# MONTMORILLONITE OR SMECTITE AS CONSTITUENTS OF FULLER'S EARTH AND BENTONITE

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#### ABSTRACT

Three conclusions are supported by the investigation outlined in this paper. (1) The two hydrous aluminum silicates, montmorillonite and smectite, appear to be identical. (2) Both may be prominent as constituents of bentonite and fuller's earth. (3) Fuller's earth from one or more long recognized European localities has been formed by the alteration of volcanic ash to smectite (montmorillonite). This is a type of origin generally relied upon to determine bentonite.

## GENERAL STATEMENT

Montmorillonite was described in 1847 by Damour and Salvétat.<sup>1</sup> Prior to that time a clay with similar physical and chemical properties had been known as smectite. This was, at that time, a common mineral name, and in the mineralogical texts of the 18th. century was used synonymously with fuller's earth. Kirwan<sup>2</sup> for example, in his second edition of Elements of Mineralogy (1794) used the words "walkererde" and "smectis" in addition to fuller's earth. Haüy<sup>3</sup> in 1801 used the terms smectite clay and fuller's earth. The general impression prevailed that smectite was a hydrous aluminum silicate containing magnesium and calcium as additional chemical constituents.<sup>4</sup> Early analyses<sup>5</sup> of smectite were somewhat questionable, although fuller's earth had been referred to in the literature since the time of Pliny,<sup>6</sup> A.D. 29.

The description of montmorillonite by Damour and Salvétat included a chemical study. Their analysis was more definite than the analyses of smectite then existing, although since that time better analyses of smectite have been recorded.<sup>7</sup> The mineral, however, appears to have escaped description by modern methods.

<sup>1</sup> Damour, and Salvétat, Ann. Chimie et de Physique, 3rd. series, vol. 21, 1847, p. 376.

<sup>2</sup> Kirwin, Richard, Elements of Mineralogy, 2nd. ed., vol. 1, 1794, p. 184.

<sup>3</sup> Haüy, Abbé René Just, Traité de Mineralogie, vol. 4, 1801, p. 444.

<sup>4</sup> Breithaupt, August, Handbuch der Mineralogie, vol. 2, 1844, p. 544.

<sup>5</sup> Thomson, Thomas, Outlines of Mineralogy, Geology, and Mineral Analysis, vol. 1, 1836, p. 246.

<sup>6</sup> The Natural History of Pliny A.D. 29. Trans. by Philemon Holland, 1601, p. 560.

<sup>7</sup> Jordan, L. A., Ann. Physik. u. Chemie, Poggendorff, vol. 77, Leipzig, 1849, p. 591.

Montmorillonite, on the other hand, has recently been extensively studied, and is generally recognized as one of the essential constituents of bentonite, in addition to other modes of occurrence.<sup>8</sup>

In connection with recent x-ray studies of bentonite<sup>9</sup> several x-ray diffraction patterns of smectite were taken which were noted to be identical with those of montmorillonite. Other comparative studies were then carried out on the two minerals with the conclusion that they appear to be identical.<sup>10</sup>

The practical significance of this conclusion is considerable. Smectite has been frequently considered to be a prominent clay mineral constituent of fuller's earth.<sup>11</sup> The clay mineral constituent of bentonite, however, is regarded as montmorillonite. If the two minerals are identical, the information should be of working value in studying technical applications of both bentonite and fuller's earth.<sup>12</sup>

The situation also raises a question of nomenclature. Which name should be retained for this clay mineral? Montmorillonite is today a well substantiated mineral name, whereas smectite, a name of prior origin is but little used at present. It would seem that the rule which calls for the least confusion in mineralogical literature would necessitate the use of the name montmorillonite, which has become common in the modern literature of clay minerals.

Examination of thin sections of smectite demonstrates that in two of the localities studied the clay has been derived by the alteration of volcanic ash. Such an origin should lead to the conclusion that, by modern definition, the clay is bentonite. We are thus placed in the apparently peculiar position of renaming a clay, bentonite, which has long been called fuller's earth. It should be pointed out, therefore, that bentonite is a rock definition while

<sup>8</sup> Ross, Clarence S. and Shannon, Earl V., *Jour. Amer. Ceram. Soc.*, vol. 9, no. 22, 1926, p. 77.

<sup>9</sup> Kerr, Paul F., Econ. Geol., vol. 26, 1931, p. 153.

<sup>10</sup> Malthacite is probably another earlier mineral name synonymous with montmorillonite. Studies of malthacite, however, are not yet complete.

<sup>11</sup> English fuller's earth, for example, has long been considered to contain smectite.<sup>11a</sup> This has been confirmed by recent reanalysis and x-ray study of clay from Woburn Sands.

<sup>11a</sup> Woodward, H. B., Jurassic Rocks of Great Britain: *Mem. Geol. Surv.*, (London), vol. **4**, 1894.

<sup>12</sup> Study of the clay mineral constituents of fuller's earth is beyond the scope of this paper. Studies are under way, however, which indicate at least a partial correlation of the clay mineral constituents of fuller's earth and bentonite.

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this term fuller's earth is based upon commercial application. A naturally adsorptive clay of standard efficiency would be known as a fuller's earth. This material might very well, at the same time, be derived from volcanic ash, and hence would be bentonite from the petrographic standpoint.

# X-RAY DIFFRACTION PATTERNS OF SMECTITE AND MONTMORILLONITE

Smectite from two recognized localities has been examined recently. Several specimens from Cilly, Styria, were presented to the Egleston Mineral Collection of Columbia University by Mr. F. R. Coudert. This locality was described by Jordan. The other smectite samples were from Woburn Sands, England, and were presented by Prof. H. Ries of Cornell University. The occurrence of smectite at Woburn Sands was mentioned as long ago as 1809 by Kidd.<sup>13</sup>

A number of x-ray diffraction patterns of montmorillonite have been taken in the last few years. These include the samples described by Ross and Shannon<sup>8</sup> together with montmorillonite from other sources. X-ray work closely confirms the results of optical and chemical studies published by Ross and Shannon as previously reported.<sup>14</sup>

Line no.	Smectite or Montmorillonite		
	Outer edge in mm. from zero beam.	Spacing in A.U. $\times$ 10 cm.	
1	18.3	4.49	
2	20.2	4.05	
3	33.0	2.48	
4	49.2	1.67	
5	56.1	1.47	
6	64.2	1.29	
7	66.2	1.250	
8	74.7	1.115	
9	82.0	1.020	
10	85.6	0.976	

TABLE 1

X-RAY DIFFRACTION MEASUREMENTS OF SMECTITE AND MONTMORILLONITE

13 Kidd, J., Outlines of Mineralogy, vol. 1, London, 1809, p. 176.

<sup>14</sup> Bonine, C. A., Report on Sedimentation, Nat'l Research Council, No. 85, 1928, p. 15.

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An x-ray diffraction pattern of montmorillonite is shown in Fig. 1. A corresponding x-ray diffraction pattern of smectite taken at the same time in the opposite side of the same film holder appears in the lower half of the figure. The measurements agree as nearly as can be determined with those previously published for montmorillonite<sup>15</sup> given in table 1.

Both represent a type of pattern due to finely crystallized material. The lines are broad and somewhat diffused. In consequence, measurements are subject to variation. Patterns are not as satisfactory as those of other clay minerals.<sup>16</sup>

Thin sections of blue fuller's earth from Woburn Sands, contain relict structures of volcanic glass fragments in a groundmass of



FIG. 1. Comparative x-ray diffraction patterns of montmorillonite and smectite

smectite.<sup>17</sup> Partially replaced fragments are also visible in places, the material of the fragments consisting of an isotropic mass with an index of refraction considerably lower than the index of refraction of smectite, presumably opal. Other less prominent isotropic remnants with an index of refraction slightly greater than smectite are probably unreplaced remnants of volcanic glass.

Thin sections of smectite from Cilly indicate that the material is more nearly pure smectite than is the case with the material at hand from Woburn Sands. Relict structures of volcanic glass are abundant, but the fragments of the glass itself or opalized glass

16 Kerr, Paul F., Econ. Geol , vol. 26, 1931, p. 153.

<sup>16</sup> Ross, Clarence S. and Kerr, Paul F., U. S. Geol. Survey, Prof. Paper No. **165E**, 1931, p. 151.

<sup>17</sup> Chemical studies indicate that the clay mineral constituent of the Woburn Sands fuller's earth may be beidellite, instead of montmorillonite on account of the presence of about 6 per cent of  $Fe_2O_3$ .

have been entirely replaced. The alteration of volcanic ash to smectite has been almost complete.

Such examination demonstrates that certain deposits of fuller's earth containing smectite have been formed by the alteration of volcanic ash. Ross and Shannon, however, define bentonite as follows:

Bentonite is a *rock* composed essentially of a crystalline clay-like mineral formed by devitrification and the accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash; . . . The characteristic clay-like mineral has a micaceous habit and facile cleavage, high birefringence, and a texture inherited from volcanic tuff or ash, and it is usually the mineral montmorillonite, but less often beidellite.

According to this definition, therefore, the clays of Cilly and Woburn Sands would now be classed as bentonite. On the other hand, from the commercial standpoint, such clays would still be classed as fuller's earth because of their natural adsorptive power.

Fuller's earth has generally been recognized as a clay with a natural high capacity for absorbing oil or grease, and also for ab-

	Smectite from Cilly		
	1	2	3
SiO <sub>2</sub>	51.21	52.43	48.60
Al <sub>2</sub> O <sub>3</sub>	12.25	15.95	20.03
Fe <sub>2</sub> O <sub>3</sub>	2.07	1.42	1.25
FeO	S	.10	
MgO	4.89	5.02	5.24
CaO	2.13	2.97	1.72
MnO			0.16
TiO <sub>2</sub>		.08	3-3
SO <sub>3</sub>		.22	3 <u></u> 2
$P_2O_5$	1 mar 1	.08	
С		.30	· (*=*
H <sub>2</sub> O	27.89	13.96 (at 110°) 7.60 (over 110°)	21.52
Total	100.44	100.13	98.52

TABLE 2

(1) Smectite, Cilly, Lower Styria, by Jordan.

(2) Smectite, Cilly, by Mr. A. M. Smoot of Ledoux & Co., N. Y.

(3) Montmorillonite, Montmorillon, France, by E. V. Shannon.

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sorbing organic and mineral bases, including coloring matter, from solution in vegetable, or mineral oils. The value of fuller's earth depends upon its ability to perform one or more of these functions. The material is usually determined by a practical test of its natural adsorptive efficiency.

## CHEMICAL ANALYSES

Chemical analyses show that both smectite and montmorillonite are hydrous silicates of aluminum with accompanying magnesium, calcium, and iron. The alkali elements either occur in such impurities as feldspar and mica, or are entirely absent. The moisture content is subject to considerable variation with an accompanying influence on the physical properties, notably on the indices of refraction.

Chemical analyses of smectite and montmorillonite are given in table 2.

The analyses by Smoot and by Shannon agree within the limits to be expected for such material. Both fall well within the range for the various constituents usually found in montmorillonite.

# Comparison of Refractive Indices of Smectite and Montmorillonite

The refractive indices of the two minerals are given in table 3. Both minerals occur in fine micaceous flakes and have moderate birefringence. The indices of refraction are in the neighborhood of 1.50 and are subject to variation with the moisture content of the min-

Montmorillonite from France	Smectite from Cilly
$\alpha = 1.485$	$\alpha = 1.490$
$\gamma = 1.506$	$\gamma = 1.506$
$\gamma - \alpha = .021$	$\gamma - \alpha = .016$
Values for sodium	n light; ± .003

TABLE 3

eral. If either mineral is allowed to stand in a desiccator the indices of refraction will be raised appreciably. It is probable that by careful drying two samples could be obtained that would have the same indices of refraction. On standing in the air, however, the values would decrease again, probably unevenly. In view of such considerations the figures given above show reasonable agreement.

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#### ACKNOWLEDGMENTS

Dr. Clarence S. Ross and Dr. Waldemar T. Schaller of the U. S. Geological Survey have kindly gone over the manuscript of this paper and have offered a number of suggestions which have been adopted. Dr. Ross has also examined thin sections of smectite from Cilly and has emphasized the origin as bentonite. The writer wishes to express his appreciation of their interest and cooperation.

#### CONCLUSION

Since the x-ray diffraction patterns, chemical analyses, and refractive indices show such close relationship it seems hardly worth while to retain the two names smectite and montmorillonite for what appears to be the same mineral. In view of the large amount of modern literature on montmorillonite it seems in the best interests of science to continue the name montmorillonite, and to drop that of smectite.

Smectite has been mentioned frequently in descriptions of fuller's earth. It would naturally follow therefore that the name montmorillonite should now replace that of smectite in referring to the clay mineral constituent of fuller's earth. It should also be emphasized that bentonite is a rock while fuller's earth is a clay having a definite commercial application. It is possible for a clay which is a bentonite by origin to have adsorptive properties which make it a fuller's earth.

## NOTES AND NEWS

### PIPERINE AS AN IMMERSION MEDIUM IN SEDIMENTARY PETROGRAPHY

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Piperine was used at least thirty years ago as an immersion medium for microscopic work, and is mentioned in several works on optical mineralogy and petrography as a suitable material for refractive index determination. Although it is probably known to most of those doing petrographic work, it has certain advantages in the examination of detrital minerals which appear to be worthy of special notice.

Directions for use of piperine together with reasons for preferring it to Canada balsam as an immersion medium for microscopic work on diatoms have been given by Chapman Jones.<sup>1</sup> Piperine is a definite chemical compound and is obtained in small crystals. Only the purified grade<sup>2</sup> is suitable for use as an immersion or mounting medium. In mounting grains in piperine it has only to be melted, not cooked, so slides may be prepared very rapidly. However, if the slides are prepared

<sup>1</sup> Jones, Chapman, Piperine as a mounting medium; *Watson's Microscope Record*, May 1925, pp. 11-12.

<sup>2</sup> Obtained from Eastman Kodak Company Rochester.