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OCCURRENCE OF BERTHIERINE IN CANADIAN ARCTIC DESERT SOILS*

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ABSTRACT

Berthierine, an iron-rich trioctahedral 1:1 layer silicate (d_{001} = 7.04 Å), is a major component in the A and C horizons of the Jaeger series, an Arctic desert soil, at Ellef Ringnes Island, Northwest Territories. Heating the powder sample to 300°C displaces the 060 reflection from 1.548 to 1.513 Å, thus indicating the transformation of the trioctahedral berthierine structure to a dioctahedral one owing to the oxidation of Fe^{2+} to Fe^{3+}. Judging from the *d* value of 060 and the relative intensities of other reflections of the unheated sample, berthierine in the soil is a mixture of monoclinic and orthorhombic polytypes having an intermediate ferrous–ferric composition. Chemical data support the proposed intermediate composition. Although berthierine is highly susceptible to weathering, the severely restricted weathering environment in the Arctic region is the main reason for the rare survival of berthierine in the Jaeger soil.

Keywords: 7-Å trioctahedral layer silicate, iron-rich serpentine mineral, chamosite, ferrous–ferric ratio, Northwest Territories, Ellef Ringnes Island.

SOMMAIRE

La berthiérine, phyllosilicate trioctaédrique (1:1) ferrifère (d_{001} = 7.04 Å), est un composant principal des unités A et C de la série Jaeger, un sol désertique arctique situé sur l'île Ellef Ringnes (Territoires du Nord-Ouest). On peut déplacer la réflexion 060 de 1.548 à 1.513 Å par chauffage à 300°C, ce qui indique la transformation de la structure trioctaédrique de la berthiérine en une autre, dioctaédrique, par oxydation du fer. A la lumière de l'equidistance d_{060} et de l'intensité relative des autres réflexions de l'échantillon non-chauffé, la composition de la berthiérine du sol se situerait entre les termes Fe^{2+} et Fe^{3+} et serait un mélange de polytypes monoclinique et orthorhombique. Les données chimiques confirment cette composition intermédiaire. Quoique la berthiérine soit très sensible à l'altération climatérique, elle persiste dans le sol Jaeger vu l'importance très restreinte du lessivage dans son environnement arctique.

(Traduit par la Rédaction)

Mots-clés: phyllosilicate trioctaédrique à 7 Å, serpentine riche en fer, chamosite, rapport Fe^{2+}/Fe^{3+}, Territoires du Nord-Ouest, île Ellef Ringnes.

INTRODUCTION

During an investigation of polar desert soils on Ellef Ringnes Island, Northwest Territories (Foscolos & Kodama 1981), a 7-Å-phase clay mineral, whose occurrence in soils is known to be unusual, was detected. Preliminary data suggested that the mineral is an iron-rich species of the serpentine mineral subgroup, and probably berthierine, with the general structural formula $(Fe^{2+},Fe^{3+},Mg,Al)_3(Si,Al)_2O_5(OH)_4$, where $Fe^{2+} + Fe^{3+} > Mg + Al$.

The mineral had often been called chamosite until it was confirmed that berthierine has priority as the name for the iron-rich 1:1 type layer silicate (kaolinite–serpentine group), and chamosite has priority for a 2:1:1 type layer silicate (chlorite group) of similar composition (Bailey *et al.* 1971). Chamosite was recently recommended as the name for the ferrous end-member of the chlorite group (Bailey *et al.* 1979).

Further detailed examination ascertained that the 7-Å-phase mineral from the Jaeger soils is berthierine. To our knowledge, no occurrence of berthierine in soils has been reported previously.

MATERIALS

Samples of the Jaeger soil series were collected at 104.5°W and 79.1°N, on the northwestern side of Ellef Ringnes Island. The Jaeger soil, developed on Jurassic ferruginous glauconitic sandstones of the Jaeger Formation, has a sandy clay-loam texture, with soil acidity (pH) of 6.1, as measured in 0.01M $CaCl_2$ solution with a

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solution-to-sample ratio of 5:1. The particle-size distribution is as follows:

	DEPTH	PARTICLE SIZE (%)		
HORIZON	(cm)	SAND	SILT	CLAY
A	0–5	49	18	33
C	5–25	50	19	31

The soils are greyish green and contain little organic matter (<0.4%). Clay fractions were collected by sedimentation, saturated with Mg^{2+} and Ca^{2+}, and freeze-dried.

Methods

X-ray analysis was done by two different techniques using Co *Kα* radiation ($\lambda = 1.7902$ Å). Basal reflection data, before and after various treatments, were obtained with a Philips diffractometer from oriented aggregates prepared by drying 1 ml of clay suspension containing 40 mg of sample on a 25 x 37.5 mm glass slide. A Guinier–de Wolff focusing camera (transmission type) was used to obtain a better record of structural changes induced by thermal treatment. Infrared absorption spectra were obtained with a Beckman IR–4250 spectrophotometer using the KBr disc technique on air-dried and thermally treated samples.

Results and Discussion

The mineral compositions of the clay fractions and the A and C horizons are similar. Therefore, the following discussion is based on the data of the A horizon sample. Figure 1 shows X-ray diffractograms obtained from oriented aggregates of Mg-saturated clay fractions before and after various treatments. The diffractogram of the air-dry sample shows sharp and strong reflections at 7.04 and 3.52 Å: these are unaffected by solvation with glycerol, whereas other weak and broad reflections show peak shifs (Figs. 1A, 1B). The *d*(001) value of 7.04 Å is smaller than those for kaolinite, greenalite and Mg-serpentine minerals. At 550°C (Fig. 1C), the 7 Å mineral, unlike kaolinites, persists, although *d*(001) contracts from 7.04 to 6.94 Å and intensities of the basal reflections are greatly reduced. At 650°C (Fig. 1D), the 7-Å-phase mineral nearly disappears.

The X-ray diffractogram (Fig. 1A) also indicates minor amounts of 14- and 10-Å-phase minerals. Glycerol treatment causes *d*(001) of the 10 Å mineral to contract from 10.3 to 9.8 Å and that of the 14 Å mineral to expand slightly from 14 to 14.2 Å. Thermal treatments up to 650°C reduce the 14 Å spacing to 13.7 Å

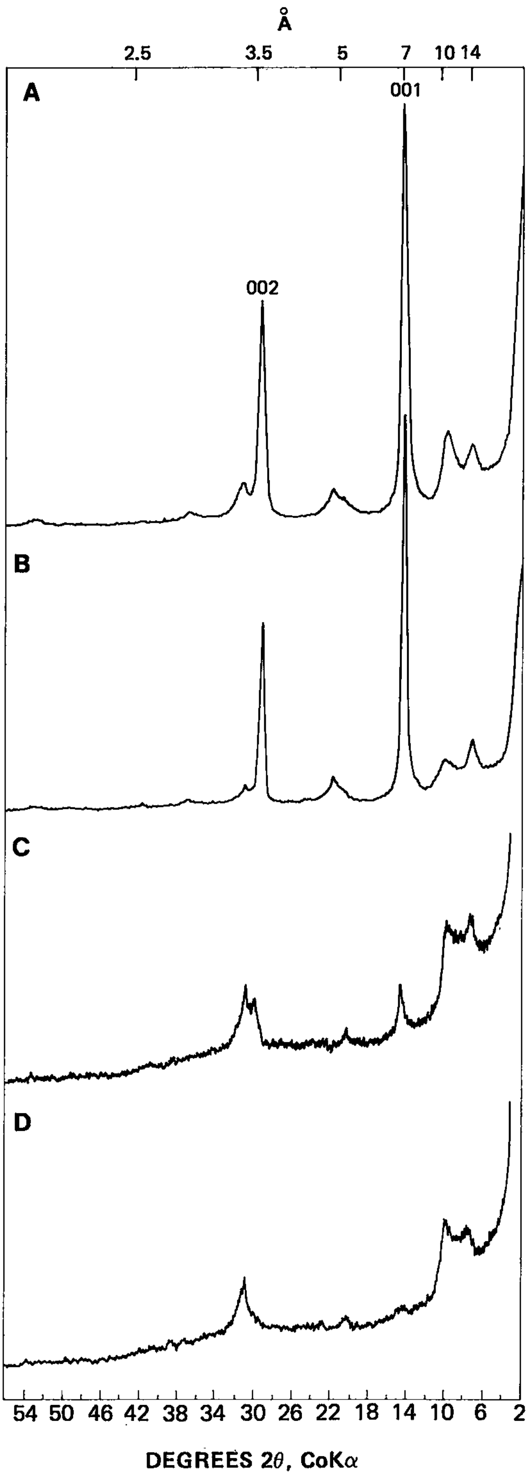

Fig. 1. X-ray diffractograms of an oriented clay fraction from the A horizon of Jaeger soil before and after various treatments. A air-dry, B glycerolation, C 550°C, D 650°C.

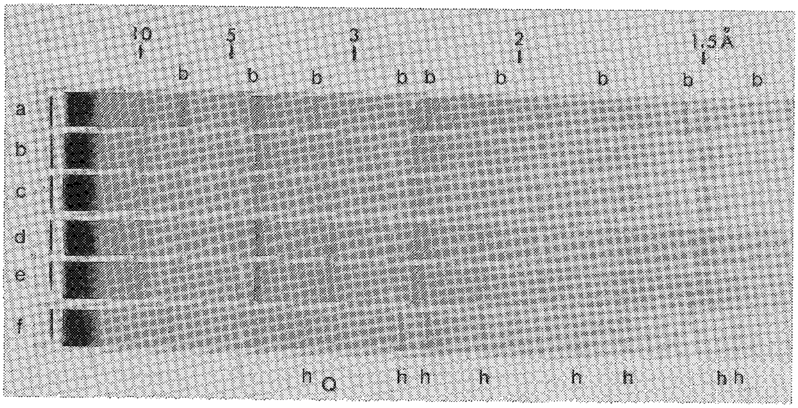

FIG. 2. Guinier–de Wolff powder-diffraction photographs of the clay fraction from the A horizon of Jaeger soil before and after heat treatments. a air-dry, b 300°C, c 400°C, d 550°C, e 650°C, f 900°C. Heated 2 hours at each temperature; b: berthierine reflections except for those overlapped with impurity reflections; h: hematite reflections; Q: quartz reflection.

and the 10.3 Å spacing to 10 Å. These features thus indicate that the 14 and 10 Å minerals are interstratified chlorite–vermiculite and interstratified mica–smectite, respectively, and that in each case the proportion of hydrated component layers is as low as 15 to 20%.

Guinier–de Wolff X-ray powder diagrams (Fig. 2) provide further information about the 7-Å-phase mineral. Besides showing a few impurity reflections, the powder diagram of the unheated sample (Fig. 2a) is in good agreement with that of berthierine [the chamosite of Brindley (1951); Table 1]. The absence of major reflections at 1.925 and 1.596 Å excludes the possibility of the mineral being amesite (Brindley *et al.* 1951). Brindley (1951) interpreted powder patterns of many berthierine samples in terms of a mixture of monoclinic and orthohexagonal structural forms. The present pattern is also considered to be such a mixture (Table 1); the ratio of monoclinic to orthorhombic polytypes is estimated to be 1:2 by reference to calculated intensities for various ratios as given by Brindley (1951).

Progressive changes in the berthierine structure upon heating were traced through the Guinier–de Wolff powder diagrams from Figures 2a to 2f. At 300°C (Fig. 2b), 001 and 002 reflections shift slightly towards smaller *d* values. Of the 20*l* reflections, those at 2.681, 1.759 and 1.474 Å disappear and others weaken. The 0*k*0 reflections at 4.64 and 1.548 Å no longer exist, probably as a result of shifting to adjacent reflections at 4.51 and 1.513 Å, respectively. This indicates a reduction of the *b* dimension. Intensities of the adjacent reflections appear to increase by approximately 15% as compared with the intensity of the quartz reflection at 3.34 Å, based on intensity data by the photodensitometric method. This enhancement would be higher if reductions in intensities

TABLE 1. X-RAY POWDER DATA FOR THE CLAY FRACTION FROM THE A HORIZON OF JAEGER SOIL

hkl⁺		Jaeger Canada		Ayrshire Scotland⁺	
monoclinic form	orthogonal form	d(Å)	I	d(Å)	I
		14.5	1*		
		10.7	2*		
001	001	7.04	9	7.05	10
020	020	4.64	2	4.67	2
110		4.51	6**	4.58	2
$11\bar{1}$		4.25	1**	4.28	½
021	021			3.90	1
002	002	3.521	5	3.520	10
		3.339	4*		
022	022	2.780	1	2.801	??
$20\bar{1}$, 130	200	2.681	2	2.678	4
		2.581	3*		
	201	2.508	10**	2.519	9
$20\bar{2}$		2.399	2	2.404	4
		2.320	½	2.337	½
201, $13\bar{2}$		2.235	1	2.273	½
	202	2.135	4**	2.141	6
$20\bar{3}$, 132		2.012	½	2.011	1
		1.969	½*		
$13\bar{3}$, 202		1.878	½	1.894	1
	203	1.759	2	1.768	4
	241	1.690	1**	1.693	?
$20\bar{4}$, 133		1.661	1	1.665	½
$13\bar{4}$, $33\bar{1}$, 060	060	1.549	7	1.555	7
330, 061	061	1.513	5**	1.521	3
		1.499	1*		
	204	1.474	2	1.473	1
331, 062	062	1.437	½	1.425	1
005	005	1.415	1	1.407	½
		1.356	½	1.361	½
$26\bar{1}$	400			1.347	½
	401	1.329	2	1.326	½

⁺After Brindley (1951). *Impurity lines
**Possibly overlapped with impurity lines

were applied to those reflections at 4.51 and 1.513 Å of berthierine after heating at 300°C, as the intensity of the 001 reflection decreases under the same conditions. Thus, it is most likely that the *d* value of the 060 reflection is converted from 1.548 to 1.513 Å. This conversion is one of the diagnostic criteria for berthierine (Brindley & Youell 1953). This change, which is due to the oxidation of Fe^{2+} to Fe^{3+}, results in a transformation of the berthierine structure from trioctahedral to dioctahedral. The specimen heated to 400°C gives a powder diagram similar to that for the specimen heated to 300°C, except that reflection intensities are diminished (Fig. 2c). At 550°C (Fig. 2d), the 001 reflection at 7 Å is extremely weak, and its second order reflection disappears. A shoulder-like reflection near 2.5 Å appears on the broad reflection at 2.56 Å. All berthierine reflections disappear at 650°C (Fig. 2e), thus confirming that berthierine decomposes between 550 and 650°C. Impurities at 14 and 10 Å, on the other hand, persist up to 650°C. At 900°C (Fig. 2f), synthetic hematite (α–Fe_2O_3) appears as a new phase along with a weak reflection of residual quartz at 3.34 Å; however, the 14- and 10-Å-phase minerals no longer exist. The appearance of hematite is a result of thermal decomposition of berthierine. These thermal reactions and products are compatible with the data of Brindley & Youell (1953) for berthierine.

The *b* parameters calculated from 060 before and after oxidation are 9.29 and 9.08 Å, respectively. The value for the ferric form is in accord with the reported value of 9.10 Å. The pre-oxidation value, however, is much smaller than 9.38 Å, reported for the ferrous form, indicating that only a part of the iron in the berthierine soil sample is in the ferrous state.

TABLE 2. CHEMICAL DATA FOR THE CLAY FRACTION FROM THE JAEGER SOIL (A HORIZON)

	(a)	(b)
SiO_2	23.16%	25.97%
TiO_2	0.66	0.74
Al_2O_3	19.30	21.64
Fe_2O_3* (free iron)	5.77	-
Fe_2O_3	13.39	15.02
FeO	18.14**	20.34
MgO	1.12	1.26
CaO	0.72	0.81
K_2O	3.27	3.67
Na_2O	0.21	0.24
L.O.I. 110°-1000°C	9.19	10.31
$H_2O(-)$ <110°C	2.10	-
C.E.C. (110°C oven-dry basis)	23.59 Meq./100 g	

*Dithionite-citrate extractable. **The value may slightly be overestimated due to the presence of a small amount of organic matter in the sample.
(a) Original analysis
(b) Scaled to 100% (after moisture. $H_2O(-)$, and free iron, Fe_2O_3*, were subtracted).

The chemical analysis of the clay fraction (Table 2) is high in Fe_2O_3, along with FeO, and supports the above interpretation of an intermediate ferrous–ferric composition for berthierine. The analysis also shows a substantial amount of K_2O, which, combined with the presence of Fe_2O_3 and the fairly weak second-order basal reflection at 5 Å, suggests that the 10-Å-phase mineral is glauconitic. The K_2O content is, however, much higher than expected from the size of the 10 Å reflection in the X-ray diffractograms. This might be due to poor crystallinity, as many glauconites are poorly crystallized. Because of impurities, no further detailed interpretation of the analysis could be made.

The infrared absorption spectrum of the air-dry sample (Fig. 3A) resembles that of berthierine (chamosite) reported by Moenke (1962). The spectrum is similar in many respects to infrared absorption spectra of iron-rich chlorites (Oinuma & Hayashi 1968). The wave numbers of absorption bands for berthierine, as reported by Moenke (1962), are 430, 462, 540, 618, 670, 990, 1080, 3410 and 3550 cm^{-1}. Of these, the major ones are 430, 462, 990 cm^{-1} and the two OH bands. The absorption band at 1080 cm^{-1} is not well defined, as it overlaps the major band at 990 cm^{-1}. These features also are present in the spectrum of Figure 3A except for minor differences where the spectrum has a small band at 815 cm^{-1} and bands on the higher frequency side of the OH band at 3500 cm^{-1}. According to Buckley *et al.* (1978), glauconites exhibit their characteristic band at 815 cm^{-1} and have a rather featureless, broad OH band with a maximum near 3540 and a skewness toward the higher frequency side. The spectrum obtained for the Arctic sample, therefore, may be a composite of berthierine and glauconite.

The sample heated at 550°C for 1 hour has a similar spectrum but with much broader absorption bands, whose frequencies are slightly shifted to the higher side (Fig. 3B). With an expanded scale and slow scanning speed (Fig. 3C), two absorption maxima were resolved at 3460 and 3600 cm^{-1}. The bands are similar to corresponding OH bands of unheated iron-rich chlorite (Oinuma & Hayashi 1968) except that the wave numbers of both absorption bands are 50 cm^{-1} higher in Figure 3C.

The results obtained above indicate that the 7-Å-phase mineral found in the Jaeger soil is a ferro-ferric berthierine with a mixture of monoclinic and orthohexagonal forms. The oc-

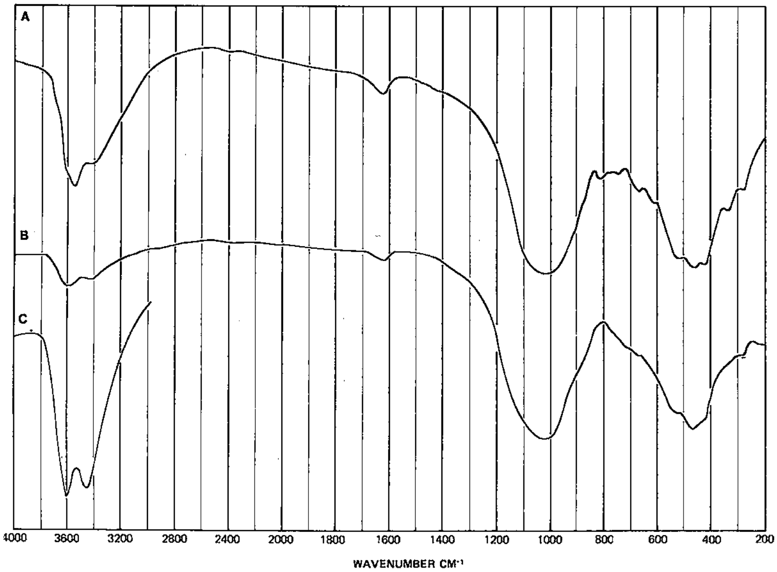

FIG. 3. Infrared spectra of the clay fraction from the A horizon of Jaeger soil. A air-dry, B 550°C, C partial record of the sample heated at 550°C at expanded scale and slow scan rate.

currence of this mineral in soils is very rare because of its high susceptibility to weathering. Soil-forming factors in Ellef Ringnes Island are classified as polar desert, *i.e.*, very low temperature and precipitation; these factors provide a severely restricted weathering environment. This may be the main reason for the survival of berthierine in this soil.

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REFERENCES

BAILEY, S.W., BRINDLEY, G.W., JOHNS, W.D., MARTIN, R.T. & ROSS, M. (1971): Summary of national and international recommendations on clay mineral nomenclature. *Clays Clay Minerals* **19**, 129-132.

———, ———, KODAMA, H. & MARTIN, R.T. (1979): Report of the Clay Mineral Society Nomenclature Committee for 1977 and 1978. *Clays Clay Minerals* **27**, 238-239.

BRINDLEY, G.W. (1951): The crystal structure of some chamosite minerals. *Mineral. Mag.* **29**, 502-525.

———. OUGHTON, B.M. & YOUELL, R.F. (1951): The crystal structure of amesite and its thermal decomposition. *Acta Cryst.* **4**, 552-557.

——— & YOUELL, R.F. (1953): Ferrous chamosite and ferric chamosite. *Mineral. Mag.* **30**, 57-70.

BUCKLEY, H.A., BEVAN, J.C., BROWN, K.M., JOHNSON, L.R. & FARMER, V.C. (1978): Glauconite and celadonite: two separate mineral species. *Mineral. Mag.* **42**, 373-382.

FOSCOLOS, A.E. & KODAMA, H. (1981): Mineralogy and chemistry of polar desert soils in Ellef Ringnes Island, Arctic Canada. *Soil Sci. Soc. Amer. Proc.* **45**, (in press).

MOENKE, H. (1962): *Mineralspektren (Aufgenommen mit Jenaer Spektralphotometer. UR10). Die Ultrarotabsorption der Häufigsten und Wirtschaftlich Wichtigsten Halogenid-, Oxyd-, Hydroxyd-, Carbonat-, Nitrat-, Borat-, Sulfat-, Chromat-, Wolframat-, Molybdat-, Phosphat-, Arsenat-, Vanadat-, und Silikatmineralien im Spektralbereich 400-4000 cm^{-1}*. Akademie-Verlag, Berlin.

OINUMA, K. & HAYASHI, H. (1968): Infrared spectra of clay minerals. *J. Toyo Univ. Gen. Educ. (Nat. Sci.)* **9**, 57-98.

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