

This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.

CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

OTTAWA

MINES BRANCH INVESTIGATION REPORT

IR 69-70

September 18, 1969

MINERALOGICAL EXAMINATION OF TWO CLAYS
FROM THE MUSQUODOBOIT RIVER VALLEY,
NOVA SCOTIA.

by

R. S. Dean

Mineral Processing Division

Mines Branch Investigation Report IR 69-70

MINERALOGICAL EXAMINATION OF TWO CLAYS FROM
THE MUSQUODOBOIT RIVER VALLEY, NOVA SCOTIA

by

R. S. Dean*

SUMMARY OF RESULTS

The two clays, of presumed Cretaceous age, were found to consist largely of quartz, disordered kaolinite, and dioctahedral mica of highly variable crystallinity. Hematite, anatase and rutile were identified as minor constituents.

* Research Scientist, Mineral Processing Division, Mines Branch,
Department of Energy, Mines and Resources, Ottawa, Canada.

CONTENTS

	<u>Page</u>
Summary of Results	i
Introduction	1
Procedure	1
Results	2
Conclusions	6
Acknowledgements	6
References	7

TABLES

No.

1. Mineralogy of Musquodoboit Valley Clay Samples	3
---	---

FIGURES

1. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Sample No. 1 clay	4
2. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Sample No. 2 clay	5

INTRODUCTION

On March 4, 1969, two samples of clay were submitted for mineralogical examination to the Mineral Processing Division, Mines Branch, by Dr. J.D. Wright, Director, Geological Division, Nova Scotia Department of Mines, Halifax, Nova Scotia. The project was assigned Laboratory Number MP-MIN-1254.

Both samples had been collected from the valley of the Musquodoboit River, Halifax County, Nova Scotia. Sample No. 1, a light red clay designated as "PB Lab No. 68-83" is a composite sample from a total of 255 feet of drill core from the clay horizon at Paint Brook. This deposit, which has been briefly described by Stevenson (1, p. 70), was sampled at various localities between approximately 0.25 and 0.5 miles north of the mouth of Paint Brook. Sample No. 2 was designated as "EL 81 [2,3] and EL 82 [1]" and is a buff composite sample of clays from two drill holes 0.35 and 0.45 miles south of the bridge at Reid. Both the Reid and Paint Brook localities are shown as clay deposits on Map 1076A, which accompanies the report by Stevenson. The clays are thought to be of Cretaceous age (1, p. 35).

PROCEDURE

Portions of each of the two samples were finely ground in an agate mortar and examined with a Guinier-deWolff 4-sample X-ray powder diffraction camera (2).

Preliminary attempts to form stable suspensions of the clays in demineralized distilled water by stirring were unsuccessful, as were attempts to reduce clay flocculation by repeated washing and centrifugation. Effective peptization of the clays was eventually accomplished by the drop-wise addition of ammonia solution which, according to Whitehouse and Jeffrey (3, p. 275), effects optimum peptization of kaolinitic clay at approximately 0.009N NH_4OH .

The peptized suspensions were separated by centrifugation into fractions consisting of mineral particles having equivalent settling diameters greater or less than 5 microns. The coarse (plus 5-micron) fractions were examined with the Guinier camera. The minus 5-micron suspensions were concentrated by centrifugation at 10,000 rpm in a Sorvall SS-3 Superspeed Centrifuge. Free iron oxides were removed by the dithionite-citrate method of Mehra and Jackson (4).

Oriented-aggregate mounts were prepared by evaporating to dryness, on glass slides, small portions of the treated minus 5-micron clay suspensions. These were scanned with a North American Philips High Angle X-ray Diffractometer when air-dry and following saturation with ethylene glycol. Guinier X-ray powder photographs were also taken of the treated, minus 5-micron clays.

Kaolin minerals were removed from the iron oxide-free clays by a slightly modified version of the differential dissolution technique of Hashimoto and Jackson (5): the samples were heated for one hour at 550°C, dispersed in a small volume of water by wet grinding in an agate mortar, and boiled for 3 minutes in 0.5N NaOH solution. A NaOH solution/clay ratio of at least 200 ml NaOH per 0.1 g clay was maintained. The residue from this treatment was collected by centrifugation, washed twice with demineralized distilled water, and analyzed with the Guinier X-ray powder camera. Oriented mounts of the treated clays were prepared on borosilicate glass slides, and these were scanned with the X-ray diffractometer before and after heat treatment for one hour at 580°C.

RESULTS

The results of the X-ray diffraction analyses of the Musquodoboit Valley clays are listed in Table 1 and show the close mineralogical similarity of the two samples. Kaolin and quartz, the two major constituents, were concentrated within the fine and coarse size fractions respectively.

The X-ray diffractograms showed that the kaolin yielded sharp basal reflections (Figure 1, Scan 1) and the X-ray powder photographs disclosed a considerable degree of layer-stacking disorder. The kaolins of both clays, and especially Sample No. 1, are probably best described as disordered members of the series extending between triclinic kaolinite and disordered dehydrated halloysite (6).

The clay micas are unusual in that very large variations in structural type occurred between the coarse and fine size fractions. The powder photographs of the plus 5-micron fractions, and particularly that of Sample No. 2, showed a sharp pattern characteristic of 2M₁ muscovite, whereas only a few very broad and indistinct polymorph lines were observed in the minus 5-micron fractions, indicating that the mica within the latter is largely 1 Md (7, pp. 236-237).

TABLE 1

Mineralogy of Musquodoboit Valley Clay Samples

Mineral	Sample No. 1			Sample No. 2		
	Size Fraction			Size Fraction		
	Whole	Plus 5-Micron	Minus 5-Micron*	Whole	Plus 5-Micron	Minus 5-Micron*
Kaolin	B	B	A	B	B	A
Mica	D	C	E	D	C	E
Quartz	B	B	F	B	B	F
Hematite	E	E	-	F	G	-
Anatase	G	G	F	G	G	F
Rutile	G	G	G	G	G	G

Abundance of minerals estimated from "A." (very abundant) to "G" (trace).

* Free iron oxides removed.

The diffractogram in Figure 1, Scan 2 shows how the clay mica pattern from the minus 5-micron fraction of Sample No. 1 was enhanced by NaOH dissolution of the dehydroxylated kaolin. Figure 2, Scan 1 is the diffractogram of the Sample No. 2 clay following the same treatment. The asymmetrical broadening toward lower Bragg angles of the 9.8A reflection from both of these residues suggests the presence of expanded layers within the mica structure. The occurrence of these following the 550°C heat treatment strongly suggests that the expanded layers originally contained interlayer material which, in view of the kaolinitic nature of the clay, would probably have been aluminous in composition (8). Such aluminous interlayer complexes would probably be dehydroxylated by the 550°C heat treatment and subsequently dissolved by NaOH (5, p. 104). Clear evidence of the collapse of the leached interlayer spaces by further heat treatment (Figure 2, Scan 2) is obscured by the low thermal stability of the minus 5-micron mica.

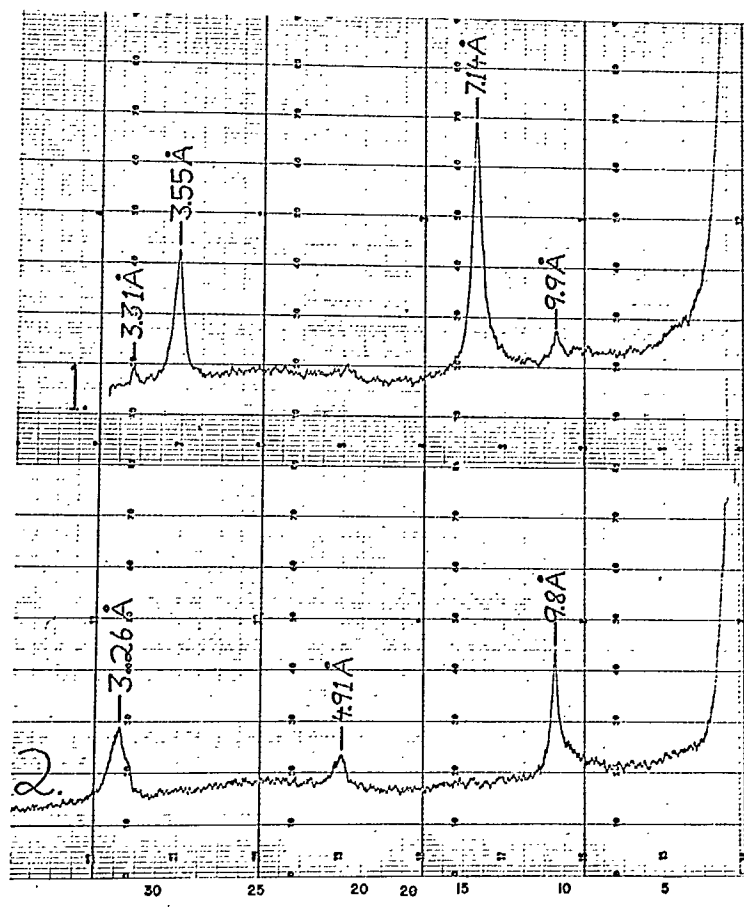


Figure 1. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Sample No. 1 clay.

Co/Fe radiation; total scale deflection - 400 counts; time constant -8; scanning speed $0.5^\circ 2\theta/\text{minute}$; 1° slits; proportional counter detector with pulse-height analyser.

Scan 1 - Iron oxides removed; air dry

Scan 2 - Iron oxides removed; heated 1 hour at 550°C ,
3 minutes 0.5N NaOH boil

Kaolin - $7.14; 3.55 \text{ \AA}$

Mica - All other reflections.

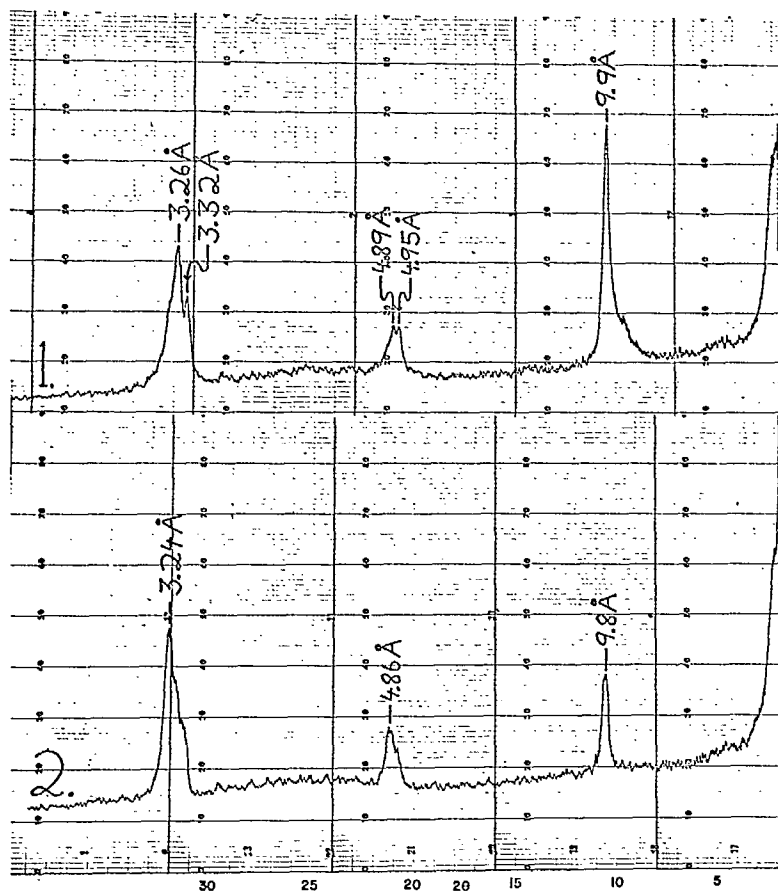


Figure 2. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Sample No. 2 clay.

Co/Fe radiation; total scale deflection - 400 counts; time constant -8; scanning speed $0.5^\circ 2\theta/\text{minute}$; 1° slits; proportional counter detector with pulse-height analyser.

Scan 1 - Iron oxides removed; heated 1 hour at 550°C ,
3 minutes 0.5N NaOH boil

Scan 2 - Iron oxides removed; heated 1 hour at 550°C ,
3 minutes 0.5N NaOH boil followed by 1 hour
heat treatment at 580°C .

Mica - All reflections.

The diffractograms in Figure 2 also illustrate a remarkable stepwise thermal collapse of the Sample No. 2 clay mica basal spacing through the sequence:

$$9.96 \overset{\circ}{\text{\AA}} \rightarrow 9.78 \overset{\circ}{\text{\AA}} \rightarrow 9.72 \overset{\circ}{\text{\AA}}$$

as calculated from the integral series of 00 ℓ reflections which were obtained from each stage. The collapse of clay mica layers to spacings below 10 \AA suggests the replacement of interlayer K^+ by smaller cations (9).

CONCLUSIONS

The Musquodoboit clay samples consist largely of disordered kaolinite, quartz and mica. The mica is notably heterogeneous. The coarser and apparently unaltered size fractions yielded X-ray powder patterns of 2M_1 muscovite whereas the finer fractions showed features consistent with rather intense mica weathering: near absence of layer-stacking order; replacement of K^+ by smaller cation(s); low thermal stability (10); and the possible intercalation of aluminous interlayer complexes.

ACKNOWLEDGEMENTS

The writer wishes to acknowledge technical assistance by C.H.J. Childe and H.C. James.

REFERENCES

1. I.M. Stevenson, "Shubenacadie and Kennetcook Map-Areas, Colchester, Hants and Halifax Counties, Nova Scotia", Memoir 302, Geological Survey of Canada (1959).
2. P.M. deWolff, "Multiple Guinier Cameras", *Acta Cryst.* 1, 207-211 (1948).
3. U.G. Whitehouse and L.M. Jeffrey, "Peptization Resistance of Selected Samples of Kaolinitic, Montmorillonitic, and Illitic Clay Materials", *in* *Clays and Clay Minerals*, Proc. Third National Conference on Clays and Clay Minerals, Nat. Acad. Sci. - Nat. Res. Council Pub. 359, 260-281 (1955).
4. O.P. Mehra and M.L. Jackson, "Iron Oxide Removal from Soils and Clays by a Dithionite-Citrate System Buffered with Sodium Bicarbonate", *in* *Clays and Clay Minerals*, Proc. Seventh National Conference on Clays and Clay Minerals, Pergamon Press, New York, 317-327 (1960).
5. I. Hashimoto and M.L. Jackson, "Rapid Dissolution of Allophane and Kaolinite - Halloysite after Dehydration", *in* *Clays and Clay Minerals*, Proc. Seventh National Conference on Clays and Clay Minerals, Pergamon Press, New York, 102-113 (1960).
6. G.W. Brindley, "Kaolin, Serpentine, and Kindred Minerals", *in* *The X-ray Identification and Crystal Structures of Clay Minerals*, Mineralogical Society, London, 51-131 (1961).
7. W.F. Bradley and R.E. Grim, "Mica Clay Minerals", *in* *The X-ray Identification and Crystal Structures of Clay Minerals*, Mineralogical Society, London, 208-241 (1961).
8. M.L. Jackson, "Interlayering of Expansible Layer Silicates in Soils by Chemical Weathering", *in* *Clays and Clay Minerals*, Proc. Eleventh National Conference on Clays and Clay Minerals, The MacMillan Company, New York, 29-46 (1963).
9. J.L. Martin Vivaldi, D.M.C. MacEwan and M. Rodriguez Gallego, "Effect of Thermal Treatment on the c Axial Dimension of Montmorillonite as a Function of the Exchange Cation", *in* Proc. International Clay Conference, Stockholm, Sweden, Aug. 12-16, 1963, The MacMillan Company, New York, 1, 45-51 (1963).

10. R. Roy, "Decomposition and Resynthesis of the Micas", Jour. Amer. Ceram. Soc. 32, 202-209 (1949).

===

RSD/cw