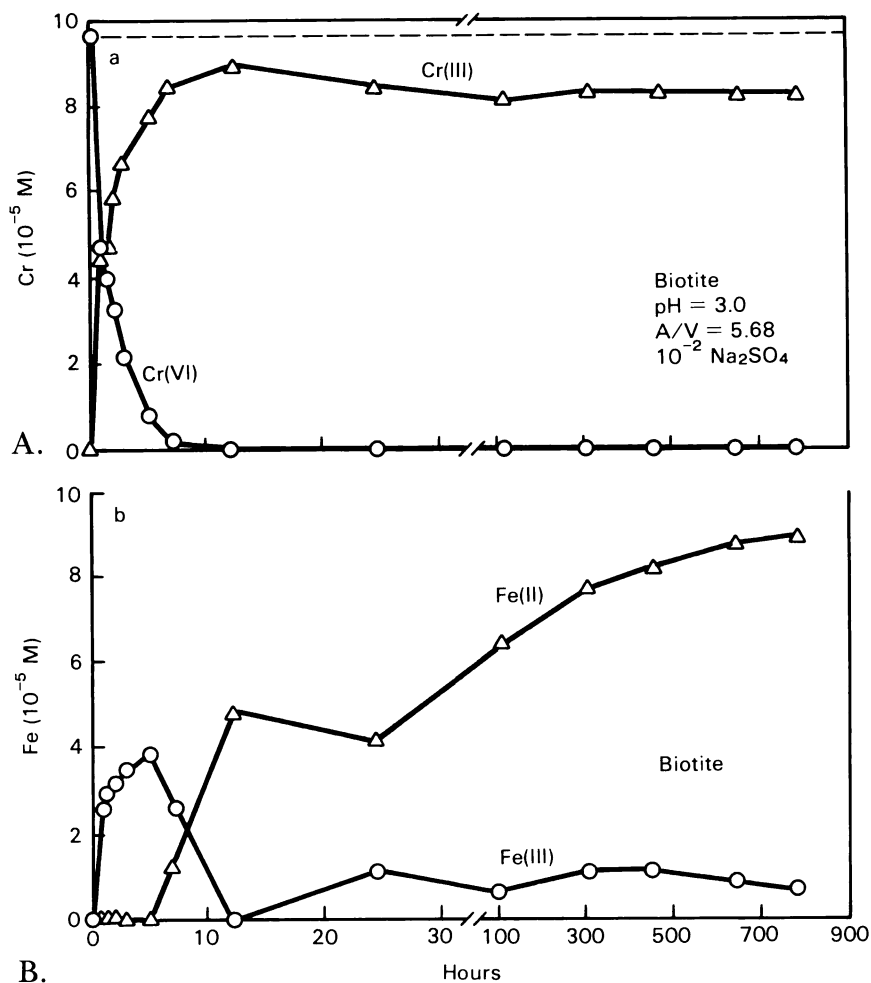


Fig. 3. Changes in (A) chromium and (B) iron concentrations with time for a biotite experiment with  $(A/V) = 5.68 \text{ m}^2 \cdot \text{liter}^{-1}$  at a pH of 3.0 in  $10^{-2} \text{ M Na}_2\text{SO}_4$ . The dashed line in (A) indicates the initial chromate concentration.

continued to dissolve. The summation of the dissolution and precipitation reactions only gives the appearance of a redox transformation. This process is illustrated by the results from an experiment in which ferric ions were added to a chromium-free suspension of hematite with a pH of 3.0. This initial ferric concentration was decreased slightly at early times, presumably because of adsorption, but then it slowly increased as the hematite was dissolved in the acidic solution (fig. 4A). In contrast,

the ferrous concentration increased rapidly as the more soluble ferrous component of the hematite dissolved, but there was no obvious conversion of the added ferric ions to ferrous (fig. 4A).

In contrast to the hematite experiments in figure 2, the solubility of  $\text{Fe}(\text{OH})_{3(s)}$  at pH 3.0 in  $10^{-2}$  M sulfate (about  $10^{-3.5}$  M  $\text{Fe}(\text{III})$ ), Baes and Mesmer, 1976) was not approached in the biotite experiment shown in figure 3, eliminating precipitation as the cause of the apparent nonstoichiometric reduction of the chromate and the continued transformation of ferric to ferrous. Instead, the experimental data suggest that the ferrous ions that were released to solution initially by dissolution of the biotite were oxidized quickly to ferric by the chromate and then reduced back to ferrous by the biotite. The dissolved iron is thus "recycled" as  $\text{Fe}^{2+}$  to react again with the chromate, so that an amount of dissolved iron that was less than that predicted by the stoichiometry of reaction (1) caused the complete reduction of the chromate. After the chromate was reduced completely to chromic, the continuing reduction cycle resulted in the conversion of most of the remaining ferric ions to ferrous. This spontaneous reduction of ferric ions by the biotite in oxygenated solutions was confirmed in the absence of dissolved chromium by adding ferric ions to a biotite suspension with a pH of 3.0 (fig. 4B). The initial ferric concentration in this solution decreased to less than the detection limit within 60 min, while the ferrous concentration showed a symmetric increase (fig. 4B). After the initial ferric concentration was reduced completely, the total iron concentration, now present totally as ferrous, increased to concentrations that were greater than the initial amount because of dissolution of the biotite (fig. 4B).

The hematite experiments in figure 2 show that the ferrous ions causing chromate reduction are derived by dissolution of the ferrous iron component of the hematite. However, two processes produce ferrous ions in the presence of the biotite, including (1) dissolution of the biotite structure, and (2) subsequent reduction of aqueous ferric ions by the biotite.

*Effects of stirring rate and surface area.*—The effect of stirring rate on chromate reduction by the hematite is shown in figure 5. The initial rates of chromate reduction were more rapid in the stirred experiments, but eventually the total amounts of chromate reduced were nearly the same for equivalent ratios of hematite surface area to solution volume ( $A/V$  in  $\text{m}^2 \cdot \text{liter}^{-1}$ ; fig. 5). This result shows that the reactive surface area of the ferrous component of the hematite was not increased by the abrading effects of stirring. Unstirred experiments with the biotite were not conducted.

The chromate concentrations versus time curves shown in figure 5 are typical of all experimental results with both the biotite and hematite. Chromate reduction is fast initially, but after approx 300 to 450 hrs, depending on the solution pH and surface areas, chromate concentrations stop decreasing and steady-state concentrations are established.

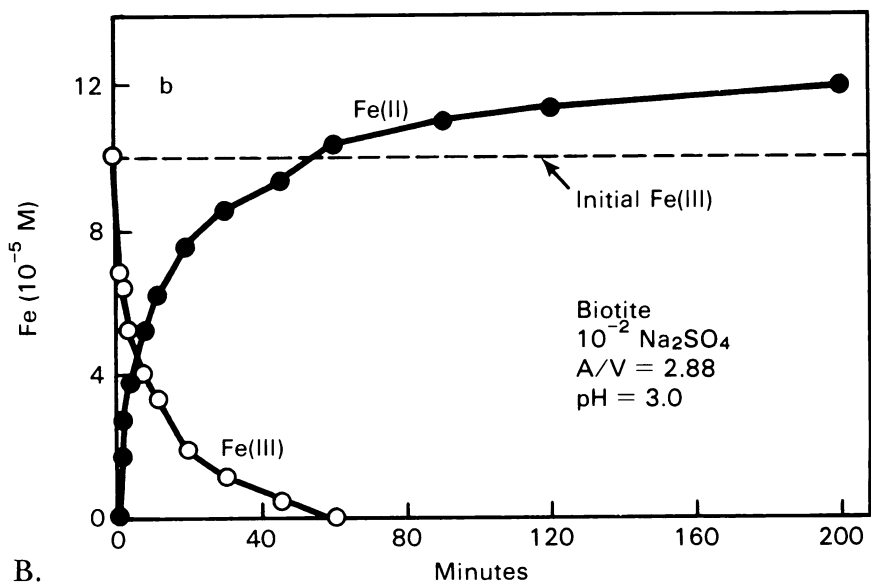
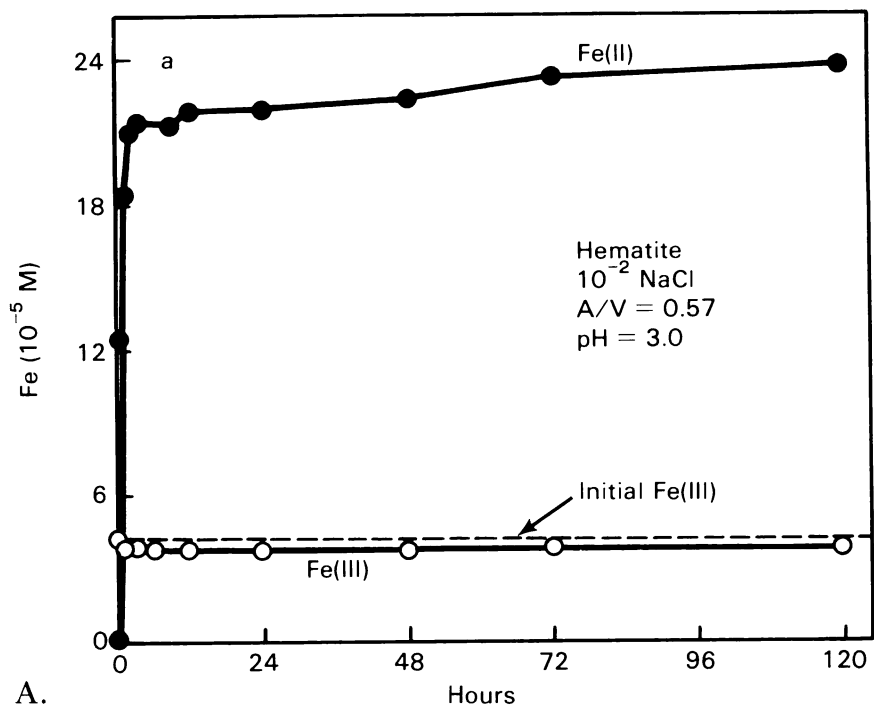


Fig. 4. Reduction of aqueous ferric iron at pH 3.0 by (A) hematite with  $(A/V) = 0.57 \text{ m}^2 \cdot \text{liter}^{-1}$  and (B) biotite with  $(A/V) = 2.84 \text{ m}^2 \cdot \text{liter}^{-1}$  in  $10^{-2}$  M NaCl and  $10^{-2}$  M  $Na_2SO_4$ , respectively.

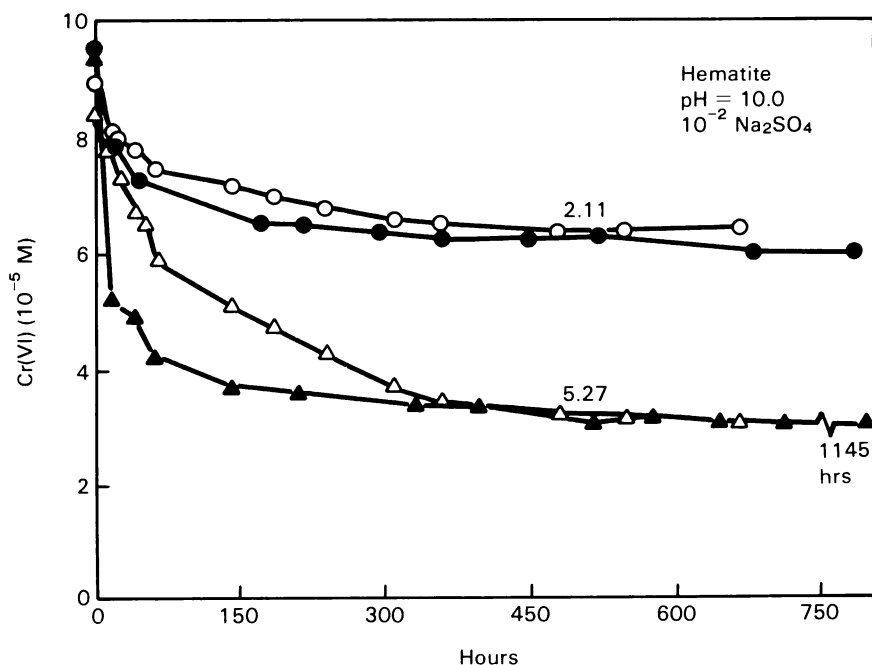


Fig. 5. Rates of chromate reduction by two ratios of hematite surface area to solution volume at a pH of 10.0 in  $10^{-2}$  M  $\text{Na}_2\text{SO}_4$  for stirred (solid symbols) and unstirred (open symbols) experiments.

The total amounts of chromate reduced by a given amount of hematite or biotite were determined by subtracting the steady-state concentrations of chromate from the initial concentrations and multiplying by the solution volumes to convert to moles. These molar amounts are shown in the log-log plot of figure 6 as a function of the ratio of surface area to solution volume ( $A/V$ ), in  $\text{m}^2 \cdot \text{liter}^{-1}$ , for the hematite and biotite. Linear regression of the data in figure 6 yielded slopes of  $0.88(\pm 0.18)$  for the hematite and  $0.95(\pm 0.17)$  for the biotite, indicating that the amounts of chromate reduced are approximately proportional to the ratio of mineral surface area to solution volume.

*Effects of pH.*—Typical changes in chromate concentration with time for are shown in figure 7 for a range of pH. The rate of chromate reduction and the amount reduced is strongly dependent on pH, being decreased as the pH is increased for both hematite and biotite (fig. 7). The effect of pH on the chromate reduction rate is best illustrated by the plot of the logarithm of the initial reduction rates versus pH shown in figure 8. These initial rates were calculated by fitting the chromate concentration versus time data for various solution pH values by a

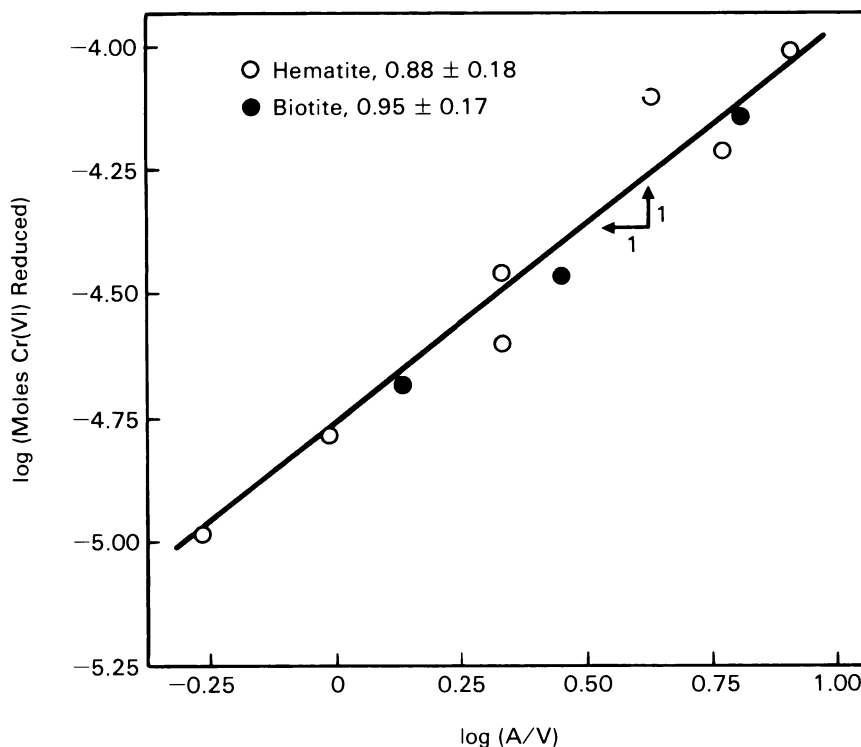


Fig. 6. Total amounts of chromate reduced by hematite at a pH of 10.0 and biotite at a pH of 4.0 in  $10^{-2}$  M  $\text{Na}_2\text{SO}_4$  as a function of  $(A/V)$ . The line indicates a slope of 1.0. The error limits for the calculated slopes indicate 95 percent confidence from the regression analysis.

method of nonlinear least-squares regression (Bevington, 1969) to an equation with the form

$$C_{(t)} = C_s + (C_0 - C_s) \exp^{-At} \quad (6)$$

In this equation,  $C_{(t)}$  is the chromate concentration at some time  $t$  (sec) after the initiation of the experiment,  $C_0$  is the initial chromate concentration,  $C_s$  is the steady-state concentration of chromate, and  $A$  is a constant that is determined from the regression analysis. This equation is not intended to imply any specific reaction mechanism but is chosen only to represent the rate data, because it describes curves that are similar to the chromate concentration versus time data observed in the experiments (fig. 7) and satisfies the boundary conditions that were evident in the experiments, that is,

$$C = C_0 \quad \text{at} \quad t = 0 \quad (7)$$



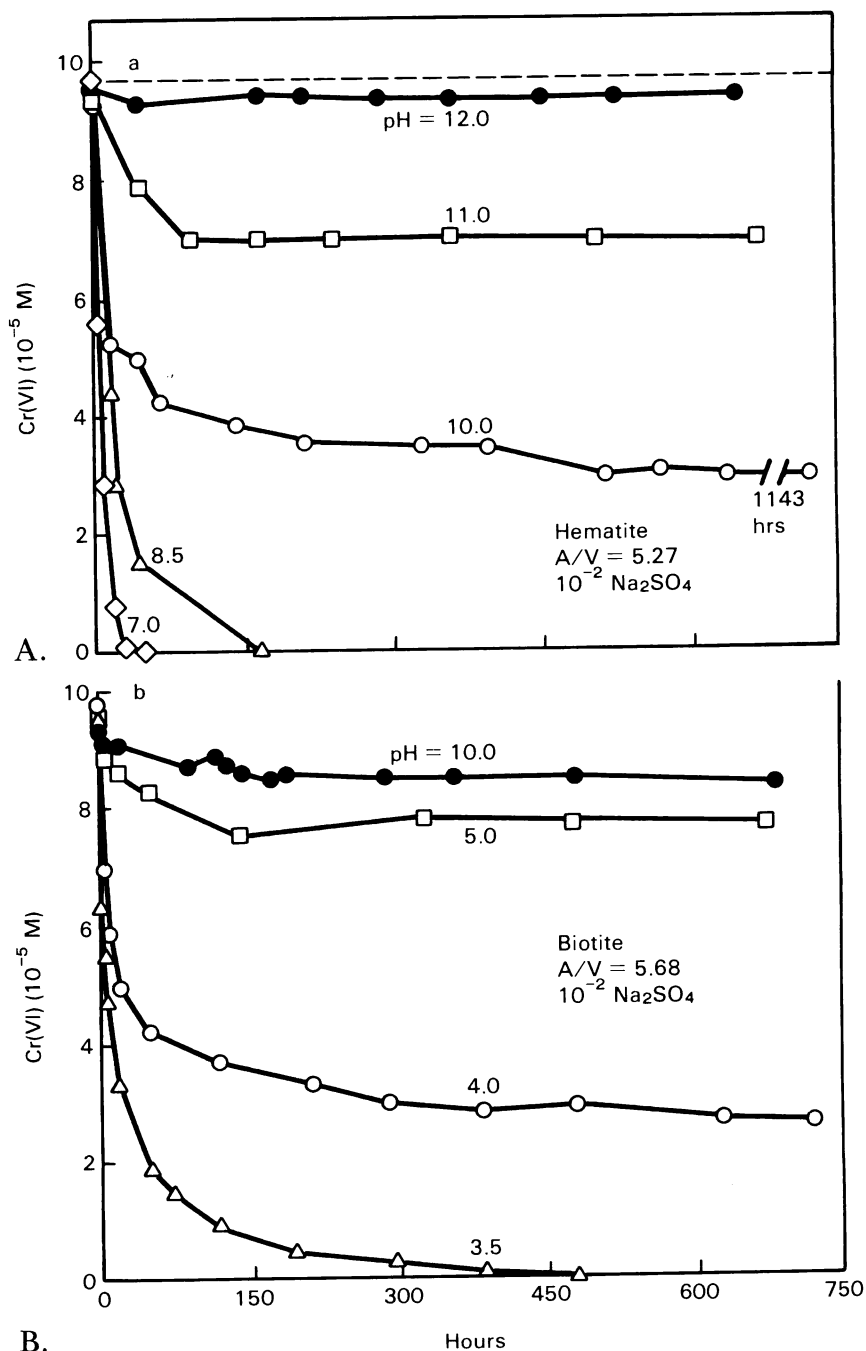


Fig. 7. Rates of chromate reduction by (A) hematite for five pH values and (B) biotite for four pH values in  $10^{-2} \text{ M Na}_2\text{SO}_4$ . The dashed line indicates the initial chromate concentration.

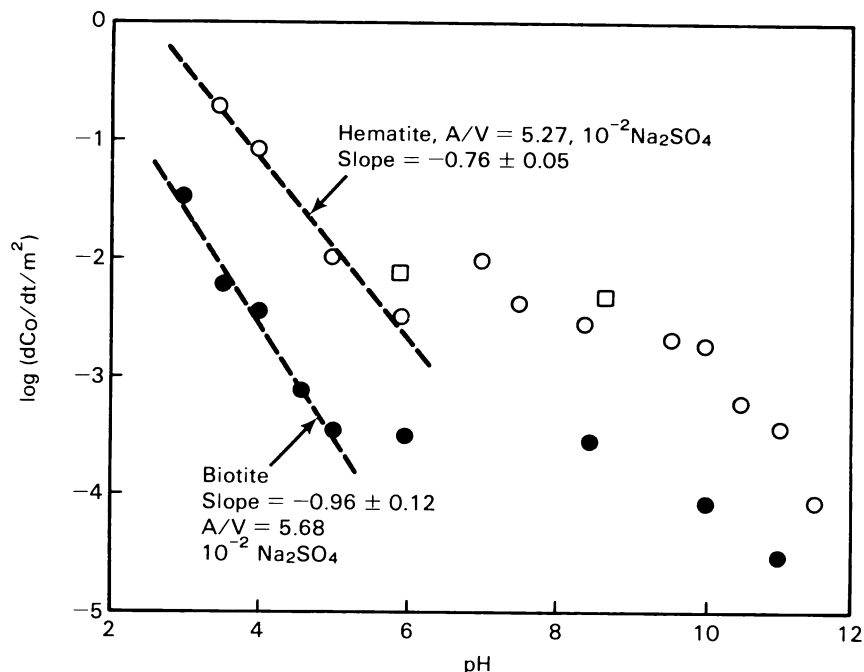


Fig. 8. Initial rates of chromate reduction in  $10^{-2}$  M  $\text{Na}_2\text{SO}_4$  which originally contained  $9.6 \times 10^{-5}$  M (circles) and  $95.05 \times 10^{-5}$  M (squares)  $\text{Cr(VI)}$  for  $(A/V) = 5.27$  and  $5.68 \text{ m}^2 \cdot \text{liter}^{-1}$  for hematite and biotite experiments, respectively. The error limits for the slopes indicate 95 percent confidence from the regression analysis.

and

$$C = C_s \quad \text{at} \quad t \rightarrow \infty \quad (8)$$

Both  $C_s$  and  $A$  were determined from the regression analysis, and the best-fit values of  $C_s$  were similar to those observed in the experiments. For the experiments in which chromate was totally reduced, the steady-state concentrations were set equal to zero. From (6), the initial rates of chromate reduction were determined from the derivative with respect to time at  $t = 0$  as follows

$$dC_0/dt = -A(C_0 - C_s) \quad (9)$$

The logarithms of these initial rates ( $\text{mol Cr(VI)} \cdot \text{liter}^{-1} \cdot \text{sec}^{-1}$ ) divided by the mineral surface area to solution volume ratio ( $\text{m}^2 \cdot \text{liter}^{-1}$ ) are shown in figure 8. In alkaline solutions, the dependence on pH is indistinct for both the hematite and biotite. Rates appear to depend on pH as the pH is lowered from 11.5 to about 9.0 to 10.0 but become nearly independent of pH for the mid-pH range of 6.0 to 9.0 (fig. 8). The slow rates of chromate reduction observed at pH greater

than 9.0 may be caused by: (1) slowed rates of dissolution of the ferrous iron components of the minerals, resulting from the decreased solubility of ferrous hydroxide which reaches a minimum between pH 8.5 and 10.5 (Baes and Mesmer, 1976), and (2) the increased rate of ferrous ion oxidation by dissolved oxygen which results in a proportionate decrease in chromate reduction (see fig. 1). For the mid-pH range of 6.0 to 9.0, rates of chromate reduction are limited by very slow rates of biotite and hematite dissolution and are nearly halted once the easily dissolved ferrous iron component has been consumed (fig. 7).

At pH less than 6.0 for the hematite and 5.0 for the biotite, the initial rates of chromate reduction are increased and clearly dependent on the hydrogen ion activity (fig. 8). The hydrogen ion dependence,  $n$ , for the rate of chromate reduction can be expressed by

$$\text{reduction rate} = k(\text{H}^+)^n \quad (10)$$

where  $k$  is a rate constant. This equation in logarithmic form becomes

$$\log (\text{reduction rate}) = \log k + n \log (\text{H}^+) \quad (11)$$

From this expression, the dependence on  $(\text{H}^+)$  for chromate reduction is determined from the slopes of plots of  $\log (\text{reduction rate})$  versus pH. These slopes are shown by the dashed lines in figure 8. Linear regression of the five initial rates determined between pH 3.0 and 5.0 gives  $n = 0.96(\pm 0.12)$  for the biotite and for the four rates between pH 3.5 and 5.0 gives  $n = 0.76(\pm 0.05)$  for the hematite.

The dependencies on pH for chromate reduction determined in figure 8 also are relevant to the initial rates of dissolution of the ferrous iron components of the biotite and hematite, because any ferrous ions produced by dissolution will quickly and quantitatively reduce chromate in solutions with pH less than about 9.0 to 10.0 (fig. 1). It is possible that the reduction of ferric ions by the biotite (figs. 3 and 4B) is also dependent on pH. However, this reaction requires an initial period of biotite dissolution to produce dissolved iron before it can proceed. A pH-dependence for biotite dissolution was not found in the literature, but the nearly linear dependence on pH obtained from figure 8 is within the range reported for the dissolution of other silicate minerals (Lasaga, 1984). For hematite, Majima, Awakura, and Mishima (1985) have reported that the dissolution rate is directly proportional to  $(\text{H}^+)$  in HCl and  $\text{HClO}_4$  solutions with pH from 2.4 to 4.0 and proportional to the square root of  $(\text{H}^+)$  in  $\text{H}_2\text{SO}_4$  solutions. We expect that our hematite experiments are most comparable to their  $\text{H}_2\text{SO}_4$  dissolution experiments, but our results imply a greater dependence on  $(\text{H}^+)$  ( $n = 0.76 \pm 0.05$ ). Majima, Awakura, and Mishima (1985) do not report whether any ferrous iron was present in their hematite sample. Given the potential differences between the morphologies and ferrous iron contents of the hematite samples used in our study and compared to those of the hematite used by Majima, Awakura, and Mishima (1985),

the difference in the rate dependence on ( $H^+$ ) does not seem unreasonably large.

*Effects of anions.*—The effects of various inorganic anions on the rate of chromate reduction are shown in figure 9A and B for the hematite at pH 10.0 and for the biotite at pH 4.0, respectively. Changes in anion concentration and type caused significant changes in the initial rates and the total amounts of chromate reduced in the order:  $10^{-1} \text{ M SO}_4^{2-} > 10^{-2} \text{ M SO}_4^{2-} > 10^{-3} \text{ SO}_4^{2-} \text{ M} > 10^{-2} \text{ M Cl}^- \geq 10^{-2} \text{ M ClO}_4^- > 10^{-2} \text{ M PO}_4^{3-}$ . The effects of the various anions on the rate are most noticeable during the first 150 hrs of reaction for both the hematite and biotite (fig. 9). After this initial period, the rates of chromate reduction are much slower in all the solutions and do not differ significantly. Because the anion effect is strongest during an initial period, we expected that it was related to the dissolution rates of ferrous components of the hematite and biotite. To test this hypothesis, a number of dissolution experiments were conducted with the hematite and biotite as a function of anion type and concentration, except that phosphate solutions were not used. In phosphate solutions, chromate reduction is affected by the accelerated rate of ferrous ion oxidation by dissolved oxygen, which results in nonstoichiometric chromate reduction (see fig. 1).

The results for the dissolution rate experiments show that the rates of ferrous ion release from both hematite and biotite are strongly affected by the anion type and composition (fig. 10). Speciation calculations with the MINTEQ model (Felmy, Girvin, and Jenne, 1984) for the experiments in figures 9 and 10 show that dissolution rates are increased in the solutions with greater affinity to complex ferrous ions (table 3). Consequently, dissolution rates are most rapid in the sulfate solutions and increase with increased sulfate concentration (table 3). For the experiments shown in figure 9, faster dissolution rates in the sulfate solutions cause more rapid rates of chromate reduction.

The possibility exists that the anion composition also might affect the rate of ferric ion reduction observed in the biotite experiments (figs. 3 and 4B). Thus, an initial concentration of  $10^{-4.34} \text{ M FeCl}_3$  was used in each of the dissolution rate experiments described in figure 10B to measure the rates of ferric ion reduction in the different anionic solutions. However, reduction was so rapid that ferric concentrations decreased to below reliable detection limits in less than 1 hr; hence, they are not well-represented on the time scale for figure 10B. In another set of shorter-term experiments with biotite, the effects of the different anions on the rates of ferric reduction were examined in more detail for a similar set of conditions (fig. 11). The rate of ferric reduction increased as a function of anion type and concentration in the same order as the dissolution rates were increased (see fig. 10). However, the total iron concentrations did not become greater than the initial concentration until all the aqueous ferric species were reduced to ferrous, except in the  $10^{-1} \text{ M SO}_4^{2-}$  solution (fig. 11A). This result indicates that

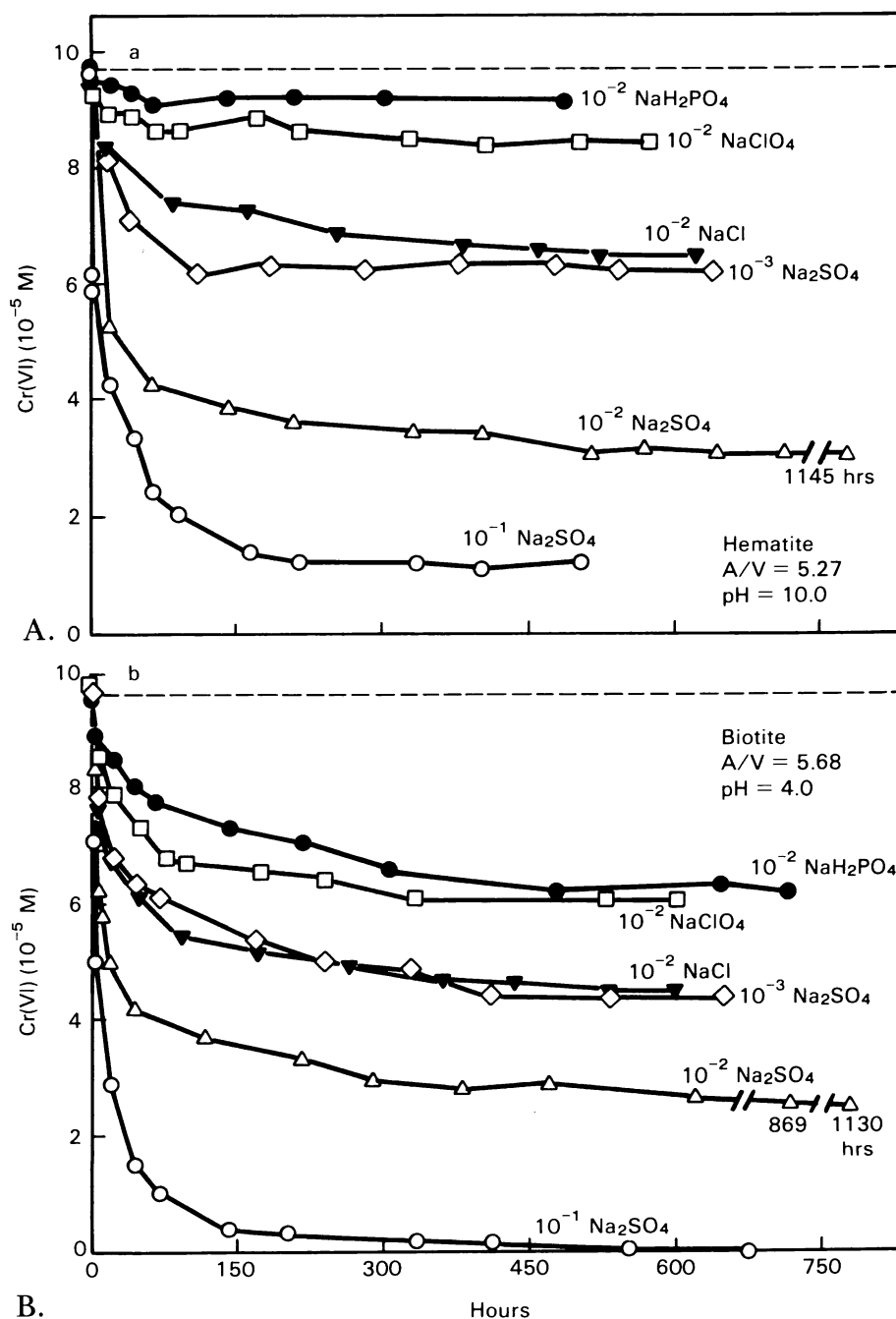


Fig. 9. Rates of chromate reduction for different ionic compositions (molar) for (A) hematite at a pH of 10.0 and  $(A/V) = 5.27 \text{ m}^2 \cdot \text{liter}^{-1}$  and for (B) biotite at a pH of 4.0 and  $(A/V) = 5.68 \text{ m}^2 \cdot \text{liter}^{-1}$ . Dashed lines indicate the initial chromate concentrations.

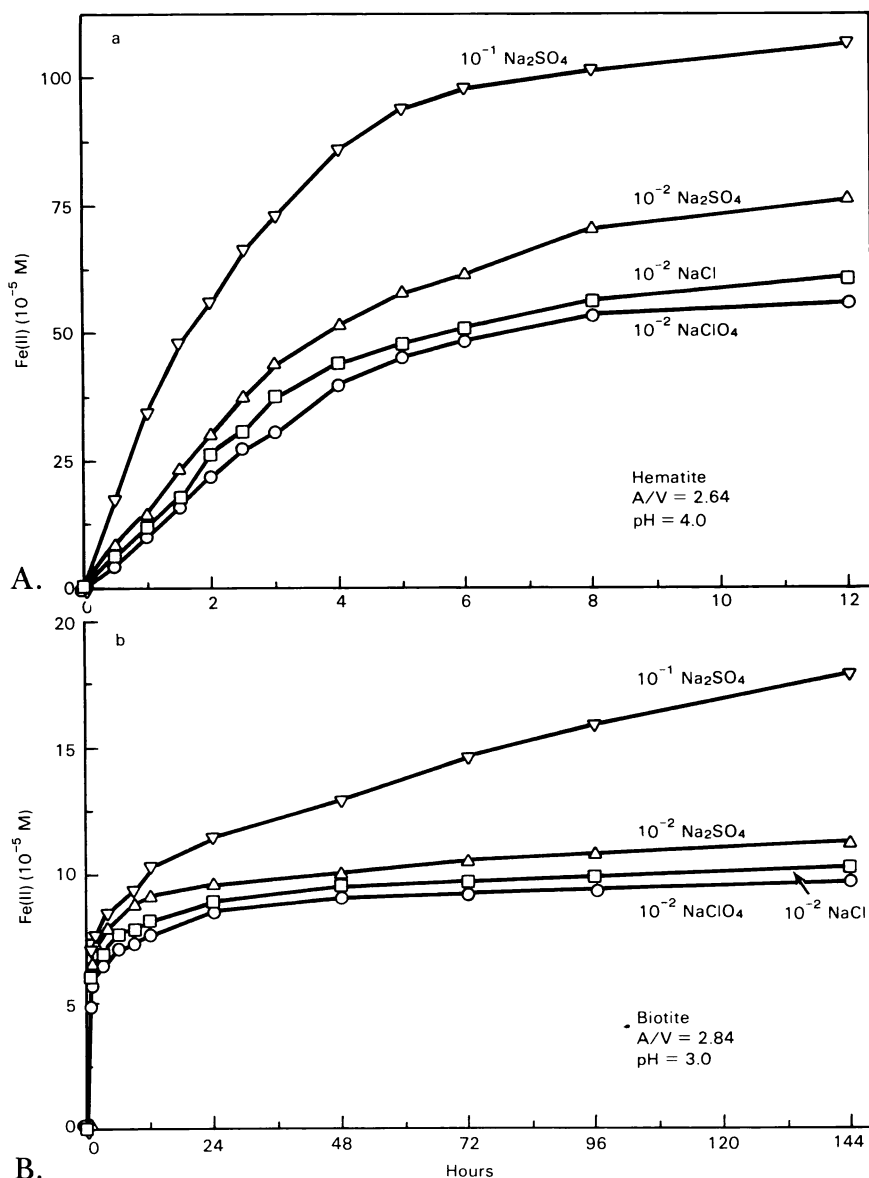


Fig. 10. Dissolution rates for (A) hematite at  $pH = 4.0$  with  $(A/V) = 2.64 \text{ m}^2 \cdot \text{liter}^{-1}$  and for (B) biotite at  $pH = 3.0$  with  $(A/V) = 2.84 \text{ m}^2 \cdot \text{liter}^{-1}$  for different ionic compositions (molar). The biotite experiments initially contained  $4.6 \times 10^{-5} \text{ M Fe(III)}$ .

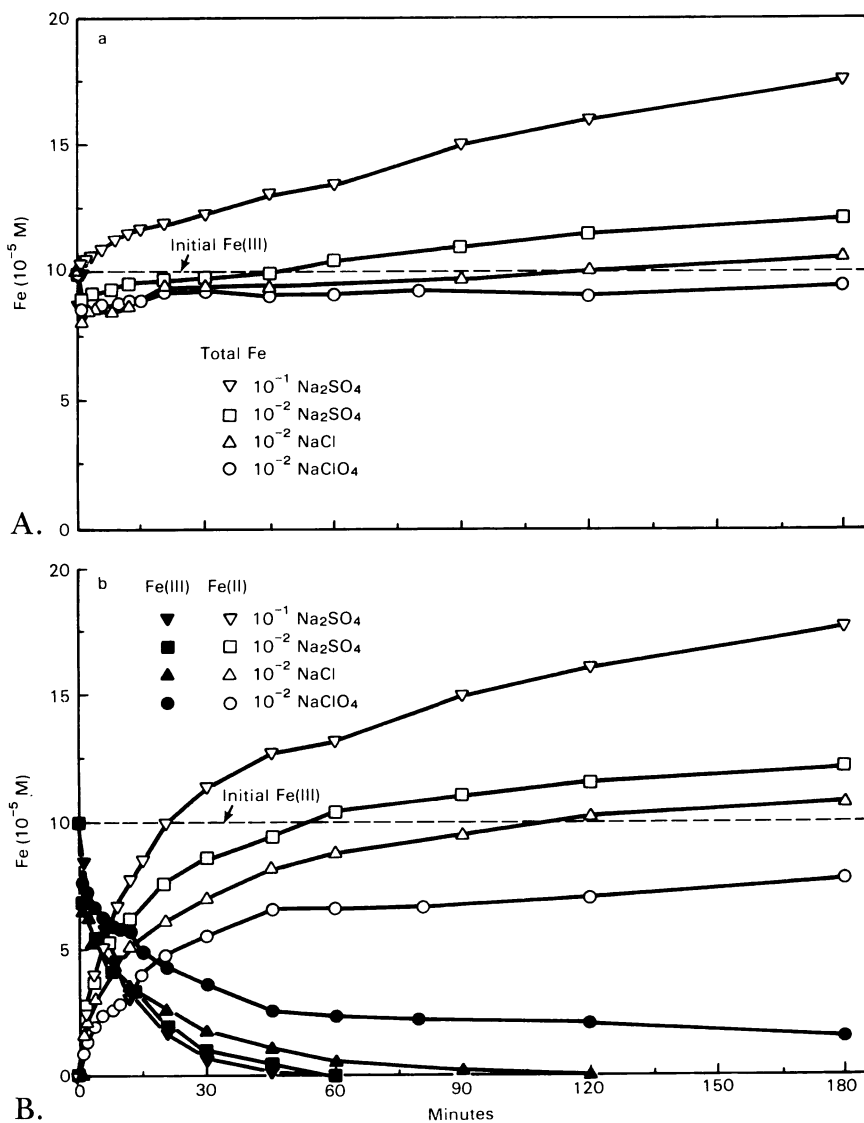


Fig. 11. Rates of (A) biotite dissolution from increases in total iron concentrations with time and simultaneous (B) rates of aqueous ferric iron reduction by the biotite as a function of ionic composition (molar) at  $\text{pH} = 3.0$  with  $(A/V) = 2.84 \text{ m}^2 \cdot \text{liter}^{-1}$ . The dashed line indicates the initial ferric concentration.

significant dissolution of the biotite matrix generally does not take place until the ferric ions are reduced. A similar result was observed in the chromate reduction experiments as well (fig. 3B). White and Yee (1985) report a similar sequence of, first, complete reduction of aqueous ferric ions and, then, mineral dissolution during the artificial weathering of biotite and augite. However, in the  $10^{-1}$  M  $\text{SO}_4^{2-}$  solution used here, biotite dissolution took place while the ferric ions were still being reduced, indicating that very high sulfate concentrations can catalyze the rate of ferrous ion release from the biotite (fig. 11A) as was found for the hematite (fig. 10A).

*Chromic and ferric hydroxide precipitation.*—Brown precipitates formed rapidly in the aqueous reduction experiments conducted to determine the stoichiometry of the reaction between ferrous and chromate ions as a function of pH (see fig. 1). Powder X-ray diffraction patterns indicated that these precipitates were amorphous. Elemental analyses of the precipitates yielded an average  $\text{Fe}(\text{OH})_{3(s)}$  to  $\text{Cr}(\text{OH})_{3(s)}$  molar ratio of  $2.90(\pm 0.35)$  as reported previously by Eary and Rai (1988). This ratio is near the ideal ratio of 3.0 that would be predicted from reaction (1) and suggests that the brown precipitates consisted of the hydroxide solid solution with a composition of  $(\text{Cr}_{0.25}\text{Fe}_{0.75})(\text{OH})_{3(s)}$ . Although we were not able to determine directly whether this solid solution had formed rather than a mixture of the pure endmembers, chromic concentrations in solutions equilibrated with these amorphous solids were consistent with the predicted solubility of  $(\text{Cr}_{0.25}\text{Fe}_{0.75})(\text{OH})_{3(s)}$  (Eary and Rai, 1988).

In the chromate reduction experiments with the hematite and biotite, it was difficult to identify any solid reaction products. In the hematite experiments, the formation of a very fine grained material which remained suspended in solution and which adhered to the sides of the bottles was apparent after 1 to 2 weeks of reaction. Powder XRD patterns for these solids showed peaks for hematite, but they were diminished in intensity compared to the unreacted hematite. The patterns also showed the broad increase in background scatter characteristic of amorphous material, suggesting that the fine grained material was a hydroxide solid. The XRD patterns for the reacted biotite were not significantly different from the unreacted material. However, White and Yee (1985) and Scott and Amonette (1988) have reported that amorphous  $\text{Fe}(\text{OH})_{3(s)}$  is the probable iron reaction product resulting from biotite weathering by aerated solutions.

The low concentrations of chromium used in the reduction experiments prevented the direct identification of any chromic hydroxide solids. However, steady-state concentrations of chromic ions were established in these experiments after variable periods of time ranging from 8 to 77 days (see figs. 2A and 3A). These steady-state concentrations are shown in figure 12 as well as the solubilities for  $(\text{Cr}_{0.25}\text{Fe}_{0.75})(\text{OH})_{3(s)}$  and  $\text{Cr}(\text{OH})_{3(s)}$  predicted from the solubility data of Sass and Rai (1987) and Rai, Sass, and Moore (1987), respectively. These authors report that



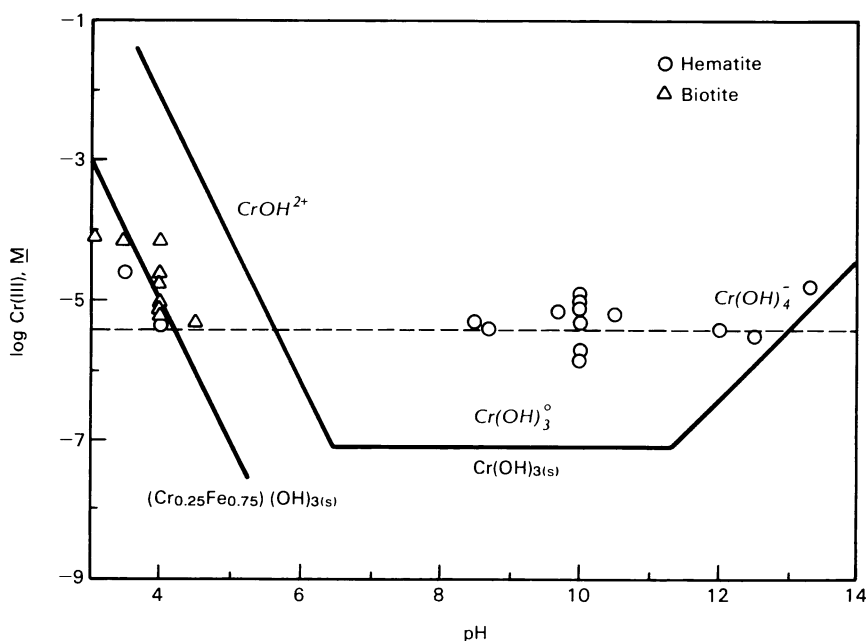


Fig. 12. Steady-state concentrations of chromic ions measured in separate reduction experiments after 8 to 77 days of equilibration. Solid lines indicate the calculated solubilities for  $\text{Cr}(\text{OH})_{3(s)}$  and  $(\text{Cr,Fe})(\text{OH})_{3(s)}$ , respectively. Chemical names in italics refer to aqueous chromium species. Dashed line indicates reliable detection limits for distinguishing chromic from chromate.

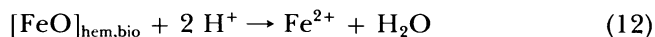
$(\text{Cr,Fe})(\text{OH})_{3(s)}$  precipitates rapidly, and solutions reach equilibrium concentrations in a matter of days, but it still should be noted that the steady-state concentrations measured in our experiments do not provide unequivocal proof of equilibrium. However, the chromic concentrations in the hematite and biotite suspensions were less than those expected from the solubility of pure  $\text{Cr}(\text{OH})_{3(s)}$  in the acidic solutions and are reasonably consistent with the predicted solubility of  $(\text{Cr}_{0.25}\text{Fe}_{0.75})(\text{OH})_{3(s)}$  (fig. 12). Concentrations are not shown for the mid-pH range, because they were too low to allow chromate to be distinguished from chromic by our analytical techniques. In alkaline solutions, the analytical chromic concentrations indicated that the solutions were oversaturated with pure  $\text{Cr}(\text{OH})_{3(s)}$  (fig. 12). However, the chromium concentrations in many of these solutions were near the detection limits, making it difficult to determine with certainty the small differences between total chromium and chromate concentrations, which was the procedure used to determine chromic concentrations. Thus, the chromic concentrations shown for alkaline solutions in figure 12 represent highest possible values. Results shown in figure 12 for chromate reduction by hematite

and biotite and those of Eary and Rai (1988) for chromate reduction solely by ferrous ions indicate that iron-rich members of the chromic-ferrous hydroxide solid solution are the primary solid products of chromate reduction in acidic solutions. In neutral to alkaline solutions, where  $\text{Fe}(\text{OH})_3(\text{s})$  is extremely insoluble, pure  $\text{Cr}(\text{OH})_3(\text{s})$  may be the more probable product of chromate reduction, although our solubility data are quite scattered for such conditions (fig. 12). The formation of these chromic hydroxides limits the concentrations of dissolved chromium to less than  $10^{-6}$  M between pH 4 and 12 (fig. 12).

#### DISCUSSION

*Reduction mechanisms.*—The experimental results presented above show that any factor that potentially can increase the ferrous ion concentration produces an increase in the rate of chromate reduction. Consequently, we conclude that chromate reduction in the presence of the hematite and biotite must occur by a two-step process that involves, first, the production of ferrous ions by dissolution or surface redox reactions and second, reaction between chromate and ferrous ions in the aqueous phase rather than on mineral surfaces. The following observations support this conclusion. (1) The rate of chromate reduction is decreased significantly at pH greater than about 9.0 to 10.0 (fig. 8) and also in phosphate solutions at lower pH (fig. 9). These are the same conditions under which the competitive rate of ferrous ion oxidation by dissolved oxygen is accelerated to the extent that fewer ferrous ions react with the chromate, resulting in nonstoichiometric reduction (fig. 1). (2) Chromate reduction is increased at low pH because of increased dissolution rates of the ferrous components of the hematite and biotite (figs. 7 and 8). (3) Increases in the concentrations of anions, such as sulfate, which complex ferrous ions (table 3), increase the rate of chromate reduction by causing more rapid dissolution of the ferrous components of the hematite and biotite (figs. 9, 10, and 11).

Dissolution of the ferrous components of hematite and biotite is the first step leading to chromate reduction and can be described by



where the subscripts hem and bio denote hematite and biotite, respectively. The ferrous ions generated by dissolution quickly and quantitatively reduce chromate to chromic under most solution conditions (fig. 1). Consequently, the addition of reactions (1) and (12) gives the overall reaction for chromate reduction caused by dissolution of the ferrous components of the hematite and biotite,



where the reaction is written with the aqueous species expected to be dominant in acidic solutions. Because the dissolution reaction consumes hydrogen ions, the rate of chromate reduction and the amount reduced

TABLE 3  
 MINTEQ calculations of ferrous and ferric ion speciation for solutions  
 described in figures 9, 10, and 11

Species	Species distributions, %				
	0.01 M ClO <sub>4</sub> <sup>-</sup>	0.01 M Cl <sup>-</sup>	0.001 M SO <sub>4</sub> <sup>2-</sup>	0.01 M SO <sub>4</sub> <sup>2-</sup>	0.1 M SO <sub>4</sub> <sup>2-</sup>
pH = 3.0 (figs. 10b and 11)					
Fe <sup>2+</sup>	100.0	100.0	90.5	66.4	46.6
FeSO <sub>4</sub> <sup>0</sup>			9.5	33.6	53.4
Fe <sup>3+</sup>		15.3		4.2	1.4
FeOH <sup>2+</sup>		65.4		15.9	4.0
Fe(OH) <sub>2</sub> <sup>+</sup>		15.9		3.4	
FeSO <sub>4</sub> <sup>+</sup>				66.0	52.7
Fe(SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup>				10.4	41.3
pH = 4.0 (figs. 9B and 10A)					
Fe <sup>2+</sup>	100.0	100.0	89.8	65.4	46.2
FeSO <sub>4</sub> <sup>0</sup>			10.2	34.6	53.8
pH = 10.0 (fig. 9A)					
Fe <sup>2+</sup>	24.0	24.0	24.3	26.1	27.4
FeSO <sub>4</sub> <sup>0</sup>			2.8	13.8	32.0
FeOH <sup>+</sup>	68.2	68.2	65.5	54.4	37.2
Fe(OH) <sub>2</sub> <sup>0</sup>	5.6	5.6	5.3	4.0	2.2
Fe(OH) <sub>3</sub> <sup>-</sup>	2.2	2.2	2.1	1.7	1.2

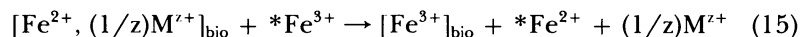
are dependent on pH and are greatly increased in acidic solutions (figs. 7 and 8). Also, anions, such as sulfate, which complex ferrous ions catalyze the dissolution reaction and, thereby, increase chromate reduction (fig. 9). Hematite dissolution has been reported to be more rapid in sulfate compared to chloride and perchlorate solutions (Majima, Awakura, and Mishima, 1985). These workers concluded that sulfate adsorption and subsequent detachment of iron sulfate complexes caused the increase in the hematite dissolution rate. In studies with biotite, numerous workers (summarized in Scott and Amonette, 1988) have reported that organic ligands can promote the dissolution rate and release of iron to solution, but studies with inorganic anions were not found. However, strongly adsorbing anions, which also have an affinity to form aqueous complexes with metal cations, can catalyze dissolution rates by decreasing the activation energy of the dissolution reaction. The activation energy ( $E_a$ ) of heterogeneous reaction has been described in general terms by Lasaga (1981) as

$$E_a = E_s + \Delta H_{ads} \quad (14)$$

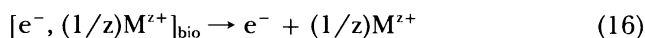
where  $E_s$  is the activation energy of the surface reaction, and  $\Delta H_{ads}$  is the heat of adsorption. According to eq (14), an anion with a negative heat of adsorption (an anion that is strongly adsorbing) causes a decrease in  $E_a$ . Sulfate is reported to adsorb strongly to iron oxides in acidic solutions (Stumm and Morgan, 1981). Thus, the increased rates of chromate reduction observed in acidic sulfate solutions (fig. 9B) may

result from a decreased activation energy of the dissolution of the ferrous components of the hematite and biotite because of sulfate adsorption and subsequent detachment as  $\text{FeSO}_4^0$  (table 3). In alkaline solutions, sulfate is not appreciably adsorbed onto iron oxides. However, sulfate still caused an increased rate of chromate reduction in the presence of the hematite at a pH of 10.0 (fig. 9). The formation of  $\text{FeSO}_4^0$  in these solutions (see table 3) may decrease the activation energy of the dissolution reaction enough to cause an increased rate of ferrous iron dissolution from the hematite even though sulfate may be only minimally adsorbed under alkaline conditions.

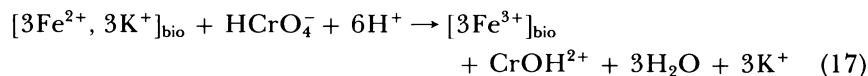
In addition to dissolution, ferrous ions also were observed to be generated by the reduction of ferric ions by the biotite (figs. 3B and 4B). This reaction was not observed in the hematite experiments. White and Yee (1985) have reported that ferric ions are reduced to ferrous in the presence of ferrous-containing silicates such as biotite, augite, and hornblende. According to these authors, ferric reduction takes place by electron transfer during the oxidation of surface ferrous iron in the silicates and occurs simultaneously with cation release from the silicate structure. These coupled electron-cation transfer reactions that take place at the surfaces of ferrous-containing silicates have been described in general terms by White and Yee (1985):



In reaction (8), M is an interlayer cation in the biotite structure with charge  $z+$ , and the asterisk denotes iron species that are conserved in solution according to the notation developed by White and Yee (1985). The release of cations to solution is required to maintain the internal charge balances of the silicate and the solution. White and Yee (1985) have correlated the rates of ferric ion reduction with the release rates of  $\text{K}^+$  from biotite and  $\text{Ca}^{2+}$  from augite and describe the charge balance as an electron-cation transfer:

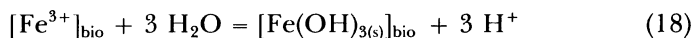


In general, a loss of  $\text{K}^+$  has been found to accompany a decrease in ferrous iron content in biotite during the initial stages of weathering (Scott and Amonette, 1988), as would be expected from the coupled electron-cation transfer process outlined above. The reduction of chromate caused by the generation of ferrous ions through coupled electron-cation transfer processes involving biotite can be described by summing reactions (1) and (15)



where the reaction is written with species that are relevant to acidic solutions and  $\text{K}^+$  as the primary exchangeable cation in the biotite structure.

Reaction (17) alone indicates that there should be a direct molar correspondence between the oxidation of structural ferrous iron and loss of  $K^+$ , which should result in neutralization of the layer charge in the  $K^+$ -depleted portions of the biotite. However, weathered biotites have been reported to have increased cation exchange capacities (Coleman, Leroux, and Cady, 1963). Also, Newman and Brown (1966) have reported that the oxidation of structural ferrous iron in biotite is not balanced by an equivalent decrease in the net negative charge in the biotite structure. To provide the missing net negative charge, other reactions must occur simultaneously with electron-cation exchange. Possible reactions include the loss of octahedral cations from the biotite structure, deprotonation of hydroxyl groups, and the incorporation of hydroxyl ions in interlayer cavities (Scott and Amonette, 1988). The most likely reaction, however, is the loss of iron from octahedral sites and subsequent precipitation in the interlayer region:

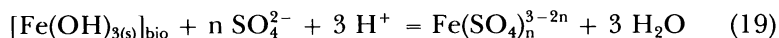


Weathered biotites often are reported to have iron hydroxide coatings along basal surfaces (Banfield and Eggleton, 1988; Scott and Amonette, 1988). Also, Newman and Brown (1966) have reported that artificially weathered biotites are more hydrated than their unweathered precursors, which is consistent with the formation of iron hydroxide in the interlayer region. In this study, the ferrous iron contents of the reacted biotites were generally observed to be decreased (table 2). The total iron contents were variable because of analytical uncertainties but, in general, did not decrease as much as the ferrous contents. This result indicates that at least part of the iron lost from the biotite structure by dissolution and electron-cation exchange reaction was precipitated as hydroxide solids in the biotite interlayers.

The effects of pH and anions on the rate of the electron-cation transfer reaction are difficult to separate from those affecting the biotite dissolution rate. The reduction of ferric ions by electron-cation transfer requires that some concentration of dissolved iron exist in solution before the reaction can be initiated. Thus, for at least a short initial period, dissolution of the ferrous component of the biotite is likely to be more important for producing ferrous ions for chromate reduction than the electron-cation transfer reaction, and the initial dissolution rate is clearly dependent on pH (fig. 8). Thus, the pH may affect the rate of any subsequent electron-cation transfer reactions by controlling the rate of depletion of oxidizable  $Fe^{2+}$  in octahedral sites in the biotite. The depletion of  $Fe^{2+}$  in octahedral sites and exchangeable  $K^+$  from interlayer sites is likely to cause a decrease in the rate of ferrous ion generation by both dissolution and electron-cation transfer reactions (Scott and Amonette, 1988; Gilkes, Young, and Quirk, 1973). In the experiments, the decreased rate of ferrous iron generation results in slower chromate reduction and the eventual establishment of steady-

state concentrations after an initial period of rapid reaction (figs. 3, 7B, 9B, and 10B).

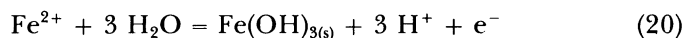
The effects of anions on the electron-cation transfer reaction are less clear. In all but the  $10^{-1}$  M sulfate solution, total iron concentrations did not increase until the initial ferric concentration had been converted to ferrous (fig. 11A), indicating that very high concentrations of sulfate are required to increase the biotite dissolution rate substantially. High concentrations of sulfate will result in the increased dissolution of any iron hydroxide that may be formed in the biotite interlayers because of complexing



where  $n = 0$  to 2. Assuming the electron-cation transfer reaction is dependent on the total ferric concentration, complexing should produce more rapid rates of ferrous ion production. Aside from any dissolution reactions, sulfate also causes a slight increase in the rate of ferric ion reduction by electron-cation transfer reactions, compared to perchlorate and chloride, (fig. 11B). Speciation calculations with MINTEQA (Felmy, Girvin, and Jenne, 1984) indicate that the ferric sulfate species,  $\text{FeSO}_4^0$  and  $\text{Fe}(\text{SO}_4)_2^-$ , were dominant in  $10^{-1}$  and  $10^{-2}$  M sulfate solutions shown in figures 10 and 11 (table 3). It is possible these species are slightly reduced more rapidly than the uncomplexed ferrous ions, which were dominant in the chloride and perchlorate solutions (table 3). The fact that the reduction rates for the two sulfate concentrations are not significantly different indicates that only a small amount of sulfate complexing of the ferric ions may be enough to increase the rate of ferric reduction by the biotite (fig. 11B). However, the results shown in figure 11B provide only circumstantial evidence supporting this conclusion. Experiments with a wider range of anion concentrations need to be conducted to determine the full dependence of the electron-cation transfer reactions on iron speciation.

*Effective oxidation potential.*—The reduction of ferric ions to ferrous by coupled electron-cation transfer reactions has been shown by White and Yee (1985) to take place at the surfaces of ferrous-containing silicates. Because electron-cation transfer reactions cause aqueous ferric ions to be reduced, the species involved in this reaction must exert a redox potential less than the aqueous ferrous/ferric couple. White and Yee (1985) calculated an oxidation potential for the ferrous/ferric couple located on the surface of hornblende that is slightly less than that calculated for the aqueous couple. However, this surface oxidation potential may be specific only to the dissolved-iron species. Our experiments indicate that the reduction of chromate is affected by dissolution and surface redox reactions which generate ferrous ions, but actually occurs in the aqueous state rather than on the mineral surfaces. Because chromate is reduced in solution by ferrous ions, the effective oxidation potential of the ferrous iron contained in hematite and biotite is defined

by the aqueous ferrous/ferric redox couple. For the pH range of most surface environments, the oxidation of ferrous ions results in the precipitation of  $\text{Fe}(\text{OH})_{3(s)}$  by the reaction



Thus, the effective oxidation potential exerted on aqueous couples by the ferrous/ferric couple in oxide and silicate minerals is defined by

$$\text{Eh} = 0.89 - 0.177 \text{ pH} - 0.059 \log (\text{Fe}^{2+}) \quad (21)$$

using thermodynamic data from Baes and Mesmer (1976) for amorphous iron hydroxide and Wagman and others (1982) for the aqueous species. The standard potential in eq (21) will vary a small amount depending on the crystallinity of the  $\text{Fe}(\text{OH})_{3(s)}$  phase.

Besides  $\text{Cr}(\text{III})/\text{Cr}(\text{VI})$ , other aqueous redox couples such as  $\text{Pu}(\text{V})/\text{Pu}(\text{VI})$ ,  $\text{Se}(\text{IV})/\text{Se}(\text{VI})$ , and  $\text{Mn}(\text{II})/\gamma\text{-MnO}_{2(s)}$  lie at higher potentials than that defined by eq (21) for all or part of the pH range of most groundwaters. These couples are compared to the  $\text{Fe}^{2+}/\text{Fe}(\text{OH})_{3(s)}$  couple in the simplified Eh-pH diagram of figure 13 in which the hydrolysis species have been omitted to focus attention on the Eh-dependent relationships. The importance of ferrous iron oxidation for controlling redox potentials in natural aqueous solutions has been discussed in detail by Sato (1960). More recently, manganese oxides (Postma, 1985),  $\text{Np}(\text{V},\text{VI})$  (Susak and others, 1983), and  $\text{Pu}(\text{V})$  (Amacher and Baker, 1982) have been found or predicted to be reduced in the presence of solids that contained ferrous iron. In addition, the transport and precipitation of gold in acidic laterites have been related to the oxidation and hydrolysis of ferrous oxides and sulfides (Mann, 1984). Based on our results with chromate, we expect that the oxidized species of these various couples can be converted to their lower oxidation states by the residual amounts of ferrous iron that may be present in oxide and silicate minerals during the early stages of weathering or that persist metastably in oxidized environments.

#### CONCLUSIONS

Our experiments on the rate of chromate reduction show that the ferrous iron contained in oxide and silicate minerals can strongly affect the redox speciation of dissolved chromium and, by analogy, other redox sensitive elements. Chromate reduction occurs in oxygenated solutions over a wide range of pH, indicating that even when chromium is introduced into groundwater environments as chromate, the residual amounts of ferrous iron commonly contained in oxide and silicate minerals can eventually cause the reduction of the chromate to chromic. In such environments, the dissolved chromium concentrations will be limited to low concentrations by the solubility of  $(\text{Cr},\text{Fe})(\text{OH})_{3(s)}$  over most of the pH range (fig. 12).

We expect that the reducing behavior of ferrous minerals is most important during the early stages of weathering before the depletion of

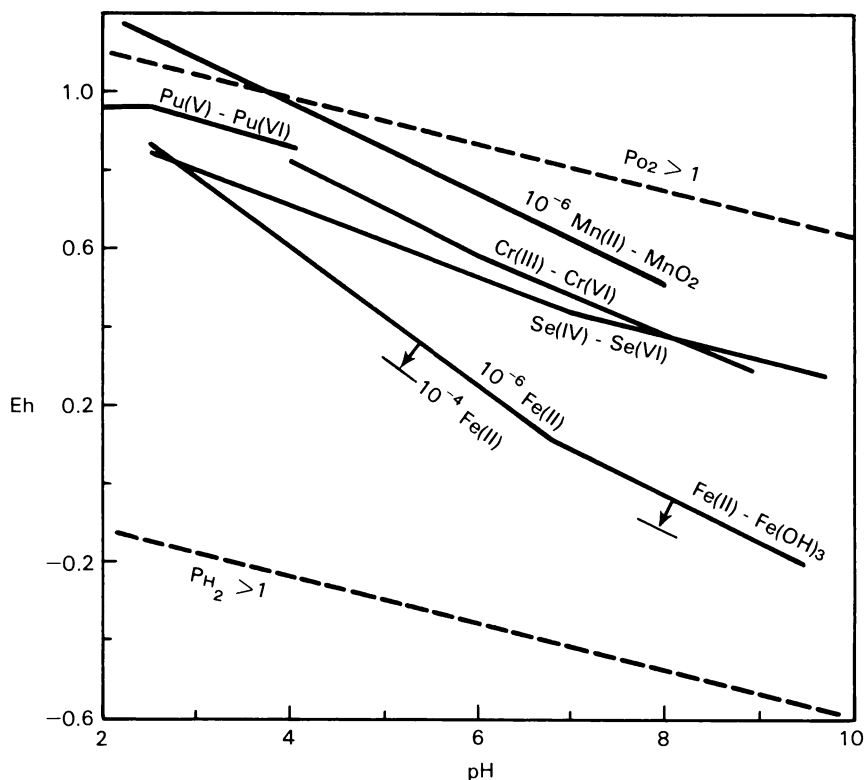


Fig. 13. Simplified Eh-pH diagram comparing various redox couples to the  $Fe^{2+}/Fe(OH)_3$  potential for  $10^{-4}$  and  $10^{-6}$  M total  $Fe(II)$  at  $25^\circ C$ . Sources of thermodynamic data include (1) iron, Baes and Mesmer (1976); (2) selenium, Wagman and others (1982); (3) plutonium, Rai (1984); (4) manganese, Wagman and others (1982) with  $\gamma$ - $MnO_2$  from Bricker (1965); and (5) chromium, Rai, Sass, and Moore (1987) and Sass and Rai (1987) with  $Cr^{3+}$  from Wagman and others (1982).

easily dissolved and structural ferrous iron. However, we suggest that further studies still need to be conducted to determine the effects of long-term weathering on the rates of ferrous ion generation from various minerals. White and Yee (1985) found that ferric ions are less rapidly reduced by weathered biotites than by fresh samples, suggesting that the rates of coupled electron-cation transfer reactions are decreased over time because of depletion of octahedral  $Fe^{2+}$  and interlayer  $K^+$ . Further studies with weathered biotites containing a range of ferrous iron and interlayer cation contents should provide insight on how long-term weathering affects the rate of ferrous ion production by dissolution and electron-cation transfer reactions.

In conclusion, our studies indicate that there are complex kinetic factors affecting the interactions between the ferrous iron contained in



minerals and aqueous ferrous and ferric species, which in turn affect the redox speciation of other redox species such as chromium. Because these interactions are kinetically controlled, they may be responsible in part for the apparent redox disequilibrium between various major and minor element redox couples often found in many dilute waters.

#### ACKNOWLEDGMENTS

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