

LEPIDOCROCITE IN A CALCAREOUS, WELL-DRAINED SOIL

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

Lepidocrocite is less common in soils than goethite or hematite. Until recently, this mineral was detected almost exclusively in hydromorphic soils in which it was thought to crystallize during the oxidation of Fe(II)-hydroxy compounds that had been precipitated in anaerobic conditions. In fact, the occurrence of lepidocrocite itself is indicative of hydromorphic conditions (van der Marel, 1951; Brown, 1953; Schwertmann, 1959; Schwertmann and Fitzpatrick, 1977; Schwertmann and Taylor, 1977; Chen *et al.*, 1980). Tarzi and Protz (1978), however, found lepidocrocite associated with mica particles in two well-drained Ontario soils developed on granite and granite-gneiss. They concluded that the Fe(II) required for lepidocrocite formation was probably derived from the structure of primary minerals, such as biotite.

Until now, lepidocrocite has been found neither in calcareous, hydromorphic soils nor in calcareous, well-drained soils. This paper reports the occurrence of lepidocrocite in a calcareous, well-drained soil developed on calcite rock and speculates on its genesis.

MATERIALS AND METHODS

Soil

Table 1 gives a description with some physical and chemical data of the sampled soil profile. Additional samples were taken from the C horizons of two similar profiles at a distance of approximately 100 m and 200 m from the described profile. The soil is formed *in situ* from Precambrian marble and occupies approximately 1500 ha in this region. It consists mainly of fine gravel and has a combined clay and silt content of less than 5%. The topography is hilly, and there is no evidence of till (Lajoie, 1962).

Methods

Most of the methods used are found in McKeague (1978) in which the methods are numbered as follows: particle size by pipet method (2.11); Fe and Al by dithionite (3.51) and by oxalate (3.52); total C by dry combustion (3.611); total analysis for some major elements (3.71); X-ray powder diffraction (XRD) after Mg saturation, glycerol solvation, and heating (5.22) using a Philips diffractometer with Fe-filtered $\text{CoK}\alpha$ radiation. The clay and silt for XRD analysis were obtained from the peroxide-treated and sodium-saturated soil. The clay was separated by sedimentation and the silt by sieving. Carbonates were not removed from the soil samples before this separation. Powder diffraction photographs were obtained with a Guinier camera. XRD data were obtained before and after heating at 310°C for 1 hr and before and after dithionite treatment to substantiate the presence of lepidocrocite and goethite by the disappearance of their reflections.

Some of these methods have been described previously, e.g., Fe and Al by dithionite (Mehra and Jackson, 1960) and by oxalate (McKeague *et al.*, 1977), and total elemental analysis (Jackson, 1958).

RESULTS

The extractable Fe content of the total soil (Table 1) is high relative to the low clay and silt contents. The amount of dithionite-extractable Fe (Fe-dith) for each horizon is about twice the amount of oxalate-extractable Fe (Fe-oxal).

Lepidocrocite in the clay and silt of the Ahk and Ck horizons (Figure 1) are indicated by peaks at 6.25 and 3.29 Å; goethite is indicated by a peak at 4.18 Å. The 6.25-Å peak is also present in the patterns of the unperoxidized <50- μm fractions of these

samples (not shown), thereby eliminating the possibility that this peak is due to calcium oxalate trihydrate which may form during peroxide treatment of calcareous soils (Brown, 1953). The lepidocrocite and goethite peaks are nearly as strong in the silt as in the clay suggesting undispersed concretions of these minerals in the silt. These peaks are absent in the XRD patterns of the unweathered underlying calcite rock (Figure 1) and of calcite-free, greenish-brown particles picked from the crushed calcite rock. Guinier densitometer recordings of the Ck horizon clay show lepidocrocite peaks at 6.23, 3.28, 2.460, 1.730, and 1.529 Å and goethite peaks at 4.17, 2.676, 2.434, 2.238, 2.179, and 1.708 Å (Figure 2). The absence of these peaks after dithionite treatment (Figures 2 and 3) and after heating to 310°C for 1 hr (not shown) provides further evidence for the presence of these iron oxides in the original samples. Essentially the same XRD data were obtained for the Ck horizon clay and silt from two similar sites nearby.

From the difference between Fe-dith and Fe-oxal, lepidocrocite + goethite appears to comprise 19% of the Ahk horizon clay and 24% of the Ck horizon clay (Table 2).

The dominant layer silicates in the clay of the soil profile are chlorite and vermiculite in discrete and in randomly and reg-

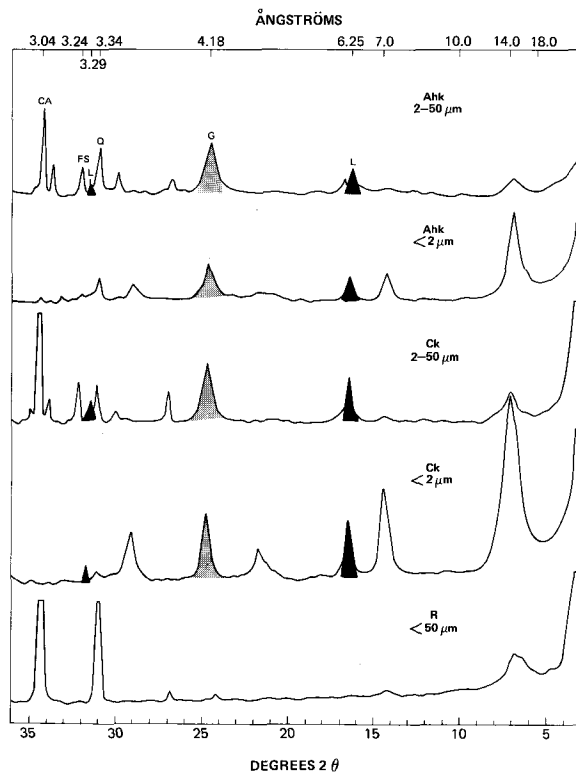


Figure 1. Smoothed X-ray powder diffraction patterns, obtained with Fe-filtered, $\text{CoK}\alpha$ radiation, of the soil profile samples after peroxide treatment and Mg saturation. The rock sample was crushed and most of its calcite removed by pH 5, 1 N NaOAc treatment. L, lepidocrocite dark-shaded peaks; G, goethite, light-shaded peaks; Q, quartz; FS, feldspars; CA, calcite.

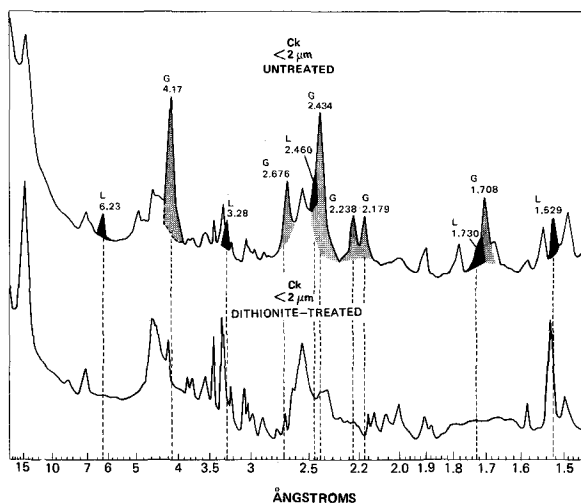


Figure 2. Guinier densitometer recordings, obtained with monochromatic $\text{CoK}\alpha$ radiation, of the Ck horizon clay. L, lepidocrocite, dark-shaded peaks; G, goethite, light-shaded peaks.

ularly interstratified forms. Some montmorillonite is present as well. The residue after treating the underlying rock with 1 N NaOAc at pH 5 contains a similar layer silicate assembly (Figure 3). Calcite is present in the silt fraction and in the rock residue along with some quartz and feldspars (Figures 1 and 3).

DISCUSSION

The occurrence of lepidocrocite in this calcareous, well-drained soil is unexpected as this mineral hitherto has been found only in non-calcareous, hydromorphic soils (Schwertmann and Fitzpatrick, 1977; Schwertmann and Taylor, 1977; Ross *et al.*, 1979; Chen *et al.*, 1980), except for its presence in two acid, well-drained soils (Tarzi and Protz, 1978).

The properties and location of the soil reported here show it to be excessively drained (Table 1), but it is not provable that it has been so in all its parts throughout its development. It is possible that hydromorphic conditions were intermittently present, particularly in cracks and pores of the weath-

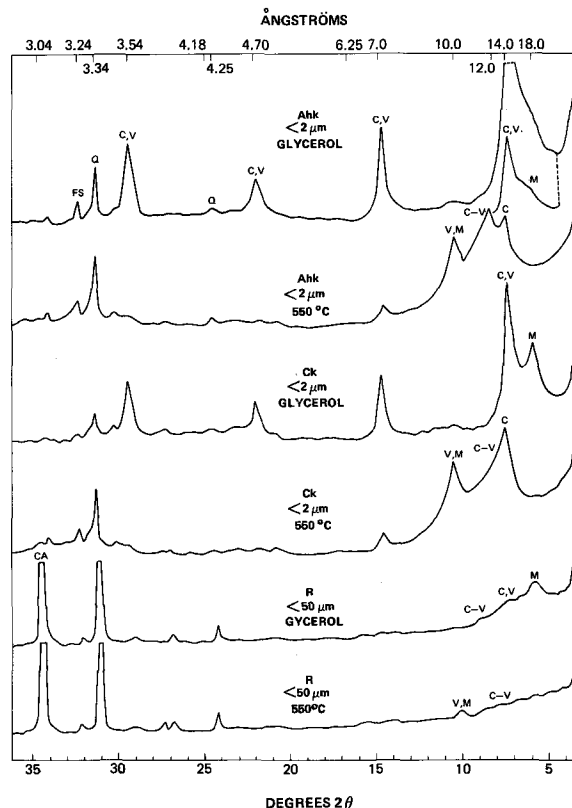


Figure 3. Smoothed X-ray powder diffraction patterns, obtained with Fe-filtered, $\text{CoK}\alpha$ radiation, of Mg-saturated samples of the soil profile. C, chlorite; V, vermiculite; C-V, interstratified chlorite and vermiculite; M, montmorillonite; Q, quartz; FS, feldspars; CA, calcite.

ering parent rock. Thus, the lepidocrocite in this soil could have formed according to the general and accepted concept of lepidocrocite formation, i.e., the Fe(II) that was oxidized to form lepidocrocite was derived from the reduction of Fe(III) oxides that were inherited from the parent rock or that formed during an earlier, aerobic stage of pedogenesis. It is more plau-

Table 1. Profile description and some physical and chemical data of the soil.¹

Particle size distribution	Dithionite extraction				Oxalate extraction		Pyrophosphate extraction		Total							pH of			
	Sand	Silt	Clay	C	Fe	Al	Fe	Al	Fe	Al	Fe	Al	Ca	K	Na	Mg	CaCO ₃ equiv- alent	<50- μm soil	<2- mm soil
(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Ahk	95.1	2.5	2.4	6.68	2.48	0.07	1.31	0.06	0.05	0.03	4.23	3.99	20.0	0.88	0.10	Nil	50	7.6	7.9
Ck	95.5	2.3	2.2	7.09	1.53	0.05	0.73	0.04	0.05	0.02	2.75	4.05	25.0	1.10	0.13	Nil	60	7.6	7.9

¹ The soil is located on the south bank of Pinks Lake in Gatineau National Park near Hull, Quebec. It is excessively drained and developed on Precambrian marble. It has a 45-90% slope. The soil is classified as a Humic Regosol in the Canadian soil classification system (Canada Soil Survey Committee, 1978) and as a Udipsamment in Soil Taxonomy (Soil Survey Staff, 1975). The area was mapped as St. Colomban Land type (Lajoie, 1962).

Ahk (soil surface horizon enriched with organic matter and carbonate) 0-22 cm, dark brown, 7.5 YR 3/2, coarse sand, weak fine subangular blocky, extremely calcareous, smooth abrupt boundary.

Ck (soil parent material containing carbonate) 22-35 cm, dark brown, 7.5 YR 5/6, coarse sand, single grain, extremely calcareous.

The horizon thickness of both Ahk and Ck is extremely variable.

Table 2. Amounts of iron dissolved from <math><2\text{-}\mu\text{m}</math> soil clay by dithionite and oxalate extractions.¹

Horizon ²	Fe-dith	Fe-oxal	FeOOH ³
Ahk	20.04	8.13	18.9
Ck	24.29	9.13	23.9

¹ Percent of air-dry sample weight.

² See Table 1.

³ Crystalline FeOOH as evaluated from the difference between Fe-dith and Fe-oxal; it consists of both lepidocrocite and goethite.

sible, however, that the Fe(II) to form lepidocrocite came directly from Fe(II)-containing primary silicates, most likely chlorite, in this soil. This source does not require anaerobic and hydromorphic conditions and was proposed by Tarzy and Protz (1978) for the formation of lepidocrocite in two well-drained Ontario soils.

According to the information available to the authors, this is the first reported occurrence of lepidocrocite in a calcareous soil. Although carbonate favors the formation of goethite, it does not seem to exclude lepidocrocite, and recent laboratory experiments have shown that it can form at room temperature in Fe(II) solutions (including carbonate solutions) at about pH 7 (Taylor and Schwertmann, 1974, 1978; Taylor, 1980). Further research, particularly on the association of lepidocrocite with chlorite, may indicate the dominant pathway to form lepidocrocite in this soil.

Considering the more numerous occurrences of lepidocrocite reported in hydromorphic soils than in well-drained soils, it is evident that anaerobic conditions favor the formation of lepidocrocite. The results presented here, however, add to previous evidence of Tarzy and Protz (1978) that lepidocrocite can also occur in well-drained, aerobic soils where it may form directly from Fe(II)-containing primary silicates, such as chlorite and biotite.

ACKNOWLEDGMENTS

The authors are grateful to R. G. Hill, G. C. Scott, J. G. Desjardins, B. C. Stone, N. M. Miles, and H. Kodama for help and advice in the experimental work and to J. A. McKeague for help and advice in the selection of samples.

*Chemistry and Biological
Research Institute*¹
Agriculture Canada
Ottawa, Ontario K1A 0C6, Canada

*Land Resource Research Institute*²
Agriculture Canada
Ottawa, Ontario K1A 0C6, Canada

G. J. ROSS

C. WANG

REFERENCES

- Brown, G. (1953) The occurrence of lepidocrocite in British soils: *J. Soil Sci.* **4**, 220–228.
- Canada Soil Survey Committee (1978) The Canadian System of Soil Classification: *Can. Dept. Agric. Pub.* **1646**, Supply and Services Canada, Ottawa, Ontario, 164 pp.
- Chen, C. C., Dixon, J. B., and Turner, F. T. (1980) Iron coatings on rice roots: Mineralogy and quantity influencing factors: *Soil Sci. Soc. Amer. J.* **44**, 635–639.
- Jackson, M. L. (1958) *Soil Chemical Analysis*: Prentice Hall, Englewood Cliffs, N.J., 498 pp.
- Lajoie, P. G. (1962) Soil Survey of Gatineau and Pontiac Counties: *Research Branch, Canada Dept. of Agric., Ministère de l'Agriculture, Service d'information*, **200-A**, Chemin Ste-Foy, Québec, Qué., 94 pp.
- McKeague, J. A. (ed.) (1978) *Manual on Soil Sampling and Methods of Analysis*: Can. Soil Sci., Ottawa, Canada, 212 pp.
- McKeague, J. A., Brydon, J. E., and Miles, N. M. (1977) Differentiation of forms of extractable iron and aluminum in soils: *Soil Sci. Soc. Amer. Proc.* **35**, 33–38.
- Mehra, O. P. and Jackson, M. L. (1960) Iron oxide removal from soils and clays by a dithionite citrate system buffered with sodium bicarbonate: in *Clays & Clay Minerals, Proc. 7th Natl. Conf., Washington, D.C., 1958*, Ada Swineford, ed., Pergamon Press, New York, 317–327.
- Ross, G. J., Miles, N. M., and Kodama, H. (1979) Occurrence and determination of lepidocrocite in Canadian soils: *Can. J. Soil Sci.* **59**, 155–162.
- Schwertmann, U. (1959) Die fraktionierte Extraktion der freien Eisenoxide in Boden, ihre mineralogischen Formen und ihre Entstehungsweisen: *Z. Pflanzenernaehr. Dueng. Bodenkd.* **105**, 194–202.
- Schwertmann, U. and Fitzpatrick, R. W. (1977) Occurrence of lepidocrocite and its association with goethite in Natal soils: *Soil Sci. Soc. Amer. J.* **41**, 1013–1018.
- Schwertmann, U. and Taylor, R. M. (1977) in *Minerals in the Soil Environment*: J. B. Dixon and S. B. Weed, eds., Amer. Soc. Agron., Madison, Wisconsin, 145–180.
- Soil Survey Staff (1975) *Soil Taxonomy*: U.S. Dept. Agric. Handbook, No. 435, U.S. Gov. Printing Office, Washington, D.C., 754 pp.
- Tarzi, J. G. and Protz, R. (1978) The occurrence of lepidocrocite in two well-drained Ontario soils: *Clays & Clay Minerals* **26**, 448–451.
- Taylor, R. M. (1980) Formation and properties of Fe(II)-Fe(III) hydroxy-carbonate and its possible significance in soil formation: *Clay Miner.* **15**, 369–382.
- Taylor, R. M. and Schwertmann, U. (1974) Maghemite in soil and its origin. II. Maghemite syntheses at ambient temperatures and pH 7: *Clay Miner.* **10**, 299–310.
- Taylor, R. M. and Schwertmann, U. (1978) The influence of Al on iron oxides I. The influence of Al on Fe oxide formation from the Fe(II) system: *Clays & Clay Minerals* **26**, 373–383.
- van der Marel, H. W. (1951) Gamma ferric oxide in sediments: *J. Sediment. Petrol.* **21**, 12–21.

(Received 10 September 1981; accepted 24 January 1982)

¹ Contribution 1270.

² Contribution 135.