

## APPLICATION OF MULTIVARIATE ANALYSIS TO MONTMORILLONITE

A. VARTY AND D. WHITE

*The Houldsworth School of Applied Science, The University, Leeds*

*Read 7th April 1964*

**ABSTRACT:** It has frequently been suggested that there is more than one structural type of montmorillonite, and the investigations of Grim and Kulbicki have supported this concept. From the data given by these authors, thirty-six characteristics have been selected and the montmorillonites compared using a multivariate analysis computer programme. The results do not support the hypothesis of two types of montmorillonite, but indicate a random distribution of the samples in an  $n$ -dimensional space.

### INTRODUCTION

The generally accepted structure for montmorillonite is that suggested by Hofmann, Endell & Wilm (1933), and the alternative structure proposed by Edelman & Favejee (1940) has not been in favour (Grim, 1953; MacEwan, 1961). The difference between the two structures is in the orientation of the silica tetrahedra which form the outer sheets of the layer. According to Hofmann *et al.* (1933) the apices of these tetrahedra are directed inwards so that the surface of the clay platelet is a sheet of oxygen atoms, whereas Edelman & Favejee (1940) believe that a certain number of the silica tetrahedra are inverted with apical hydroxyl groups projecting from the clay surface. A full discussion of these concepts and their subsequent modifications is given by MacEwan (1961).

A recent paper by Grim & Kulbicki (1961) has revived interest in this topic, for after an intensive investigation into forty montmorillonites they concluded that there were two different types conforming to the two different structures outlined above. The samples with the Hofmann-Endell-Wilm structure they refer to as Wyoming type and the samples with inverted tetrahedra as Cheto type. This extensive investigation has also drawn attention to papers which have suggested the existence of different types of montmorillonite on fairly limited experimental data.

In 1954 Byrne investigated the X-ray and differential thermal analysis characteristics of fifteen montmorillonites and he concluded that all montmorillonites are interstratifications; namely, that adjacent layers differ from one another in composition, structure or some other factor. Similarly, Beavers & Larsen (1953) have reported several discrete mobilities in electrophoresis, suggesting the presence of different types of particles, in what appeared to be a homogeneous clay.

Of those publications which suggest that there may be more than one type of montmorillonite the most disturbing is one by McAtee (1958) in which he suggests that Wyoming Bentonite, one of the best known montmorillonites, is a mixture of structures. The evidence for this conclusion was drawn from X-ray studies of centrifuged fractions of the clay. The heavier fractions of the clay had calcium as the exchangeable ion whereas the lighter fractions were predominantly sodium clays. This is not surprising as it is known that calcium clays settle more readily than sodium clays, but it is difficult to explain why the ions are not randomly distributed throughout the clay. From this evidence McAtee (1958) inferred that the segregation of the two ions into different fractions of the clay was a consequence of underlying structural difference.

The major evidence of Grim & Kulbicki (1961) for structural differences within montmorillonite came from the products formed during destructive heating, variations in the cation-exchange capacity and differences in the chemical constitution.

The assessment of this data is rather difficult, as in addition to the various interpretations which may be given to the same data, there is also the problem that the existence of different types of montmorillonite has been proposed from differing experimental data. Montmorillonite samples do differ in their properties, but these differences do not necessarily mean that there are two or more structural types of this clay mineral. It would be expected that if different structural types did occur, then the differences between them could be correlated, and the evidence given by the many authors would consequently form part of a much larger set of data.

The investigation of this type of problem requires the measurement of many different properties on a large number of samples, preferably by the same laboratory. It is then possible to analyse the results mathematically and determine, with little or no personal bias, whether the differences in the properties of the samples are correlated. The very comprehensive paper by Grim & Kulbicki (1961) has supplied the necessary data for such an analysis.

## METHOD

*General theory*

The mathematical basis of multivariate analysis is very simple; a table of  $n$  rows of the samples and  $r$  columns of their features is drawn up, and the scoring is + or - according to the presence or absence of the feature concerned. The first row is then compared with each successive row, counting the ++, -- and +- combinations for each comparison. The numbers of these combinations are then used to calculate a similarity index, which is usually expressed as a percentage, and which gives the percentage similarity between the two samples with respect to the features scored. Inevitably, when tables of this magnitude are drawn up some data are missing, or cannot be scored for some other reason, and in these instances the feature is scored to indicate a null count. This procedure does not detract from the analysis unless the proportion of such scorings becomes unduly large.

The work of Sneath (1957, 1962) has led to the widespread use of this technique in the biological sciences, and the literature on this topic is now fairly extensive (Kendall, 1958; Sneath & Sokal, 1962).

*Practical application*

The features used and the method of scoring may be seen in the data table in the Appendix. With unit features, such as the occurrence of quartz as a high temperature phase, the scoring is simply + or - according to the presence or absence of this material at high temperature. With the quantitative data such as the alumina content of the clay or the cation-exchange capacity, the range is divided into classes, and a positive scoring given for each class up to and including the one in which the sample falls.

Although the counting and calculation may be carried out in the laboratory this is extremely tedious and time consuming, and a more suitable method is to use a computer. For this work a Ferranti Pegasus 2 was used, and this was programmed to calculate the similarity coefficient from the formula

$$S = \frac{n_{++}}{n_{++} + n_{+-} + n_{--}}$$

Details of other similarity coefficients which are sometimes used will be found in the literature referred to above. The results obtained were linearly grouped according to the  $S$  values and this grouping is shown in Table 1. Sample numbers 17-23 and 37-41 were omitted from this analysis because of inadequate data or atypical samples. A two-dimensional plot of the results was made using  $d = \log_2 1/S$  to convert the similarity values to the distances shown in Fig. 1.

TABLE 1. A linear arrangement of the similarity values.

	16	34	32	35	33	30	11	10	9	8	13	36	15	14	12	27	26	24	31	28	3	4	6	29	25	2	5	7	1
16	00																												
34	84	00																											
32	83	85	00																										
35	76	83	83	00																									
33	78	58	83	83	00																								
30	62	52	67	73	90	00																							
11	68	57	75	75	89	89	00																						
10	70	67	71	76	76	80	88	00																					
9	71	76	62	70	70	65	75	76	00																				
8	65	62	73	72	76	82	89	74	71	00																			
13	65	62	64	78	78	81	80	73	67	81	00																		
36	56	60	56	75	83	74	76	67	64	75	87	00																	
15	61	58	47	71	74	73	75	65	62	73	95	91	00																
14	62	62	62	75	78	82	80	74	64	62	00	83	91	00															
12	80	76	65	68	62	65	70	73	67	67	82	68	71	83	00														
27	59	57	56	58	70	78	70	68	67	68	70	71	65	71	71	00													
26	72	68	79	71	75	68	65	58	59	68	67	71	59	68	68	62	00												
24	67	69	85	75	75	61	69	65	58	61	65	58	56	61	65	58	86	00											
31	57	62	71	62	76	77	75	71	65	74	68	70	58	70	70	83	68	72	00										
28	65	55	69	62	68	77	67	67	58	67	68	56	50	70	70	83	76	75	82	00									
3	48	46	54	60	61	54	52	54	50	58	52	62	54	52	50	73	62	63	75	71	00								
4	52	50	69	55	58	48	50	52	43	53	56	55	52	55	55	69	63	75	71	75	86	00							
6	55	52	77	65	76	71	57	61	46	65	61	63	54	50	50	68	62	71	73	71	76	82	00						
29	57	55	69	64	68	68	59	57	57	61	61	65	64	61	59	81	79	80	80	89	80	85	75	00					
25	59	57	71	62	70	68	58	52	54	54	62	62	58	62	62	80	67	76	75	79	81	88	76	99	00				
2	44	42	69	48	57	60	44	41	47	47	48	48	45	48	48	72	65	75	74	78	77	84	73	90	91	00			
5	42	41	62	48	54	58	42	44	46	46	46	50	48	46	44	70	67	73	71	76	75	86	76	85	86	95	00		
7	50	53	57	57	62	62	54	47	50	50	47	57	50	47	47	69	67	69	77	75	90	91	57	91	77	91	00	00	
1	39	38	59	45	56	62	46	43	48	48	43	50	42	45	45	73	60	61	75	72	75	78	75	77	77	84	91	91	00

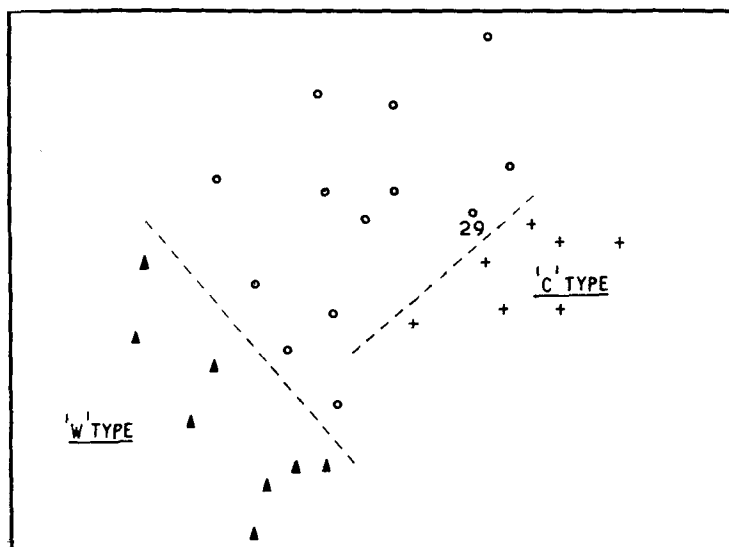


FIG. 1. A two-dimensional diagram of the similarity values.

## DISCUSSION

If the clay samples examined formed a linear series the similarity values given in Table 1 should increase fairly regularly towards the diagonal line, where each sample plotted against itself must have a similarity value of 100%. As Table 1 is the optimum linear arrangement which could be obtained, it is fairly obvious from the many similarity values which are out of place, that the samples do not form a linear series. To some extent, however, the groupings suggested by Grim & Kulbicki (1961) have been maintained. The proposed Cheto types, samples 1-7, are together at the lower end of the Table with only samples 25 and 29 interpolated in the middle of the group. The Wyoming samples 8-16 are together towards the top of the Table except for sample 16 which is removed from the group as a whole.

A more satisfactory evaluation of the similarity values may be obtained using two dimensions as shown in Fig. 1. In this case the only difficulty arose with sample 16 which could not be fitted into the diagram whilst maintaining the correct distances between this sample and the others. Therefore this sample has been omitted. Again, the groups suggested by the original authors are present as shown by the dotted lines, but without prior knowledge of these groupings there appears little justification for drawing boundary lines anywhere on the diagram.

In the original paper, sample 29 was selected as an example of a mixture of the two types and separated into two fractions by sedimentation in a centrifuge. The coarse fraction was found to have the characteristics of the Cheto type, and the fine fraction the characteristics of the Wyoming type. In the two-dimensional diagram this sample almost falls within the confines of the Cheto group, but this might be explained if the characteristics exhibited by a mixture are dominated by those of the Cheto type.

Reviewing the results as a whole it is rather unexpected that on this type of analysis the similarity coefficients should extend down to 39%, with a fairly large proportion in the 40-60% region. This is emphasized by the comparatively small range in the chemical composition of the samples included in this analysis; the silicon in the tetrahedral layer lies between 3.75 and 3.98, and the aluminium between 1.28 and 1.73 per half unit cell. It appears unlikely that such small changes in the chemical composition of the montmorillonites would effect such large changes in their characteristics, and the cause of this variation is to be sought elsewhere. Good evidence is given by Grim & Kulbicki (1961) for the inversion of some of the silica tetrahedra in the Cheto type, but they do not rule out the possibility of other structural types. This analysis is in broad agreement with these conclusions, but indicates that the variation

in the characteristics of these clays may be continuous as indicated by the random scatter on the two-dimensional diagram. An alternative suggestion is that most montmorillonites are mixtures of at least two structural types in varying proportions, but such a conclusion would add further confusion to an already complex problem.

#### ACKNOWLEDGMENT

The authors wish to thank Mr C. B. A. Price of this University for writing the computer programme for this work.

#### REFERENCES

- BEAVERS A.H. & LARSEN B.L. (1953) *Proc. Soil Sci. Soc. Amer.* **17**, 22.  
BYRNE P.J.S. (1954) *Clays and Clay Minerals* (A. Swineford and N. Plummer, editors). Nat. Acad. Sci.—Nat. Res. Council, Washington. Publ. 327, 241.  
EDELMAN C.H. & FAVEJEE J.C.L. (1940) *Z. Kristallogr.* **102**, 417.  
GRIM R.E. (1953) *Clay Mineralogy*, p. 55. McGraw-Hill, New York.  
GRIM R.E. & KULBICKI G. (1961) *Amer. Min.* **46**, 1329.  
HOFMANN U., ENDELL K. & WILM D. (1933) *Z. Kristallogr.* **86**, 340.  
KENDALL M.G. (1958) *A Course in Multivariate Analysis*. Griffin, London.  
MCATEE J.L. (1958) *Clays and Clay Minerals* (A. Swineford, editor). Nat. Acad. Sci.—Nat. Res. Council, Washington. Publ. 566, 279.  
MACÉWAN D.M.C. (1961) *The X-ray Identification and Crystal Structures of Clay Minerals*, 2nd edn (G. Brown, editor), p. 146. Mineralogical Society, London.  
SNEATH P.H.A. (1957) *J. gen. Microbiol.* **17**, 184.  
SNEATH P.H.A. (1962) *Microbial Classification*, p. 259. Cambridge University Press.  
SNEATH P.H.A. & SOKAL R.R. (1962) *Nature, Lond.* **193**, 855.

## APPENDIX

Numerical key to features used in constructing data Table

*A. High temperature phases*

1. Quartz
2. Beta Cristobalite
3. Cordierite
4. Felspar
5. Mullite
6. Enstatite

*C. Chemical analysis*

(Content/half unit cell)

- |    |     |             |
|----|-----|-------------|
| Si | 13. | 3.60-3.70   |
|    | 14. | 3.71-3.79   |
|    | 15. | 3.80-3.89   |
|    | 16. | 3.90-4.0    |
| Al | 17. | 1.10-1.30   |
|    | 18. | 1.31-1.50   |
|    | 19. | 1.51-1.60   |
|    | 20. | 1.61-2.00   |
| Fe | 21. | 0.000-0.120 |
|    | 22. | 0.121-0.220 |
|    | 23. | 0.220-0.500 |
| Mg | 24. | 0.000-0.340 |
|    | 25. | 0.341-1.000 |
|    | 26. | 1.000-3.000 |

*B. Peaks on differential thermal curve*

7. 500-600°C (endo.)
8. 600-700°C (exo.)
9. 700-900°C (endo.)
10. 1000-1100°C (endo.)
11. 1200-1300°C (endo.)
12. 1300-1400°C (exo.)

*D. Cation-exchange capacity**Measured*

27. 80-95
28. 96-105
29. 105-120
30. 120-140

*Measured—calculated theoretically*

31. —20.0
32. 0-30
33. 30-50

*E. Unit cell b-dimension*

34. 8.940-9.600
35. 8.961-8.990
36. 8.991-9.050

Table of

Samples	Features	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1		+	+	+	+	—	—	—	+	+	—	+	+	+	+	+	+	+	+
2		+	+	+	—	—	—	—	+	+	+	+	+	+	+	+	—	+	+
3		+	+	+	—	—	—	—	+	+	0	0	0	+	+	+	+	+	—
4		+	+	+	—	—	—	—	+	+	+	+	+	+	+	+	—	+	+
5		+	+	+	—	—	—	—	+	+	0	0	0	+	+	+	+	+	+
6		+	+	+	—	—	—	—	+	+	+	0	0	+	+	+	+	+	+
7		+	+	+	—	—	—	—	+	+	+	0	0	0	0	0	0	+	+
8		—	+	—	—	+	—	+	+	+	—	+	—	+	+	+	+	+	+
9		—	+	—	—	+	—	+	+	+	—	—	—	+	+	+	+	+	+
10		—	+	—	—	+	—	—	+	+	—	+	0	+	+	+	+	+	+
11		—	+	—	—	+	—	—	+	+	0	0	0	+	+	+	+	+	+
12		—	+	—	—	+	—	—	+	+	—	+	+	+	+	—	—	+	+
13		—	+	—	—	+	—	—	+	+	0	0	0	+	+	+	—	+	+
14		—	+	—	—	+	—	—	+	+	—	+	0	+	+	+	—	+	+
15		—	+	—	—	+	—	—	+	+	—	—	—	+	+	+	—	+	+
16		—	+	—	—	+	—	—	+	+	0	0	0	+	—	—	—	+	+
17		—	+	—	—	+	—	—	+	+	—	—	—	0	0	0	0	0	0
18		—	+	—	—	+	—	—	+	+	0	0	0	0	0	0	0	0	0
19		—	+	—	—	+	—	—	+	+	0	0	0	0	0	0	0	0	0
20		—	+	—	—	+	—	—	+	+	0	0	0	0	0	0	0	0	0
21		—	+	—	—	+	—	—	+	+	—	+	—	0	0	0	0	0	0
22		—	+	—	—	+	—	—	+	+	0	0	0	0	0	0	0	0	0
23		—	+	—	—	+	—	—	+	+	—	+	—	0	0	0	0	0	0
24		+	+	—	—	+	—	—	+	+	+	0	0	+	+	—	—	+	+
25		+	+	+	—	+	—	—	+	+	+	+	+	+	+	+	—	+	+
26		+	+	—	—	+	—	—	+	+	—	+	—	+	+	—	—	+	+
27		—	+	+	—	+	—	+	+	+	—	+	+	+	+	+	+	+	+
28		—	+	+	—	+	—	—	+	+	—	+	+	+	+	+	—	+	+
29		+	+	+	—	+	—	—	+	+	0	0	0	+	+	+	—	+	+
30		—	+	+	—	+	—	—	+	+	—	+	0	+	+	+	+	+	+
31		+	+	+	—	+	—	—	+	+	—	+	+	+	+	+	+	+	+
32		+	+	—	—	+	—	—	+	+	+	+	+	0	0	0	0	+	+
33		+	+	—	—	+	—	—	+	+	0	0	0	+	+	+	+	+	+
34		+	+	—	—	+	—	—	+	+	0	0	0	+	—	—	—	+	+
35		+	+	—	—	+	—	—	+	+	—	—	+	+	+	—	—	+	+
36		+	+	—	—	+	—	—	+	+	—	—	0	+	+	+	+	+	+
37		+	+	+	—	—	—	—	+	+	—	—	+	+	+	+	—	+	—
38		—	+	—	—	—	—	—	+	+	—	+	+	—	—	—	—	+	—
39		—	+	—	—	—	—	—	+	+	—	+	—	0	0	0	0	0	0
40		—	—	—	—	—	+	—	—	—	—	—	0	+	+	+	+	0	0
41		—	+	—	—	—	+	+	—	—	—	—	—	+	+	+	+	0	0



