Canadian Mineralogist
Vol. 14, pp. 159-163 (1976)

MIXED-LAYER KAOLINITE-MONTMORILLONITE FROM SOILS NEAR DAWSON, YUKON TERRITORY[1]

H. KODAMA, N. MILES, S. SHIMODA,[2] AND J. E. BRYDON[3]
Soil Research Institute, Agriculture Canada, Ottawa, Ontario K1A 0C6

ABSTRACT

Clay fractions of soils at two sites, which are 21 km apart, near Dawson contain a mineral having a broad X-ray diffraction reflection at about 7∼8Å. A mineralogical study of one representative soil sample was carried out with X-ray diffraction, chemical and infrared-absorption methods. The results indicate that the mineral is a mixed-layer kaolinite-montmorillonite with an irregular stacking manner and with an approximate proportion of 0.6∼0.7 for the kaolinite component.

SOMMAIRE

La fraction argileuse de sols prélevés aux environs de Dawson, en deux sites distants de 21 km contien un minéral caractérisé par une raie diffuse de diffraction des rayons-X correspondant à un espacement d'environ 7 à 8Å. L'étude minéralogique d'un échantillon typique du sol, effectuée par diverses méthodes des rayons-X, analyse chimique et absorption infra-rouge indique que le minéral consiste en un empilement de irrégulier couches mixtes kaolinite-montmorillonite, dans lequel la fraction de kaolinite atteint ∼0.6 à 0.7.

(Traduit par le journal)

INTRODUCTION

Brydon & Shimoda (1970) summarized the occurrence of disordered kaolinite minerals in Canadian soils, and briefly mentioned an interstratified clay mineral with kaolin and 2:1-type layers in a soil (SSG 13) from the Yukon Territory. This sample was later examined by L. G. Schultz (personal communication, 1972). Subsequent study of the mineral has attested that it is a mixed-layer kaolinite-montmorillonite with an irregular stacking manner. Similar mixed-layer minerals were also found in different horizons and in other soils in the Yukon Territory. To our knowledge, this is the first report of the occurrence of such minerals in Canada. The purpose of this paper is to describe the mixed-layer kaolinite-montmorillonite found in the soils, which is believed to be relatively uncommon and may have been related to a specific mineral transformation process.

A combination of kaolinite and smectite as component layers of an interstratified mineral was first reported from Japan by Sudo & Hayashi (1956) and Sudo (1959). Shimoyama *et al.* (1969) established further mineralogical data for the Japanese clays and concluded that the minerals were complicated interstratifications of montmorillonite-halloysite (10Å)-metahalloysite (7Å). Altschuler *et al.* (1963) demonstrated the case of the transformation of montmorillonite into kaolinite in Florida in which kaolinized montmorillonite was mentioned. A relatively well-crystallized mixed-layer kaolinite-montmorillonite has recently been reported from Mexico by Schultz *et al.* (1971) and from Poland by Wiewiora (1971, 1973). These recent reports and the calculated X-ray diffraction profiles for such a combination (Cradwick & Wilson 1972) facilitated the identification of this type of mineral in Canadian soil samples.

SAMPLE STUDIED

The original soil samples were collected by J. Day of the S.R.I. in cooperation with O. Hughes

TABLE 1. DESCRIPTION OF THE SOIL SAMPLES

Site 1			Site 2		
51 km southeast from Dawson on Klondike Highway			72 km southeast from Dawson on Klondike Highway		
Lab Sample Number	Horizon	Depth (cm)	Lab Sample Number	Horizon	Depth (cm)
SSG 9	Bm 1	0-3	SSG 16	Ae	0-14
SSG 10	Bm 2	3-29	SSG 17	Bfj	14-21
SSG 11	II Bf	29-54	SSG 18	C	21-36
SSG 12	II Bfc	54-109	SSG 19	II Bf	36-58
SSG 13	II Bm	109-139	SSG 20	II BC_1	58-80
SSG 14	II Bc	139-199	SSG 21	II BC_2	80-130
SSG 15	II C	199^+	SSG 22	II C	130^+

---

[1] Contribution No. 562 (SRI).

[2] Present address (S.S.): Geological and Mineralogical Institute, Faculty of Science, Tokyo University of Education.

[3] Present address (J.E.B.): Environmental Protection Service, Environment Canada Ottawa, Ontario K1A 0H3.

of the Geological Survey of Canada at two sites near Dawson, Yukon Territory on the basis of the paper by Bostock (1966). Coarse and fine clay fractions were separated from the various soil horizons (Table 1) by a combination of sedimentation and centrifugation. Preliminary X-ray diffraction data indicated that the mixed-layer kaolinite-montmorillonite was concentrated in the fine clay fractions (<0.2 μm) from all horizons at both sites except for the two top horizons at site 1 (SSG 9 and 10). The mixed-layer mineral was associated commonly with mica, chlorite-vermiculite intermediate, quartz, and traces of chlorite and kaolinite. Because of its relative purity, the fine clay fraction of sample SSG 11 from the IIBf horizon was chosen for the present study.

Experimental Results

Figure 1 shows X-ray diffraction patterns obtained on oriented aggregates of the Ca-saturated, fine clay fraction (< 0.2 μm) of SSG 11 before and after various treatments. An air-dry sample (Fig. 1a) gave three major broad reflections near 13, 10 and 7.8Å in the low 2θ region. The background of the diffraction pattern in this region was high and steeply increased as the 2θ angle approached zero, which suggests the pre-

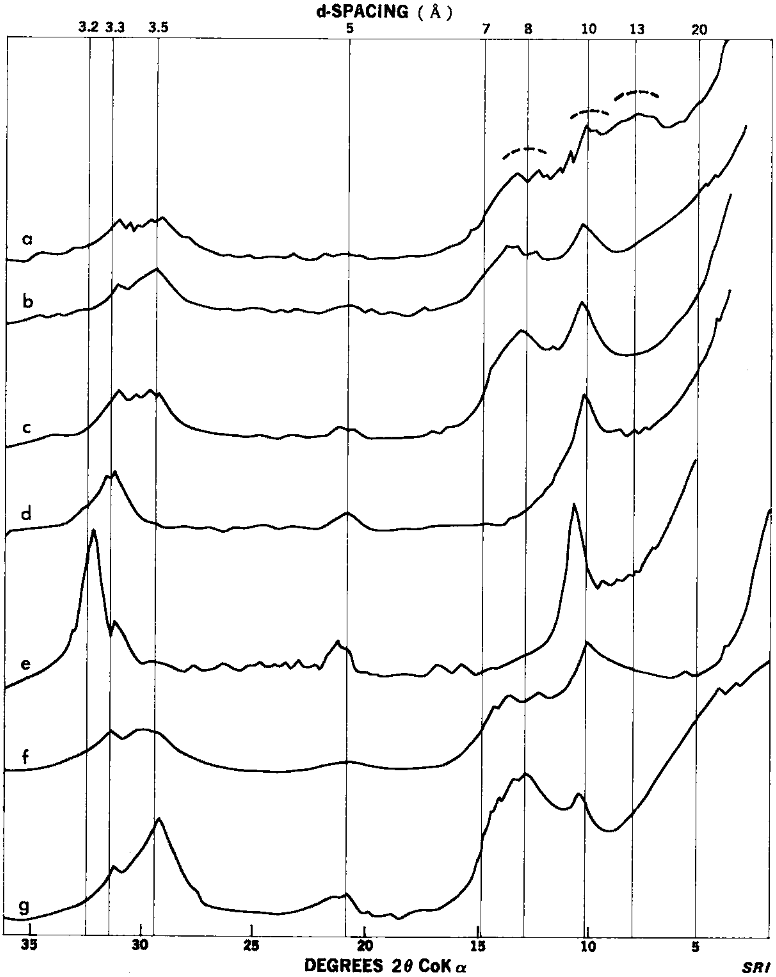

FIG. 1. X-ray diffraction patterns of oriented specimen of the Ca-saturated <0.2 μm clay fraction from sample SSG 11. (a) Air-dry; (b) glycerol-saturated; (c) after heating the air-dry specimen at 300°C; (d) after heating at 500°C; (e) after heating at 700°C; (f) air-dry sesquioxide-free; (g) glycerol-saturated sesquioxide-free.

sence of non-crystalline and fine particle-size material. Solvation with glycerol (Fig. 1b) diffused the 13Å reflection into a part of the background to leave a continuous wide diffraction band around 4° - 6° 2θ range (Co$K\alpha$, λ = 1.7902Å), whereas the 10Å and 7.8Å reflections remained virtually unchanged. Heating at 300°C (Fig. 1c) eliminated the 13Å reflection, left the 10Å reflection unchanged, and enhanced slightly the height of the 7.8Å reflection. Heating at higher temperatures produced only 10Å reflections (Fig. 1d and e). At higher 2θ values, the 3.4Å and 3.5Å reflections remained largely unchanged until the sample was heated at 500°C, whereupon the reflection near 3.5Å was eliminated. On heating at 700°C (Fig. 1e), a new and well-defined reflection appeared at 3.24Å. This was closely related to the spacing for the 3rd-order basal spacing of collapsed montmorillonite or vermiculite ($\simeq$9.7Å) rather than that of heated mica (10Å). Other X-ray diffraction data for a non-oriented powder specimen showed no detectable feldspar or quartz. These data also indicated that the layer silicates present were dioctahedral since the sample had a major reflection at 1.50Å.

After removal of free sesquioxides by the dithionite-citrate extraction method (Mehra & Jackson 1960), the height of the background of the low 2θ region was substantially reduced (Fig. 1f). Although the 13Å reflection was poorly defined in the diffraction pattern of the sesquioxide-free sample (Fig. 1f), glycerolation produced the same broad diffraction band in the 4°-6° 2θ (Co$K\alpha$) region (Fig. 1g) as in the diffraction pattern of glycerolated sample from which free sesquioxides were not removed (Fig. 1b). The reflection near 8Å was rather intense and well-defined after solvation with glycerol and its posititon moved to 8.2Å from 7.8Å which was the *d*-spacing under air-dry condition.

DISCUSSION AND CONCLUSIONS

The following interpretations may be derived from the above results. The 10Å component was ascribed to a discrete mica. The 13Å and 7.8Å reflections appeared to indicate random interstratifications (no superstructure). A chloritic component should be excluded from the 13Å phase, since it collapsed to 10Å upon heating ($\geq$ 300°C). An expansion by solvation with glycerol indicated the presence of expanding layers in the 13Å phase. A humid condition of $>$ 95% r.h. (data not given here) also caused an expansion similar to that on glycerolation. This suggested that the expanding layers were montmorillonitic rather than vermiculitic. Thus, it is likely that the 13Å phase is an interstratification of mica and montmorillonite.

Although the 7.8Å phase did not appear to be sensitive to various experimental conditions such as dry, wet and solvation with glycerol, heating at 300°C exhibited a small but definite expansion of spacing from 7.8 to 8.0Å. This reflection disappeared on heating at 500°C. These features were markedly similar to those described by Schultz *et al.* (1971) for mixed-layer kaolinite-montmorillonite from Mexico. In fact, they stated that the features most diagnostic of the mixed-layer character was an X-ray reflection near 8Å after heating at 300°C. Similar interpretations may be applied to confirm that the 7.8Å phase in SSG 11 is a mixed-layer kaolinite-montmorillonite. Under air-dry condition (30~50% r.h.), Ca-saturated montmorillonite has its first-order basal reflection at 15.4Å and the second-order at 7.7Å. If such montmorillonite layers are interstratified with kaolinite layers having the first-order basal reflection at 7.2Å, diffraction interference phenomena could produce a composite reflection between 7.7 and 7.2Å. When the Ca-saturated montmorillonite is solvated with glycerol, its layer expands to 18Å. An interference reflection may then appear between 9 (=18Å/2) and 7.2Å. Upon heating at 300°C, the layer contracts to 9.6Å. Therefore, the interference reflection may appear between 9.6 and 7.2Å. The positions of reflection maxima are a function of the mixing ratio of the two components, kaolinite and montmorillonite. Thus, it is possible to evaluate an approximate ratio from an observed *d*-spacing by reference to calculated data. The data after heating at 300°C, which are the most diagnostic, gave a reflection maxima at 8Å and that was plotted on the calculated reflection migration curve of Cradwick & Wilson (1972). The plotting corresponded to a ratio of 0.6:0.4 for kaolinite to montmorillonite. A similar ratio was also obtained from data after glycerolation.

Infrared data (Fig. 2) provided useful additional information (Kodama & Oinuma 1963; Oinuma & Kodama 1964). In the OH-stretching region there are three distinct absorptions at 3700, 3625, and 3430 cm^{-1} and a shoulder-like absorption at 3650 cm^{-1}. The 3700 and 3625 cm^{-1} and the shoulder-like absorption bands are characteristic of kaolinite. The major band at 3625 cm^{-1} is also common to muscovite and montmorillonite. The absorption at 3430 cm^{-1} can be assigned to hydrogen-bonding OH vibrations which may originate from interlayer water in montmorillonite or related minerals. In the region 1200-300 cm^{-1}, two large broad absorption maxima appeared around 1000 and 500 cm^{-1}, and were associated with small but well-defined absorption bands at 1100, 1035, 1010, 912, 750, 693, 530, 468, 430 and 350 cm^{-1}. Overall, the pattern resembled a composite spectrum of three minerals, kaolinite, muscovite and montmorillonite (Farmer 1974). The absorption at 430 cm^{-1} may be another indication of the presence of kaolinite, since the two other minerals do not have a distinct band at that wave-number. An absorption band at 833 cm^{-1} which belongs to muscovite was missing. The quantity of muscovite, therefore, should not be high. Although the spectra strongly indicate the presence of kaolinite, X-ray data showed only an indistinct hump at around 7.2Å, which might be due to a small amount of discrete kaolinite. Thus, the major portion of the infrared spectra belonging to kaolinite should be assigned to the component with a kaolinitic structure of the mixed-layer mineral.

To account for some impurities, some corrections were made based upon chemical analysis. The air-dry sample contains 1.8% amorphous Al_2O_3, 6.9% amorphous Fe_2O_3, and 4.7% moisture (<100°C). On the sesquioxide-free and moisture-free basis, the sample consisted of 47.6%, SiO_2, 26.1% Al_2O_3, 7.6% Fe_2O_3, 1.0% MgO, 1.2% CaO, 0.7% K_2O, 0.1% Na_2O and 15.7% ignition loss. Assuming that the mica component in the sample is similar to so-called illite having an idealized formula, $(K,Na)_{0.66}Al_2(Si_{3.34}Al_{0.66})O_{10}(OH)_2$, (using the average illite K content as 8% K_2O, *c.f.* Weaver 1965), the total composition mentioned above was corrected for the mica compostiton after the total alkalis had been allocated to the mica composition. The corrected values are 47.1% SiO_2, 25.1% Al_2O_3, 8.4% Fe_2O_3, 1.1% MgO, 1.3% CaO and 16.9% ignition loss which are similar to those expected for the mixed-layer kaolinite-montmorillonite minerals (Shimoyama *et al.* 1969; Schultz *et al.* 1971). The SiO_2/Al_2O_3 ratio of ideal kaolinite is 1.18. An average $SiO_2/(Al_2O_3+Fe_2O_3+MgO)$ ratio of Wyoming-type montmorillonite is about 1.9 (*c.f.* Weaver & Polland 1973). If we ignore the small montmorillonite component in the mixed-layer mica-montmorillonite, the proportion of the kaolinite component (X) in the mixed-layer kaolinite-montmorillonite can be evaluated from the equation, $1.18X + 1.9\,(1\text{-}X) = SiO_2/(Al_2O_3 + Fe_2O_3 + MgO)$ where the ratio is 1.4 in this case. This calculation indicates that 70% of the mixed-layer is a kaolinite component. The cation exchange capacity of SSG 11 was 37 meq/100g. The value is slightly higher than expected for a 30% montmorillonite content but closer to the 40% montmorillonite content from the peak migration curve, although a small amount of the montmorillonitic component in the mixed-layer mica-montmorillonite should also contribute to this value.

In conclusion, the 8Å-phase in SSG 11 is a mixed-layer kaolinite-montmorillonite with an irregular stacking manner and with an approximate mixing ratio of 0.6~0.7 for the kaolinite component. Similar conclusions can be extended to 8Å-phases of soils in different horizons at the two sites. No substantial variation in the mixing ratio was found among those samples.

ACKNOWLEDGMENTS

We gratefully acknowledge the technical assistance of D. Graham, M. Jaackimainnen, G. C. Scott, and R. Hill. Particular thanks are due to J. Day, Soil Research Institute, for providing valuable soil samples. We also thank L. G. Schultz, U.S.G.S. Denver, Colorado for kindly

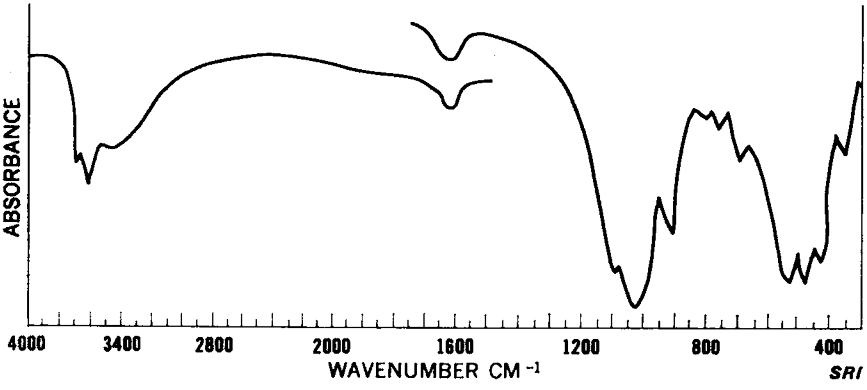

FIG. 2. Infrared absorption spectra of Ca-saturated specimen of the <0.2 μm clay fraction from sample SSG 11.

furnishing preliminary information of sample SSG 13 and his interpretation. Critical reviews by G. J. Ross are greatly appreciated.

REFERENCES

ALTSCHULER, Z. S., DWORNIK, E. J. & KRAMER, H. (1963): Transformation of montmorillonite to kaolinite during weathering. *Science* **141**, 148-152.

BOSTOCK, H. S. (1966): Notes on glaciation in central Yukon Territory. *Geol. Surv. Can. Pap.* **65-36**.

BRYDON, J. E. & SHIMODA, S. (1970): Disordered kaolin-like minerals in Canadian soils. Presented at 7th Meet. *Clay Minerals Soc.* Miami, Florida, U.S.A.

CRADWICK, P. D. & WILSON, M. J. (1972): Calculated X-ray diffraction profiles for interstratified kaolinite-montmorillonite. *Clay Minerals* **9**, 395-415.

FARMER, V. C. (1974): Chapter 15. The layer silicates. *In* The Infrared Spectra of Minerals (V. C. Farmer, ed.). 331-363.

KODAMA, H. & OINUMA, K. (1963): Identification of kaolinite minerals in the presence of chlorite by X-ray diffraction and infrared absorption spectra. *Clays Clay Minerals* **11**, 236-249.

MEHRA, O. P. & JACKSON, M. L. (1960): Iron oxide removed from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Minerals* **8**, 317-327.

OINUMA, K. & KODAMA, H. (1964): Infrared absorption spectra of clay minerals in the region from 2800 to 700 cm^{-1}. *J. Tokyo Univ. Nat. Sci.*, No. 5, 1-22 (in Japanese).

SCHULTZ, L. G., SHEPARD, A. O., BLACKMON, P. D. & STARKEY, H. C. (1971): Mixed-layer kaolinite-montmorillonite from the Yucatan Peninsula, Mexico. *Clays Clay Minerals* **19**, 137-150.

SHIMOYAMA, A., JOHNS, W. D. & SUDO, T. (1969): Montmorillonite-kaolin clay in acid clay deposits from Japan. *Proc. Int. Clay Conf. Tokyo*, **1**, 225-231.

SUDO, T. (1959): *Mineralogical Study on Clays of Japan.* Maruzen, Tokyo. 328 p.

——— & HAYASHI, H. (1956): A randomly interstratified kaolin-montmorillonite in acid clay deposits in Japan. *Nature* **178**, 1115-1116.

WEAVER, C. E. (1965): Potassium content of illites. *Science* **147**, 603-605.

——— & POLLARD, L. D. (1973): *The Chemistry of Clay Minerals.* Elsevier Scientific Publ. Co., New York, 213 pp.

WIEWIORA, A. (1971): A mixed-layer kaolinite-smectite from lower Silesia, Poland. *Clays Clay Minerals* **19**, 415-416.

——— (1973): Mixed-layer kaolinite-smectite from Silesia, Poland. Final Rep. *Proc. Int. Clay Conf., Madrid.* 75-88.

Manuscript received August 1975, emended November 1975.