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THE OCCURRENCE OF LEPIDOCROCITE IN TWO WELL-DRAINED ONTARIO SOILS

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Abstract—Lepidocrocite was identified associated with mica particles and in the clay fraction of two well-drained Ontario soils developed on a granite and a granite-gneiss. The occurrence of lepidocrocite is rare outside the tropics and there are no reports on its existence in well-drained soils.

Key Words—Anaerobic, Iron, Goethite, Lepidocrocite, Soil.

INTRODUCTION

Lepidocrocite (γ-FeOOH), a polymorph of goethite (α-FeOOH), is a rare form of iron oxide. According to Deer et al. (1962) it occurs typically under oxidizing conditions as a weathering product of Fe-bearing minerals. There are only a few reports on its occurrence in temperate regions where its presence has been associated with hydromorphic and poorly drained soils (Brown, 1953; Fitzpatrick, 1971; Schwertmann, 1973). It also occurs in bog ores where Fe(II) forms due to anaerobic environment (Jackson, 1964). Peacock (1942) reported lepidocrocite to occur in clusters with micaceous cleavage. To the authors' knowledge, the mineral has not been reported to occur in well-drained soils and there is only one published report on its occurrence in Canada in a Fera Eluviated Gleysol from Alberta (Pawluk, 1971). For this reason, the occurrence of lepidocrocite in two well-drained Ontario soils is important.

THE SOILS

The soils in which lepidocrocite occurs are residually developed on a granite in Methuen Township and a granite-gneiss in Cavendish Township near Lake Catchacoma, Peterborough County, Ontario. The Methuen granite is a medium grained, granular to granoblastic rock that weathers deeply to yellow-brown feldspathic gravel (Hewitt, 1960). Biotite and hornblende are the main dark minerals, and plagioclase and microline are the feldspars. Oligoclase, quartz, and microcline are the main constituents of the granite-gneiss. Hornblende, pyroxene, and biotite are accessories. Brief profile description and some chemical properties for the Methuen granite soil are given by Gillespie and Protz (1969), and for a soil similar to the Catchacoma granite-gneiss in Protz et al. (1974). The Methuen granite soil has been classified as Lithic Dystric Brunisol (Gillespie and Protz, 1969). The Catchacoma granite-gneiss soil is degraded Dystric Brunisol.

IDENTIFICATION OF LEPIDOCROCITE

Lepidocrocite was identified in the course of the study of weathering of mica minerals in the soils under consideration. Its presence associated with mica particles and in the clay fraction was indicated by both the oriented and X-ray powder diffraction patterns. The oriented specimens produced a single 6.23–6.27 Å peak (Figure 1). The second and third order reflections were not apparent either because of preferred orientation, especially since lepidocrocite often exists in nature as flakes or in micaceous form (Pawluk, 1971; Schwertmann, 1973) or due to superimposition of the second and third order reflection peaks on the 3.33 Å peak of mica and quartz, and 2.50 Å peak of mica, respectively. The heat treatment substantiated the presence of the mineral in that the 6.27 Å peak disappeared after heating to 300°C for 2 hr (Rooksby, 1961; Deer et al., 1962; Tarzi, 1976).

To obtain a positive evidence for the presence of lepidocrocite, X-ray random powder diffraction data were obtained for the mica particles separated from the Methuen and the Catchacoma soil profiles. The results confirmed the presence of the mineral as the four strongest reflections 6.27, 3.29, 2.47, and 1.93 Å (Table 1) were clearly produced. Goethite was not detected in the soils studied, but hematite was identified associated with Methuen mica particles. The most diagnostic reflections were 2.69, 1.69, and 3.67 Å.

DISCUSSION

The almost exclusive occurrence of lepidocrocite in soils in which anaerobic conditions prevail, and the ease with which lepidocrocite is synthesized through the oxidation of Fe(II) led many workers (e.g., Schwertmann and Thalmann, 1976) to conclude that its formation in soils requires Fe(II). However, this Fe(II) need not come exclusively from Fe(III) reduced as a result of anaerobic environment. Fe(II) from the structure of minerals (e.g., biotite) could serve as starting

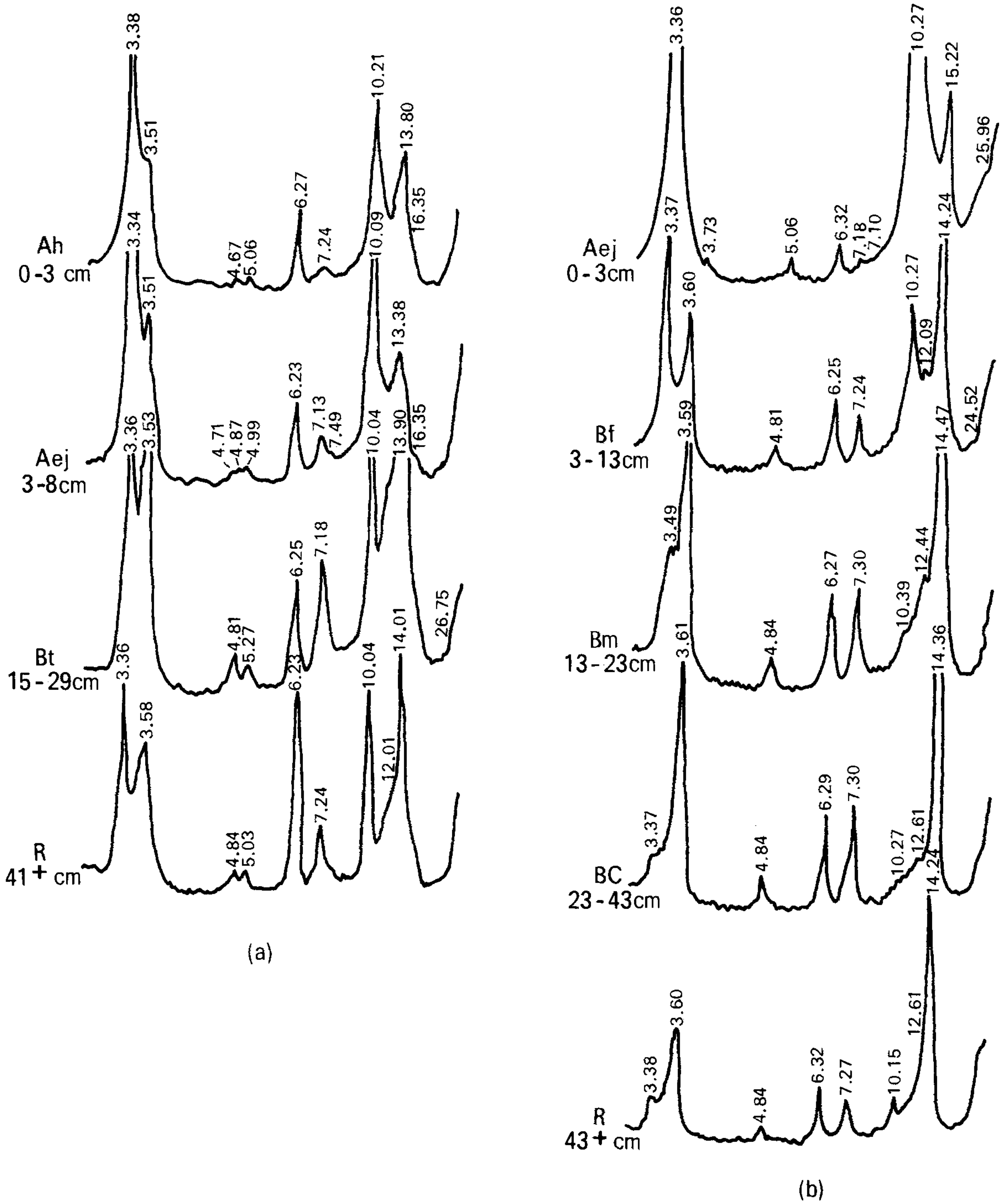

Fig. 1. X-ray diffractograms of air-dry micaceous particles: (a) from the Methuen granite soil profile; (b) from the Catchacoma granite-gneiss soil profile.

material. Furthermore, occasional formation of lepidocrocite in pure Fe(III) systems has been reported (Fordham, 1970). The green rust which is a mixture of Fe(II, III) also yields lepidocrocite if enough O_2 is present (Taylor and Schwertmann, 1974). The green rust, however, has not been identified in soils.

In nature, lepidocrocite is less stable than its polymorph goethite (Chesworth, 1975) and normally it

Table 1. X-ray powder diffraction data of micaceous particles from the Methuen granite and the Catchacoma granite-gneiss soil profiles.

	Methuen granite				Catchacoma granite-gneiss			
Horizon depth (cm)	Ah 0–3		R 41+		Bf 3–13		R 43+	
	d Å	I/I₁	d Å	I/I₁	d Å	I/I₁	d Å	I/I₁
	13.59	100	14.15	100	14.06	100	14.25	100
	10.27	100	10.21	46	10.11	48	10.16	27
	6.27	14	6.26	24	8.59	<1	7.06	2
	4.59	26	4.59	18	6.23	10	6.29	13
	4.27	6	4.26	1	4.62	21	4.61	20
	3.68	20	3.66	5	4.29	8	4.27	15
	3.34	66	3.53	9	3.68	4	3.53	5
	3.30	14	3.34	33	3.34	31	3.34	36
	3.15	3	3.28	20	3.30	3	3.30	5
	2.94	1	2.78	1	3.14	6	2.83	8
	2.69	26	2.70	8	2.89	6	2.64	30
	2.62	57	2.62	32	2.62	40	2.55	6
	2.52	6	2.51	5	2.52	4	2.46	15
	2.44	34	2.46	18	2.45	20	2.37	11
	2.29	17	2.30	6	2.28	8	2.29	4
	2.19	17	2.20	6	2.17	13	2.24	4
	2.08	10	2.00	8	2.00	12	2.12	6
	2.02	10	1.93	8	1.94	4	2.09	6
	1.93	9	1.82	10	1.81	5	1.98	7
	1.84	6	1.81	6	1.73	12	1.93	4
	1.82	6	1.73	8	1.67	13	1.82	5
	1.71	16	1.69	11	1.53	34	1.73	8
	1.68	11	1.53	24	1.37	10	1.67	8
	1.53	51	1.37	6	1.32	8	1.53	35
	1.49	10					1.37	10
	1.45	10					1.32	13
	1.37	9						

transforms to the latter. What then causes it to persist for long periods of time in soils and sediments is not fully understood. Laboratory studies (Schwertmann and Taylor, 1972a, 1972b; Schwertmann and Thalmann, 1976), while throwing some light on the formation and stability of lepidocrocite, have been unable, thus far, to answer many questions relative to its persistence in soils and sediments. This form of iron oxide should not persist, especially in the presence of ferrous iron which, according to Oosterhout (1967) acts to increase the solution rate of lepidocrocite. If this is presumed to partly explain the persistence of lepidocrocite in the Methuen and Catchacoma soil profiles, as they are well drained and thus lack Fe(II), its persistence in waterlogged soils cannot be explained with the abundance of Fe(II). The presence of silicate ions cannot often be held responsible for the inhibition of the conversion to goethite since it interferes only in the nucleation stage of goethite formation (Schwertmann and Taylor, 1972a). The latter has frequently been found associated with lepidocrocite, an indication that nucleation of goethite has already started. The possible effect of Al has not been investigated yet.

Assuming that the experimental results obtained by Schwertmann and Taylor (1972a, 1972b) are valid for field conditions, several possible explanations could be suggested for the persistence of lepidocrocite in the Methuen and the Catchacoma soil profiles. Although goethite was not detected in these soil profiles, its presence cannot be excluded, as X-ray may not detect it if present in trace amounts. If goethite is present, then inhibited or retarded dissolution of lepidocrocite could be responsible for its persistence. The absence of anaerobic conditions and extreme pH values would act to minimize its dissolution. Furthermore, dissolution of lepidocrocite rather than nucleation of goethite is the conversion rate determining process at temperatures and pH values prevailing in nature as shown by Schwertmann and Taylor (1972a). If goethite, however, is absent, silicate ions may be responsible for the persistence of lepidocrocite through retardation of goethite nucleation. It is possible that retardation of both lepidocrocite dissolution and nucleation of goethite combined might be effective.

If any of the hematite detected in the Methuen soil profile originated from lepidocrocite, which decreased towards the surface of the soil profile with an increase in hematite, then the conversion to hematite of lepidocrocite possibly can be explained by the observation of Schwertmann and Taylor (1972a). These investigators observed that during conversion of lepidocrocite to goethite some hematite formed from poorly crystalline FeOOH at 80°C in M KOH, as well as at lower KOH concentration (0.1 M KOH). In the latter case, the supersaturation of Fe was much lower for goethite to form while favorable for hematite formation. It is not easy to see how this system can be applied to natural environment. Nevertheless, if the dissolution of lepidocrocite in the soils under consideration is low, then the soil solution may not reach the degree of saturation relative to Fe required for goethite formation while being sufficient for the formation of hematite. The fact that experimental evidence is in favor of conversion via a solution phase (Oosterhout, 1967; Schwertmann and Taylor, 1972a) rather than a topotactic reaction, may support this.

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Резюме- Лепидокрокит был обнаружен в ассоциации с частицами слюды и в глинистых фракциях двух хорошо дренированных разновидностях почв из Онтарио, развитых на граните и гранито-гнейсе. Лепидокрокит редко встречается вне тропиков,и до сих пор не было сообщений о его существовании в хорошо дренированных почвах.

Kurzreferat- Es wurde gefunden,daß Lepidokrokit mit Glimmerteilchen verbunden ist und in den Tonfraktionen von zwei gut entwässerten Ontarioerden,auf einem Granit und Granitgneis entwickelt,vorkommt.Das Vorkommen von Lepidokrokit außerhalb der Tropen ist selten und es gibt keine Berichte über seine Existenz in gut entwässerten Erden.

Résumé-La lepidocrocite a été identifiée associée avec des particules de mica et dans les fractions argileuses de deux sols bien drainés d' Ontario,développés sur un granite et un granite-gneiss.On trouve rarement la lepidocrocite en dehors des tropiques et il n'y a pas de rapport de son existence dans des sols bien drainés.

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