

NOTE

INFLUENCE OF TRANSITION METALS ON THE FORMATION OF IRON OXIDES DURING THE OXIDATION OF Fe(II)Cl₂ SOLUTION

Key Words—Goethite, Iron oxide, Lepidocrocite, Oxidation, Transition metal.

Among the most common iron oxides in hydro-morphic soils are goethite and lepidocrocite which result from the weathering of pre-existing iron minerals. Si and Al strongly interfere with lepidocrocite formation, whereas Si alone favors ferrihydrite and Al-goethite formation (Schwertmann and Thalmann, 1976; Karim, 1977).

Different proportions of Al, Ca, Mg, and Si and low concentrations of Mn, Zn, Cu, Mo, and Ni ($\sim 10^{-6}$ M) have been observed in soil solution (Russell, 1973). Reduction of Fe(III) and Mn(IV) oxides in seasonally waterlogged soils has been reported to increase soil solution concentration of Mn, Co, Cu, Mo, and Zn (Ponnamperuma, 1972). Upon aeration, Fe(II) oxidizes to lepidocrocite, goethite, or ferrihydrite, depending on soil pH and the presence of Al and Si in solution. Nalovic and Segalen (1973) reported that the sum of the transitional metals present with iron inhibits the crystallization of iron oxides. They did not explain, however, the specific effect of individual elements on iron oxide crystallization. The present study was initiated to elucidate the influence of Mn, Zn, Cu, Co, Ni, and Mo on the crystallization of iron oxides through the oxidation of Fe(II) solutions.

EXPERIMENTAL

Preparation of oxides

Distilled water was boiled vigorously and allowed to cool under a flow of N₂ gas which had been passed through an alkaline pyrogallol solution to remove oxygen. A 0.05 M Fe(II)Cl₂ solution was prepared using this oxygen-free H₂O. The standard metal solutions were prepared by dissolving their chlorides in 0.25 N HCl. Standard molybdate solution was prepared by dissolving crushed ammonium molybdate in distilled water.

The N₂ gas was continuously bubbled through a calculated volume of 0.05 M Fe(II)Cl₂ solution to which varying amounts of different standard metal solutions had been added to obtain different atomic ratios of Mn/Fe, Zn/Fe, Co/Fe, Ni/Fe, and Mo/Fe. These mixtures were brought to pH 7 under a flow of N₂ gas by adding CO₃²⁻-free NaOH solution.

Air was passed through the NaOH solution to remove CO₂, and blown through the green suspensions at the rate of 2-3 bubbles per second. The oxidation

took about 48 min at which time the pH had decreased to about 3.8 (± 0.2). The oxides formed were dialyzed against distilled H₂O until the H₂O gave a negative test for Cl⁻ with AgNO₃. This process usually took 2-3 days.

X-ray powder diffractometry

Known proportions of lepidocrocite prepared by the oxidation of 0.05 M Fe(II)Cl₂ solution were mixed with known amounts of goethite prepared by ageing of precipitates from Fe(III) solution at pH 12 for 4 days at 50°C. The mixtures were finely powdered in an agate mortar, packed into aluminum holders, and were pressed against filter paper to minimize orientation effects. X-ray powder diffraction (XRD) patterns were obtained with a Philips goniometer using Fe-filtered CoK α radiation. The areas of 120 reflection of lepidocrocite and the 130 reflection of goethite were measured and plotted against known proportions of lepidocrocite and goethite. The areas of the 120 reflection of lepidocrocite and the 130 reflection line of goethite were measured in unknown samples, and the proportions of these minerals were ascertained by reference to these standard curves.

Chemical analysis of oxides

An acid oxalate treatment was used (Schwertmann, 1964) in which 70-100 mg of the oxide were shaken with 100 ml of NH₄-oxalate-oxalic acid (pH 3.0) mixture for 2 hr in the dark to determine the "noncrystalline" fraction of oxides (Fe₀). A duplicate sample was dissolved completely by gently heating in a few milliliters of approximately 12 N HCl and the total metal content of the oxide was determined by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

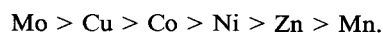
The oxidation of 0.5 M Fe(II)Cl₂ solution yielded mainly lepidocrocite with an Fe₀/Fe_t ratio about 0.40 (± 0.2). The addition of Mn, Zn, Cu, Co, Ni, and Mo tended to increase the proportions of goethite or noncrystalline oxides and to decrease the amount of lepidocrocite (Table 1). Lepidocrocite was the principal product, when only Mn or Zn was added. As the proportion of Mn to Fe was increased, some goethite formed and the crystallinity of the lepidocrocite de-

Table 1. Influence of initial concentrations of trace elements on the oxidation products of 0.05 M Fe(II)Cl₂ solutions.

Elements added to Fe(II)Cl ₂ solution	Atomic ratios × 10 ⁻³			Fe _o /Fe _t	Approximate proportions and HW ¹ of lepidocrocite and goethite			
	In solution	In oxidation product	In oxide after oxalate treatment		Lepidocrocite		Goethite	
					(%)	HW (°2θ)	(%)	HW (°2θ)
0	0	0	0	0.40	100	0.41	0	
Mn	3.08	1.66	0.98	0.41	65	0.48	0	
	27.30	9.13	6.41	0.43	40	0.52	10	0.45
	80.00	18.83	14.66	0.51	20	0.57	15	0.50
Zn	3.06	2.05	1.86	0.47	50	0.47	3	0.43
	30.60	22.90	8.60	0.60	25	0.58	0	
	70.00	31.86	21.14	0.69	0		trace	
Cu	3.15	7.82	6.97	0.29	25	0.51	30	0.41
	31.50	52.02	48.60	0.22	3	0.62	35	0.38
	70.00	84.27	14.23	0.60	0		trace	
Co	3.39	2.16	1.96	0.34	35	0.49	25	0.44
	20.00	14.71	14.60	0.22	20	0.54	35	0.41
	67.87	24.28	22.36	0.37	10	0.56	25	0.47
Ni	3.41	2.01	1.88	0.38	45	0.48	10	0.42
	19.52	8.60	7.68	0.23	26	0.53	25	0.43
	68.13	38.80	28.16	0.22	10	0.55	40	0.45
Mo	2.08	3.50	3.11	0.20	10	0.55	25	0.48
	10.40	8.90	7.82	0.13	0		35	0.42
	30.00	24.84	22.42	0.07	0		40	0.38
	40.00	33.20	25.36	0.12	0		25	0.49

¹ Uncorrected width at half height of 120 reflection of lepidocrocite and 130 reflection of goethite.

creased, as indicated by the width of 120 reflection of lepidocrocite. Copper largely induced the formation of goethite. At Cu/Fe = 31.5 × 10⁻³, about 35% goethite formed, and only 3% lepidocrocite was present. At Cu/Fe = 70 × 10⁻³, the main product was noncrystalline material, with a trace of goethite. Molybdate strongly inhibited the formation of lepidocrocite, but favored goethite. No lepidocrocite was formed at the atomic ratio of Mo/Fe = 10.4 × 10⁻³. All of these transition elements suppressed lepidocrocite but favored the formation of goethite mostly between the atomic ratios of 3.08 × 10⁻³ and 31.5 × 10⁻³. The inhibitory effect of elements on lepidocrocite formation was in the following order:



The amounts of Mn, Zn, Cu, Co, Ni, and Mo in the iron oxides left after oxalate extraction varied greatly. The maximum amount of Cu in the oxide corresponded to Cu/Fe = 48.6 × 10⁻³ and was achieved from a solution with Cu/Fe = 31.5 × 10⁻³. The coprecipitation of Cu at the lowest Cu/Fe ratio (3.15 × 10⁻³) was much higher than that of any other metal at a similar Me/Fe ratio added. The formation of 30–35% of goethite at low and medium Cu/Fe ratio in solution vs. high Cu/Fe appears to be dependent on the amounts of Cu²⁺ coprecipitated. Cu²⁺ has a d⁹ electronic configuration which is likely to affect its coprecipitation with goethite.

The fraction of oxides other than lepidocrocite and goethite increased with increasing addition of trace

metals. Nalovic and Segalen (1973) reported that the association of trace metal with iron during crystallization leads to the formation of microcrystals of oxides containing trace metals. Slow oxidation of Fe(II)Cl₂ solution usually gives lepidocrocite, but oxidation in the presence of Si yields ferrihydrite (Schwertmann and Thalmann, 1976; Karim, 1977). No ferrihydrite was detected in the oxides formed through the oxidation of mixed solutions containing trace metals. Because ferrihydrite gives very weak and broad XRD lines, it is difficult to detect in low concentrations by XRD (Schwertmann *et al.*, 1982). Lepidocrocite and goethite have the same mass absorption coefficient; the amount of either mineral present should be proportional to the intensity of a particular XRD peak, but the presence of poorly crystalline material may cause an increase of the absorption coefficient (Schwertmann and Taylor, 1972). It appears, however, that the goethite fraction in the Mo-series of oxides was underestimated, possibly because of mismatch of goethite formed in the Mo-series and the standard goethite. Goethite formed at Mo/Fe = 10.4 × 10⁻³ has much larger surface area (109 m²/g) than the standard goethite (51 m²/g).

CONCLUSIONS

Mn, Zn, Cu, Ni, and Mo had specific effects on the formation and crystallinity of the iron oxides produced by the oxidation of precipitates formed by the neutralization of Fe(II)Cl₂ solutions with CO₃²⁻-free NaOH. Lepidocrocite was the principal product up to atomic ratios of Mn/Fe = 27.30 × 10⁻³ and Zn/Fe = 3.06 ×

10^{-3} , but at higher ratios, some goethite formed and the crystallinity of the lepidocrocite decreased. Copper mostly favored goethite at $\text{Cu/Fe} = 31.50 \times 10^{-3}$. Molybdenum at $\text{Mo/Fe} = 10.4 \times 10^{-3}$ completely inhibited the formation of lepidocrocite but strongly favored goethite. The inhibitory effects of these transition elements on the formation of lepidocrocite were in the order: $\text{Mo} > \text{Cu} > \text{Co} > \text{Ni} > \text{Zn} > \text{Mn}$.

ACKNOWLEDGMENT

I am grateful to Dr. A. C. D. Newman for advice on the experiments during the tenure of research work at Rothamsted Experimental Station, Harpenden, Herts, United Kingdom.

Bangladesh Agricultural Research
Institute
Joydebpur, Dhaka, Bangladesh

ZAHURUL KARIM

REFERENCES

Karim, Z. (1977) The control of iron hydrous oxides crystallization by traces of inorganic components in soil solution: Ph.D. thesis, University of Reading, 100–119.

Nalovic, L. and Segalen, P. (1973) Relations entre le fer et les éléments traces de transition dans un certain nombre de minéraux ferrifères: *Cah. ORSTOM, serie pedol.* **XI**, 181–191.

Ponnamperuma, F. M. (1972) The chemistry of submerged soils: *Adv. Agron.* **24**, 29–96.

Russell, E. W. (1973) *Soil Conditions and Plant Growth*. 10th ed., Longman, London, 641–653.

Schwertmann, U. (1964) Differenzierung der Eisenoxide des Bodens durch photochemische Extraktion mit saurer Ammoniumoxalat-Lösung: *Z. Pflanzenernaehr., Dueng. Bodenkd.* **10**, 194–202.

Schwertmann, U. and Taylor, R. M. (1972) The transformation of lepidocrocite to goethite: *Clays & Clay Minerals* **20**, 159–164.

Schwertmann, U. and Thalmann, H. (1976) The influence of Fe(II), Si, and pH on the formation of lepidocrocite and ferrihydrite during oxidation of aqueous Fe(II)Cl₂ solutions: *Clay Miner.* **11**, 189–199.

Schwertmann, U., Schulze, D. G., and Murad, E. (1982) Identification of ferrihydrite in soils by dissolution kinetics, differential X-ray diffraction, and Mössbauer spectroscopy: *Soil Sci. Soc. Amer. J.* **46**, 869–875.

(Received 25 April 1982; accepted 19 August 1983)