

REACTION SCHEME FOR THE OXIDATION OF As(III) TO As(V) BY BIRNESSITE

JOHNNIE N. MOORE

Department of Geology, University of Montana, Missoula, Montana 59812

JEFFREY R. WALKER

Department of Geology, Vassar College, Poughkeepsie, New York 12601

THOMAS H. HAYES

Department of Chemistry, University of Montana, Missoula, Montana 59812

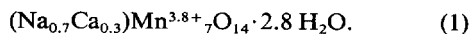
Abstract—The oxidation of As(III) to As(V) by K-birnessite was examined at different temperatures, pHs, and birnessite/As(III) ratios. Experiments ranged in duration from 5 to 64 hr, and solution and solid products were determined at several intervals. All experiments showed that the reaction produced large amounts of K⁺ to solution and very little Mn²⁺. As(V) was released to solution and incorporated into the K-birnessite. The oxidation was initially rapid and then slowed. The oxidation of As(III) was probably facilitated initially by autocatalytic Mn-As(V) reactions occurring mostly in the interlayer, in which large amounts of As(V) and K⁺ could be easily released to solution. The reaction also slowed when interlayer Mn was exhausted by forming Mn-As(V) complexes. Mn(IV) could only be acquired from the octahedral sheets of the birnessite. The two-stage reaction process proposed here depended on the layered structure of birnessite, the specific surface, and presence of exchangeable cations in K-birnessite.

Key Words—Arsenic, Birnessite, Oxidation, Potassium, Solution.

INTRODUCTION

The oxidation of As(III) to As(V) by manganese oxide minerals is an important means of altering the toxicity of arsenic in aquatic environments (Oscarson *et al.*, 1980, 1981a, 1981b, 1983). As common particulates in fresh and marine environments, various forms of manganese oxides mediate these reactions (Jenne, 1968; Murray, 1975; Martin and Meybeck, 1979; Wangersky, 1986; Lind, 1988). Birnessite, a frequently encountered, natural form of manganese oxide in modern sediments and soils (Jones and Milne, 1956; Giovanoli *et al.*, 1970a), is an important component in the natural oxidation of As(III) to As(V) (Oscarson *et al.*, 1980). Because As(III) is more toxic than As(V) (Coddington, 1986), this reaction controls arsenic toxicity.

The structure of birnessite is not well known, because the mineral does not form grains large enough for single crystal analysis and is variable in composition. Birnessite was originally identified from Mn-rich pans at Birness, Scotland, by Jones and Milne (1956); they equated the mineral to δ -MnO₂. Their chemical analysis established an O:Mn ratio of 1.9, and they calculated the following formula:



Giovanoli *et al.* (1970a) proposed a probable sheet-like structure for birnessite similar to that of chalcophanite (Giovanoli *et al.*, 1970a; Burns and Burns, 1977;

Golden *et al.*, 1986; Stouff and Boulegue, 1988). Each sheet consists of edge-sharing MnO₆ octahedra. Mn⁴⁺ occupies five of every six octahedral sites; the sixth site is vacant. Between the octahedral sheets, an interlayer may contain Mn³⁺, metal cations (M⁺/M²⁺), and water molecules. Mn³⁺ ions are presumably located above and below the vacant positions, octahedrally coordinated by water molecules of the interlayer and oxygen atoms of the MnO₆ octahedral sheets. The position of the M⁺/M²⁺ cations is unclear, but they are thought to be positioned between the MnO₆ octahedral sheets and the interlayer water sheets. The total layer thickness, *d*(001), of this arrangement is about 7.2 Å.

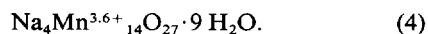
Based on water content determined by dehydration at 600°C, the data of Giovanoli *et al.* (1970b) give the following formula for synthetic Na-birnessite:



This data gives an O:Mn ratio of 1.8. Data based on dehydration at 300°C give an O:Mn ratio of 1.98 (Giovanoli *et al.*, 1970b), and would produce a somewhat different formula:

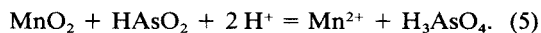


Giovanoli *et al.* (1970b), however, used neither of these formulae; instead, they presented the following generalized formula:



Charge balance in birnessites of different compositions is probably achieved by substitution of Mn^{3+} for Mn^{4+} in the octahedral sheets and Mn^{3+} in the interlayer and by altering the number of M^+/M^{2+} cations in the structure. The high layer charge density in birnessite results in a high cation-exchange capacity (CEC) of 240 meq/100 g for Na-birnessite (Golden *et al.*, 1986). Interlayer cations are easily exchanged and may be any one of several monovalent and divalent cations (e.g., K, Na, Ca, Mn, Ba, Cs); naturally occurring birnessite specimens typically contain a combination of Na, Ca, Mn and K as interlayer cations.

Previous investigations of the oxidation of As(III) to As(V) by birnessite and other manganese oxides considered Mn to be the electron acceptor; however, these studies did not consider the role of the structure of manganese oxide minerals in the reaction, other than to note that more crystalline forms slow the oxidation (Oscarson *et al.*, 1983). In their initial descriptions of the reaction, Oscarson *et al.* (1981a), suggested that As(III) oxidized to As(V) as Mn(IV) in MnO_2 in lake sediments was reduced to Mn(II) by the reaction:



Oscarson *et al.* (1981b) experimentally demonstrated the effectiveness of birnessite in oxidizing arsenic, but reported the absence of a mole-for-mole release of Mn^{2+} with the formation of As(V). In fact, using the data of Oscarson *et al.* (1981b) to calculate molar ratios, only a relatively small amount of Mn^{2+} was apparently released for every mole of As(V) formed (maximum of 1:17 and minimum of 1:145). Oscarson *et al.* (1981b) attributed this loss to adsorption and/or complexation and, possibly, to the formation of "sparingly soluble $Mn_3(AsO_4)_2$ " within the birnessite, but they did not isolate this compound or determine the composition of the reacted birnessite. To understand this disparity more fully and determine the reaction scheme of the oxidation, experiments were designed to determine the rate of the arsenic oxidation and the production of solute and solid-phase reactants during the reaction.

METHODS AND MATERIALS

K-birnessite was prepared by the reduction of potassium permanganate with HCl using the methods of McKenzie (1971). Different rates of addition of the reactants resulted in different K concentrations in the products: 1.7% K-birnessite and 8.2% K-birnessite. The reaction rates of the arsenic-birnessite system were determined at 5°, 25° and 40°C, at pHs of 3.5, 7.5, and 11.0, and for different mixtures of birnessite and As(III) (made by dissolving $NaAsO_2$). Experiments were conducted for as long as 64 hr. Different weights of birnessite were combined with 100 ml of As(III) solution for each experiment. Reactants were determined in the solution and solid phase at specific intervals by extracting samples and analyzing them by induc-

tively coupled argon plasma-emission spectrometry (ICAPES). Birnessite from these samples was dissolved in HCl in a microwave digestion vessel and the solutions analyzed by ICAPES. As(III) and As(V) in solution were separated with ion-exchange columns (Ficklin, 1983) and analyzed by ICAPES. As(III) and As(V) in birnessite was determined by dissolving the solid in hot 4 M HCl and separating the two oxidation states by ion exchange (W. C. Ficklin, U.S. Geol. Survey, Geochemistry Branch, Denver, Colorado, personal communication). The mean amounts of As(III) and As(V) (from Na_2HAsO_4) recovered from quality-control experiments were 91% (relative standard deviation (RSD) = 0.6%) and 98% (RSD = 2.1%), respectively. Based on internal standards, the average error of the ICAPES analyses was about 2%. Triplicate experiments showed an overall difference of $\leq 10\%$ for the determination of As(III) and As(V) and $\leq 15\%$ for Mn and K in solution and $\leq 12\%$ for solid-phase As, K, and Mn in birnessite.

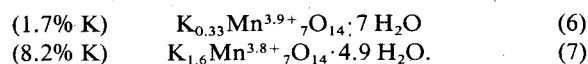
The chemical composition and crystal structure of the birnessite were determined before the reaction and at intervals during the reaction. For X-ray powder diffraction analysis, samples were lightly packed into well mounts and analyzed with a Philips Norelco diffractometer using $CuK\alpha$ radiation and a graphite monochromator. Scans from 10° to $65^\circ 2\theta$ were made at rates of 0.25° and $0.5^\circ 2\theta/\text{min}$. Four peaks were noted at 7.21, 3.60, 2.44, and 1.414 \AA in the synthetic birnessite. For the unreacted sample, $d(001)$ (average) was 7.20 \AA (Figure 1). A two-dimensional hk diffraction band was noted on the high-angle side of the 2.44-\AA peak indicative of random stacking of the MnO_6 octahedral sheets. On heating to 300°C , $d(001)$ (average) decreased slightly to 7.08 \AA . Unfortunately, these changes were near the error of measurement (about 2%), but for a specific sample a small decrease in $d(001)$ was seen after heating and reaction, suggesting that interlayer water was driven off by heating, causing minor collapse of the mineral structure (Figure 1).

Water content was determined by thermal gravimetric analysis of 6- to 8-mg samples. The decrease in weight on heating was measured from 30° to 600°C at a rate of $15^\circ\text{C}/\text{min}$, with a hold time of 1 min between temperature changes. The percentage of water was calculated from the weight loss after heating to about 300°C .

RESULTS AND DISCUSSION

Modifications during reaction

Two synthetic K-birnessite products were used in this study, one containing 1.7% K and one containing 8.2% K. Chemical analyses gave an O:Mn ratio of 2.0 for both products and yielded the following formulae:



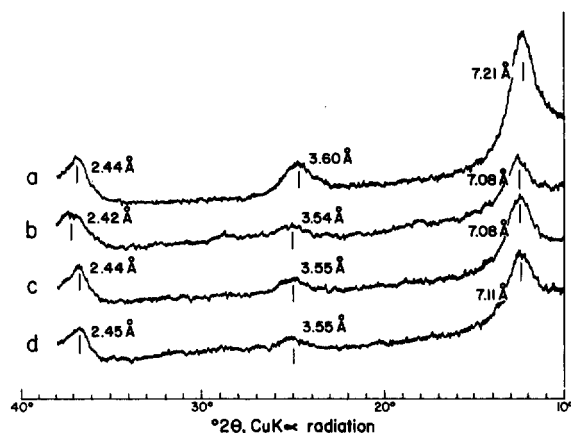


Figure 1. X-ray powder diffraction patterns for 1.7% K-birnessite product: (a) before reaction; (b) after heating to 300°C for 12 hr; (c) after 6 hr of reaction; and (d) after 64 hr of reaction. Error is about $\pm 2\%$.

These formulae were calculated on the basis of seven Mn. Total oxygen was determined by difference after measuring all other components analytically. The two birnessite products (Table 1) had higher Mn-oxidation states than the birnessite samples reported by Giovanoli *et al.* (1970b), but the oxidation states were similar to those described by Jones and Milne (1956).

Reactions extending for 64 hr using the 1.7% K-birnessite showed distinct trends of As(III) oxidation to As(V) and incorporation of As(V) into the birnessite (Figure 2, Table 2). As the oxidation reaction proceeded, As(III) in solution rapidly decreased and As(V) in solution increased (Figure 2a). Although As(III) in solution continued to decline, after eight hours, the As(V) concentration in the solution reached a maximum and then declined slightly with continued reaction. As(V) continued to be produced, but it was incorporated into the solid phase, as shown by the increase in As content in the birnessite (Figure 2c, Table 2). Substantial quantities of K^+ were released to solution during oxidation (Figure 2b). For the first 8 hr of reaction, 1 mole of K^+ was released from the birnessite for every 5 moles of As(V) in solution, decreasing to about 1 mole of K^+ for every 4 moles after 8 hr of reaction (Table 3, column d). The ratio of As(V)/ Mn^{2+} in solution was much greater; about 350 in the first

Table 1. Composition of two birnessite products used in reactions.¹

	K	Mn	H ₂ O	O
1.7% K-birnessite	1.7	51.5	17.0	29.8
8.2% K-birnessite	8.2	50.7	11.6	29.5

¹ Concentrations in wt. % based on three analyses for the 1.7% K-birnessite product and four analyses for the 8.2% K-birnessite product.

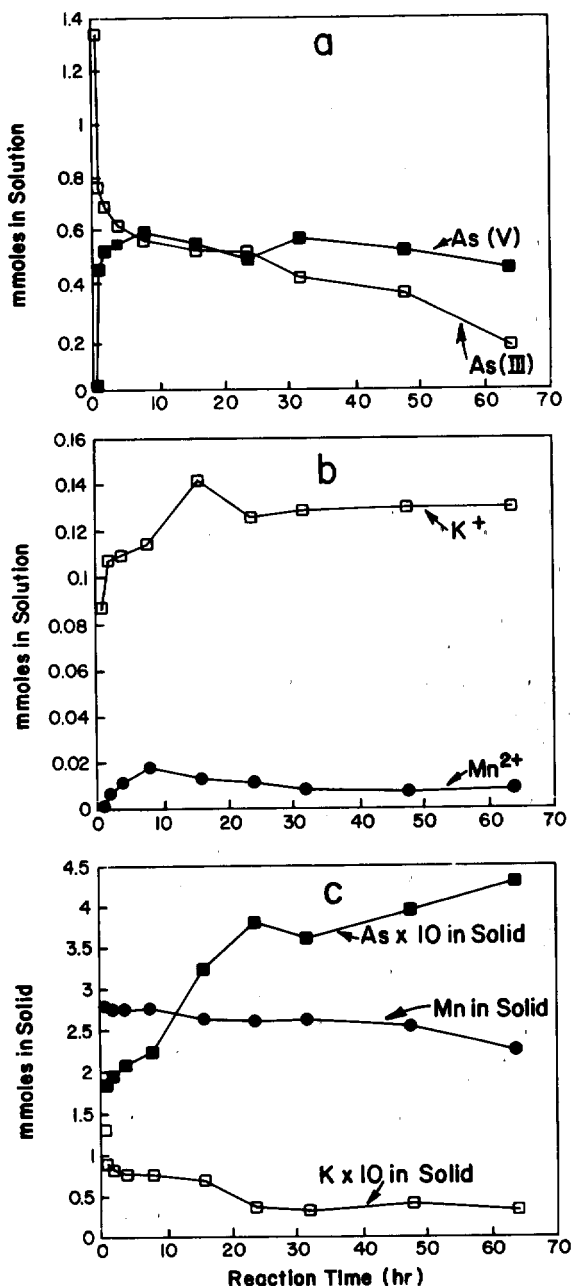


Figure 2. Change in elemental content (mmoles in solution and solid) vs. time (64-hr reaction) for 100 ml of 1000 mg/liter As(III) (1.34 mmole) and 0.3 g of 1.7% K-birnessite product; values reported in mmoles in the system (not as concentration) for direct comparison between solution and solid phases; at pH 7.5 and 25°C: (a) solution content of As(III) and As(V); (b) solution content of K^+ and Mn^{2+} ; and (c) solid content of As, K, and Mn (As and Mn times 10).

hour of the reaction, decreasing to about 40–80 thereafter (Table 3, column c).

The Mn content in the birnessite decreased slightly as the reaction proceeded (Figure 2c), but K was re-

Table 3. Molar ratios in solution and solid during reaction.¹

a Time (hr)	b As(V)/(III) in solution	c As(V)/Mn ²⁺ in solution	d As(V)/K ⁺ in solution	e K ⁺ /Mn ²⁺ in solution	f As(V)/(III) in solid	g Mn/K in solid	h As/K in solid	i Mn/As in solid
1	0.6	350	5.2	68	62	21.6 ² 31.1	2.1	15.0
2	0.8	77	4.8	16	63	33.9	2.4	14.0
4	0.9	48	5.0	10	66	36.1	2.7	13.2
8	1.1	34	5.2	6	68	36.8	3.0	12.4
16	1.1	43	3.9	11	125	38.4	4.7	8.1
24	1.0	44	3.9	11	131	76.8	11.3	6.8
32	1.4	72	4.4	16	308	86.4	11.9	7.2
48	1.5	79	4.1	20	393	67.0	10.4	6.4
64	2.8	58	3.5	16	330	77.4	14.9	5.2

¹ From same experiment presented in Table 2.

² Starting ratio.

leased at a much faster rate, resulting in initial birnessite Mn/K ratios of about 22, which increased to about 80 (Table 3, column g) as the reaction proceeded. Increases in the molar ratios of Mn/K and As/K and a decrease in the molar ratio of Mn/As (Table 3, columns g, h, and i respectively) in the birnessite indicate that K was released from the birnessite interlayer and that As was taken up in the solid phase. Arsenic in the solid products was dominated by As(V) after reaction and As(V)/As(III) molar ratios increased with time (Table 3, column f).

Birnessite products having different K contents showed similar rates of oxidation (Figure 3), and their Mn:As ratios were nearly identical after reaction. Reactions with both the 1.7% and 8.2% K birnessite materials all resulted in a rapid decrease of As(III) in solution in the first hour of reaction, followed by a slower rate of decrease (Figure 3).

Oscarson *et al.* (1983) reported that the rate of As(III) oxidation increased with increasing temperature. In experiments with the 1.7% K birnessite product, the rate of oxidation of As(III) during the first hour of

reaction increased with increasing temperature (Figure 4a). Little difference, however, was noted between reactions at 5° and 25°C (differences are within the 10% error), but the initial rate increased noticeably at 40°C. After 1 hr of reaction, the rates were similar at all three temperatures.

Oxidation was more rapid in experiments at pH 3.5 than those at pH 11.0 within the first 10 min of reaction (Figure 4b). After 10 min, however, the rate curves were similar for reactions at different pHs, and error of measurement overlapped for all experiments after 1 hr of reaction.

The data above suggest a two-stage process in the oxidation of As(III) to As(V) by birnessite. Presumably, the reaction began with a rapid oxidation of As(III), followed by slower rates of oxidation. The early, rapid stage released most of the As(V) to solution. During the second stage, As(V) solution concentrations stabilized and As(V) was mainly incorporated into the solid phase. At no stage was Mn²⁺ released to solution in significant quantities, but instead remained in the solid phase. K⁺ was released rapidly during the early stage of reaction and then stabilized. The early stage of the reaction proceeded more rapidly at higher temperatures, but the second stage rate was not significantly affected by temperature. The oxidation of As(III) under acid conditions proceeded more rapidly than under basic conditions during the first minutes of the reaction, but pH had no effect afterward. Different K contents of the birnessite had no significant effect on rate.

Reaction scheme

Oscarson *et al.* (1981b) suggested that, in the oxidation of As(III) to As(V) by birnessite, K⁺ was released into solution because "... the addition of As(III) disrupts the crystal structure at the surface of the oxide ...". They assumed that most of the K released was exchangeable at or near the surface of the birnessite and that the total amount of K⁺ originated from "...

Table 2. Solution and solid As content (mmole) during reaction.¹

Time (hr)	As(III) in solution	As(V) in solution	Total As in solid	As(V) in all phases	Total As all phases
0	1.34*	—	—	—	—
1	0.759	0.450	0.184	0.631	1.393
2	0.687	0.517	0.195	0.709	1.399
4	0.615	0.546	0.208	0.751	1.369
8	0.559	0.591	0.223	0.811	1.373
16	0.521	0.546	0.323	0.869	1.390
24	0.515	0.487	0.380	0.867	1.382
32	0.418	0.566	0.360	0.926	1.344
48	0.355	0.521	0.393	0.914	1.269
64	0.160	0.452	0.428	0.880	1.040

¹ For an experiment of 100 ml of 1000 mg/liter As(III) (* initial content, 1.34 mmole As(III)) with 0.3 g of 1.7% K-birnessite, pH 7.5 and 25°C.

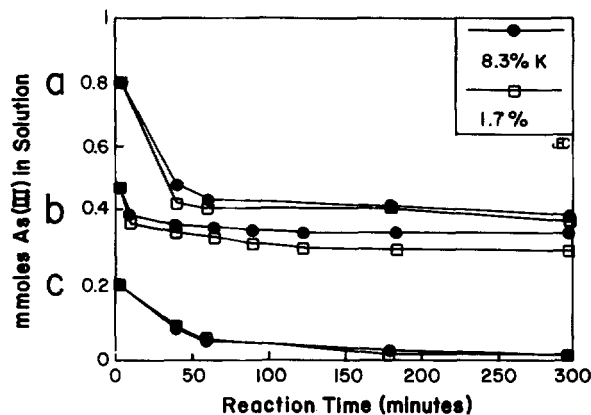
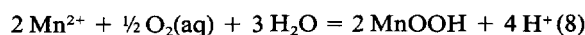


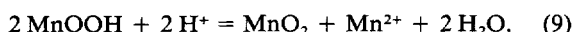
Figure 3. Change in As(III) content in solution vs. time (300-min reaction) for different K-birnessite products (1.7% K and 8.2% K): (a) 100 ml of 600 mg/liter As(III) and 0.2 g K-birnessite product, 2.3 Mn:As ratio; (b) 100 ml of 350 mg/liter As(III) and 0.1 g K-birnessite product, 2.0 Mn:As ratio; and (c) 100 ml of 150 mg/liter As(III) and 0.1 g K-birnessite product, 4.65 Mn:As ratio.

exchangeable and structural K . . .". In birnessite, K is included in the structure as an interlayer cation to balance charge and, therefore, is in an excellent position to be exchanged with aqueous species. Golden *et al.* (1986) found that several cations were easily exchanged with Na in Na-birnessite and that substituting K, Na, and Li in the structure did not significantly change the $d(001)$ value of birnessite. Only by addition of Cs, which is larger than the interlayer H_2O molecules, did the basal spacing change significantly.

Hem (1979), Crowther *et al.* (1983), and Krishnamurti and Huang (1987) established that birnessite can act as a catalyst to oxidize aqueous metal ions. Hem (1979, 1980) proposed an autocatalytic process to explain how such reactions can occur without releasing large amounts of Mn^{2+} to solution. In the presence of oxygen, aqueous Mn^{2+} reacts to form Mn(III) oxyhydroxide by:



Disproportionation of the Mn(III) oxyhydroxide results in the formation of Mn(IV) oxide and Mn^{2+} :



In this process the disproportionation of Mn(III) oxyhydroxides leads to autocatalytic coprecipitation of Mn(IV) and metal ions if they are present. Integrated with compositional changes seen in the present experiments, these concepts can be applied to the oxidation of As(III) by birnessite.

The birnessites used in the present experiments have average Mn-oxidation states of 3.8 to 3.9. Although not measured directly, the calculated Mn-oxidation states during the 64-hr reaction showed an initial de-

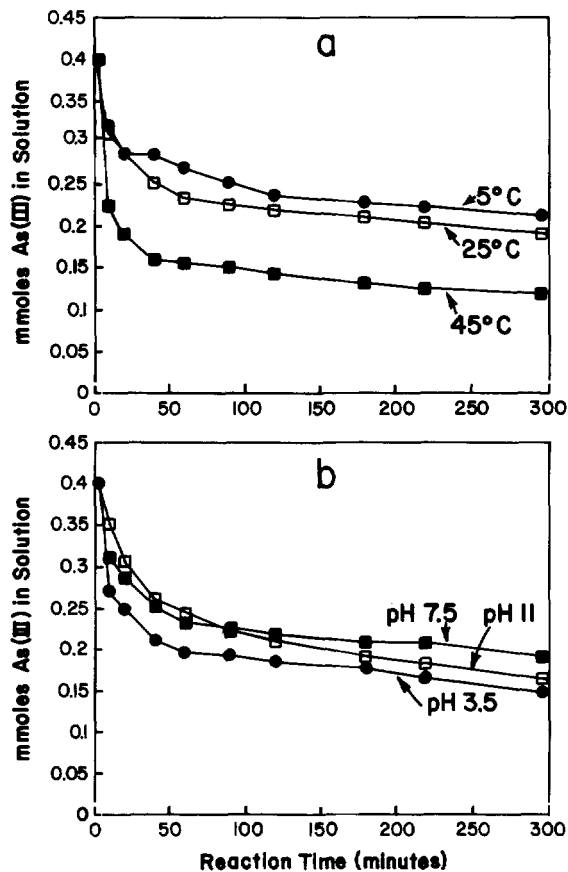
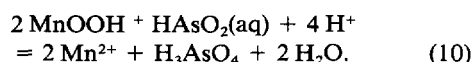


Figure 4. Change in As(III) content in solution vs. time (300 min reaction) for 100 ml of 30 mg/liter As(III) (0.4 mmole) and 0.1 g of 1.7% K-birnessite product (see Methods section for experimental error): (a) reactions at different temperatures; and (b) reactions at different pHs.

crease as Mn was reduced, presumably from Mn(III,IV) to Mn(II) via a reaction analogous to Eq. (5). In this scheme, the As(III) might have reacted with solid-state Mn(III) oxyhydroxides present in the birnessite (J. D. Hem, U.S. Geological Survey, Menlo Park, California, personal communication). These Mn(III) species would have been strong electron acceptors and might have oxidized As(III) in solution to As(V), with or without disproportionation (Eqs. (8) and (9)):



Mn^{2+} was not released to solution, however, during the oxidation, but instead may have reacted with H_3AsO_4 to form relatively insoluble manganese-arsenic complexes, possibly similar to $Mn_3(AsO_4)_2$ (Oscarson *et al.*, 1981a; Pascal, 1966). The concentrations of Mn^{2+} in solution would then have been controlled by the solubility of these manganese arsenates, leaving less Mn^{2+} available for recycling to Mn^{3+} through oxidation. As-

suming interlayer Mn was available, this reaction could have taken place rapidly. As oxidation proceeded, all the easily available Mn would have been consumed, and the substitution of As(V) in the interlayer would have released K^+ to solution, as seen in these experiments.

If such a reaction was important, the concentration of Mn^{2+} in solution should have been controlled by the disproportionation processes of the mixed valence Mn during the early stages of the reaction and the solubility of the manganese arsenate complexes during the later stages. In the first stage of the reaction, in which the Mn-oxidation state was reduced to 3.6, about 4×10^{-6} mole/liter Mn^{2+} would have been expected based on only the Mn disproportionation relationships (Hem, 1980, Figure 3). In the first 2 hr of the 64-hr reaction (Table 2), the Mn^{2+} concentration was 1.3 to 6.7×10^{-6} mole/liter, which brackets the predicted concentration of Mn^{2+} from Hem's (1980) disproportionation reactions. The concentration of Mn^{2+} at the same experimental conditions before As(V) addition was 1.7×10^{-7} mole/liter, extremely close to the concentration of 1.5×10^{-7} mole/liter predicted by Hem's (1980) disproportionation reactions. These relationships suggest that autocatalytic Mn-As(V) reactions occurred in the early stages of the reaction. These reactions probably occurred mostly in the interlayer, where a large amount of As(V) and K^+ could be easily released to solution, and the reaction could have proceeded rapidly.

In this model, when interlayer Mn was exhausted by forming manganese-arsenate complexes, the reaction slowed because Mn(IV) could only be acquired from the octahedral sheets. During this second stage, Mn^{2+} concentration in solution decreased (Figure 2) as it was incorporated into the solid phase with As(V), possibly forming $Mn_3(AsO_4)_2$ and/or a compound similar to krautite, $Mn(H_2O)(AsO_3OH)$ (Catti and Franchini-Angela, 1979). The existence of such a compound is supported by the chemical composition of products formed during long-term reactions. In reactions longer than 4 hr, a gel commonly formed, which was not seen in shorter experiments. The gel had As/Mn molar ratios of 0.9 to 1.0, similar to that expected for krautite. Moreover, the oxidation state of arsenic in the birnessite residue was predominantly As(V) (Table 3), and the As(V)/As(III) ratio increased with time, substantiating the presence of a manganous arsenate complex. As these compounds formed, K was depleted from the solid phase (Table 3) and released to solution (Figure 2, Table 2).

The zero point of charge of birnessite is near pH 2 (Healy *et al.*, 1966; Oscarson *et al.*, 1983). At all pHs used in our experiments (pH 3.5, 7.5, and 11), birnessite should therefore have a highly negative surface, accounting for the minimal difference in rates at different pHs. Negativity would have increased, however,

with increasing pH. At pH 3.5 and 7.5 the dominant As(III) species was H_3AsO_3 ; at pH 11 it was $H_2AsO_3^-$ (Ferguson and Gavis, 1972). Thus, the initial decreased oxidation rate at pH 11 may have resulted from repulsion of the As(V) aqueous species. At decreased pH the surface negativity would have decreased, and the noncharged species, H_3AsO_3 , would have been more reactive because of the polar nature of this pyramidal form. Also, at lower pH, birnessite is more soluble and could have produced more Mn^{2+} for the autocatalytic reaction. As(V) species also change with pH (Ferguson and Gavis, 1972). At pH 3.5 and 7.5, the dominant species is $H_2AsO_4^-$; at pH 11 it is $HAsO_4^{2-}$. By lowering pH (and thereby decreasing the negative charge on the birnessite) the charge on the As(V) species would have also decreased, allowing more access to the surface by the As(V) to produce manganese-arsenate complexes. Because no measurable differences in rate at most stages of the reactions were noted, however, these changes could not have been of great importance during later stages of reaction.

Reactions possibly involving interlayer atoms appear to have been superseded by reactions that involved other structural elements of the birnessite. The reaction rate probably slowed because arsenic oxidation required Mn which was tightly bound in the octahedral sheets, instead of the easily accessible interlayer Mn. Such a mechanism may also explain data from experiments carried out at different temperatures. The first stage of the reaction increased with increasing temperature, but not the second stage. Increased available energy at elevated temperatures would have increased the rate of initial reaction with interlayer Mn(III,IV) and the precipitation of arsenic manganese compounds (Hem, 1981). To reach Mn(IV) in the octahedral sheets, during the second stage, however, reaction would require diffusion, a process which was apparently not as dependent on temperature, because later rates were similar at different temperatures.

The two-stage process proposed here for the oxidation of As(III) to As(V) by birnessite depended on the mineral structure. The layered structure, resulting specific surface and the presence of exchangeable cations was likely essential in determining reaction rates. Thus, reaction rates for arsenic oxidation by pyrolusite are slow (Oscarson *et al.*, 1983), because pyrolusite is more crystalline, has a structure of corner-sharing (MnO_6) octahedra, and no interlayer, resulting in a smaller specific surface. Oscarson *et al.* (1981a) showed that the kinetics of the oxidation of As(III) to As(V) by Fe(III)-oxyhydroxides are extremely slow "... despite the thermodynamic favourability ..." (Oscarson *et al.*, 1980, p. 701; Oscarson *et al.*, 1981a, p. 50). The three-dimensional framework of goethite, the most common Fe(III)-oxyhydroxide, does not have interlayer positions for exchangeable cations. Also, disproportionation reactions may not be important in iron

oxyhydroxides. Therefore, any oxidation reaction would have to dissolve the iron polyhedra in order to gain access to Fe(III) and would proceed slowly without the autocatalytic reactions available in Mn-oxide precipitation processes. Alternatively, manganese oxides containing tunnel structures (hollandite, romanecheite, todorokite) (Turner and Buseck, 1981) may be extremely effective substrates for arsenic oxidation reactions. If so, exchange of these large cations with As should damage the framework, resulting in easily detectable structural changes.

REFERENCES

- Burns, R. G. and Burns, V. M. (1977) The mineralogy and crystal chemistry of deep-sea manganese nodules, a poly-metallic resource of the twenty-first century: *Phil. Trans. R. Soc. Lond. A*, **286**, 283–301.
- Catti, M. M. and Franchini-Angela, M. (1979) Krautite, $Mn(H_2O)(AsO_3OH)$: Crystal structure, hydrogen bonding and relations with haidingerite and pharmacolite: *Amer. Mineral.* **64**, 1248–1254.
- Coddington, K. (1986) A review of arsenals in biology: *Tox. Environ. Chem.* **11**, 281–290.
- Crowther, D. L., Dillard, J. G., and Murray, J. W. (1983) The mechanism of Co(II) oxidation on synthetic birnessite: *Geochim. Cosmochim. Acta* **47**, 1399–1403.
- Ferguson, J. F. and Gavis, J. (1972) A review of the arsenic cycle in natural waters: *Water Research* **6**, 1259–1274.
- Ficklin, W. H. (1983) Separation of arsenic(III) and arsenic(V) in ground waters by ion-exchange: *Talanta* **5**, 371–373.
- Giovanoli, R., Stähl, E., and Feitknecht, W. (1970a) Über Oxidhydroxide des vierwertigen Mangans mit Schichtengitter, 2. Mitteilung: Mangan(III)-manganat(IV): *Helv. Chim. Acta* **53**, 453–464.
- Giovanoli, R., Stähl, E., and Feitknecht, W. (1970b) Über Oxidhydroxide des vierwertigen Mangans mit Schichtengitter, 1. Mitteilung: Natriummangan(II, III)manganat(IV): *Helv. Chim. Acta* **53**, 209–220.
- Golden, D. C., Dixon, J. B., and Chen, C. C. (1986) Ion exchange, thermal transformations, and oxidizing properties of birnessite: *Clays & Clay Minerals* **34**, 511–520.
- Healy, T. W., Herring, A. P., and Fuerstenau, D. W. (1966) Effect of crystal structure on the surface properties of a series of manganese dioxides: *J. Colloid Interface Sci.* **21**, 435–444.
- Hem, J. D. (1979) Redox processes at surfaces of manganese oxide and their effects on aqueous metal ions: *Chemical Geol.* **21**, 199–218.
- Hem, J. D. (1980) Redox coprecipitation mechanisms of manganese oxides: in *Particulates in Water*, M. C. Kavanaugh and J. O. Leckie, eds., *Adv. Chem. Ser.* **189**, American Chemical Society, Washington, D.C., 45–72.
- Hem, J. D. (1981) Rates of manganese oxidation in aqueous systems: *Geochim. Cosmochim. Acta* **45**, 1369–1374.
- Jenne, E. A. (1968) Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and waters: American Chemical Society, Washington, D.C., *Adv. Chem. Ser.* **73**, 337–387.
- Jones, H. L. P. and Milne, A. A. (1956) Birnessite, a new manganese oxide mineral from Aberdeenshire, Scotland: *Mineral. Mag.* **31**, 283–288.
- Krishnamurti, G. S. R. and Huang, P. M. (1987) The catalytic role of birnessite in the transformation of iron: *Can. J. Soil Sci.* **67**, 533–543.
- Lind, C. J. (1988) Hausmanite (Mn_3O_4) conversion to manganite (γ - $MnOOH$) in dilute oxalate solution: *Envir. Sci. Tech.* **22**, 62–70.
- Martin, J. M. and Meybeck, M. (1979) Elemental mass balance of material carried by major world rivers: *Mar. Chem.* **7**, 173–206.
- McKenzie, R. M. (1971) The synthesis of birnessite, cryptomelene, and some other oxides and hydroxides of manganese: *Mineral. Mag.* **38**, 493–502.
- Murray, J. W. (1975) The interaction of cobalt with hydrous manganese dioxide: *Geochim. Cosmochim. Acta* **39**, 635–647.
- Oscarson, D. W., Huang, P. M., Defosse, C., and Herbillo, A. (1981a) Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments: *Nature* **291**, 50–51.
- Oscarson, D. W., Huang, P. M., and Liaw, W. K. (1980) The oxidation of arsenite by aquatic sediments: *J. Envir. Qual.* **9**, 700–703.
- Oscarson, D. W., Huang, P. M., and Liaw, W. K. (1981b) The role of manganese in the oxidation of arsenite by freshwater lake sediments: *Clays & Clay Minerals* **29**, 219–225.
- Oscarson, D. W., Huang, P. M., Liaw, W. K., and Hammer, U. T. (1983) Kinetics of oxidation of arsenite by various manganese dioxides: *Soil Sci. Amer. J.* **47**, 644–648.
- Pascal, P. (1966) *Nouveau Traité de Chimie Minerale*, Vol. 26: Masson, Paris, 453 pp.
- Stouff, P. and Boulegue, J. (1988) Synthetic 10Å and 7Å phyllosulfates: Their structures determined by EXAFS: *Amer. Mineral.* **73**, 1162–1169.
- Turner, S. and Buseck, P. R. (1981) Todorokites: A new family of naturally occurring manganese oxides: *Science* **212**, 1024–1027.
- Wangersky, P. J. (1986) Biological control of trace metal residence time and speciation: A review and synthesis: *Mar. Chem.* **18**, 269–297.

(Received 6 February 1989; accepted 22 January 1990; Ms. 1881)