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A SCHEME FOR RECALCULATING THE CHEMICAL ANALYSES OF ARGILLACEOUS ROCKS FOR COMPARATIVE PURPOSES

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ABSTRACT

A scheme for recalculating chemical analyses of argillaceous rocks is proposed in which, in the initial stages, no attempt is made to recalculate in terms of the actual mineral compositions present. Instead a series of "normative" formulae is introduced (*e.g.* $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$, $Na_2Al_4(Si_6Al_2)O_{20}(OH)_4$, $Al_4Si_8O_{20}(OH)_4$, $Mg_{12}Si_8O_{20}(OH)_{16}$ and $Fe_{12}Si_8O_{20}(OH)_{16}$), from which the probable mineralogical composition can be readily calculated if the nature of the clay minerals present is known. Even in the absence of such information, regrouping the "normative" formulae into "normative" minerals affords a basis of comparison of large numbers of analyses of argillaceous rocks.

INTRODUCTION

Petrological and geochemical investigations of the argillaceous rocks are hampered by the fine grain size of most of the constituents of these sediments. Mineralogical studies by such methods as *x*-ray diffractometry and differential thermal analysis disclose the nature of the principal minerals present but are, at best, semi-quantitative. Minerals present in very small amounts may escape detection by these techniques but may nevertheless be of considerable importance in any attempt at elucidating the physico-chemical conditions under which sedimentation occurred. Chemical analysis of the rocks yields data on their overall compositions, which, in so far as they must be related to the proportions and compositions of the minerals present, should be of mineralogical as well as geochemical interest. But variability in clay mineral composition makes the interpretation of the chemical analyses in terms of probable mineral composition difficult. Numerous workers have attempted such interpretations, *e.g.* Imbrie and Poldervaart (1959) recalculate their analysis in terms of the minerals probably, or known to be, present. There are difficulties about applying such schemes generally, principally because of the variation in clay mineral composition previously mentioned. In the course of geochemical work on argillaceous rocks conducted in the Department of Geology, the University of Manchester, a scheme of recalculating chemical analyses of such rocks has been used in which, in the initial stages, no attempt is made to recalculate in terms of the actual mineral compositions present. This permits the retention of flexibility in the scheme and thus its possible application to large numbers of analyses of argillaceous rocks. If desired, and data on probable mineralogical composition are available, it is possible to extend the recalculations in terms of such mineralogical composition. However, for general comparative purposes, it appears wiser to adopt a more general scheme of recalculation in the same way that igneous geochemists have adopted the igneous "norm."

SCHEME FOR RECALCULATION

Chemical analyses of argillaceous rocks should include the determination of such minor constituents as CO_2, S, SO_3 and organic C as well as the usual major constituents. FeO should be reported independently of Fe_2O_3 and in the presence of organic matter may be determined by a method recently published (Nicholls, 1960). During interpretation of the analysis it must be remembered that when this method is used the sulfide minerals remain unattacked, and any sulfide iron is reported as Fe_2O_3. Consequently it is the ferric iron content which must be assigned to sulfur when forming iron sulfide in the course of the recalculation. In addition, it is desirable to determine free silica in argillaceous rocks, for which various methods are available, (Trostel and Wynne, 1940; Bulycheva and Mel'nihova, 1958; Polezhoev, 1958) and to quote free and combined SiO_2 separately.

Since chemical analyses are usually expressed as weight percentages of oxides (except for S and C), the first stage in the recalculation is the expression of the constituents in molecular proportions, by dividing weight percentages by appropriate molecular weight (Table 1, line 2). Certain constituents, *viz.* free SiO_2, organic C, H_2O- and TiO_2 are not recast in the recalculation, and the calculation of their molecular proportions may be omitted. The molecular proportion of MnO is combined with that of FeO.

Sulfur is assigned to Fe_2O_3 in the molecular ratio 2:1 to form FeS (Table 1. line 3). Should there be insufficient Fe_2O_3 to satisfy the sulfur, these two constituents are distributed between FeS and FeS_2 by solving the equations $2x+4y=$ molecular proportion of sulfur, $x+y=$ molecular proportion of Fe_2O_3 where 2x is the molecular proportion of FeS and 2y is the molecular proportion of FeS_2. If Fe_2O_3 remains after making FeS it is reported as "excess Fe_2O_3."

P_2O_5 is assigned to CaO and H_2O+ in the ratio 3:10:1 to form $Ca_5(PO_4)_3(OH)$ (Table 1, line 4). SO_3 is assigned to CaO and H_2O+ in the ratio 1:1:2 to form $CaSO_4 \cdot 2H_2O$. CaO remaining after these operations is assigned to CO_2 in the ratio 1:1 to form $CaCO_3$ (Table 1, line 5). If insufficient CO_2 is present to satisfy the CaO the excess CaO over that which can be combined with CO_2 is reported simply as "excess CaO."

In most cases an excess of CO_2 will remain at this stage. If so, a molecular proportion of MgO equal to that of CaO recast into $CaCO_3$ is assigned to CO_2 in the ratio 1:1 to form $MgCO_3$ (Table 1, line 6). If there is insufficient CO_2 for this operation to be carried through all the available

TABLE 1. RECALCULATION OF THE CHEMICAL ANALYSIS OF A MUDSTONE OF UPPER CARBONIFEROUS AGE TAKEN FROM A BOREHOLE AT BERSHAM, NORTH WALES, 265 FT. BELOW THE POWELL COAL SEAM (*i.e.* ABOUT 1260 FT. BELOW THE GROUND SURFACE)

	Free SiO_2	Combined SiO_2	Al_2O_3	TiO_2	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	H_2O+	H_2O-	CO_2	C	P_2O_5	SO_3	S	Line No.
	34.40	28.16	20.60	0.94	0.66	2.60	0.02(5)	1.25	0.34	0.62	3.35	4.86	0.79	0.90	0.40	0.17	n.d.	0.02	1
		.4693	.2020		.0041	.0361	.0003	.03125	.0061	.0100	.0356	.2700		.0205		.0012		.0006	2
						.0364													
FeS					.0003													.0006	3
					.0038 (excess Fe_2O_3)														
$Ca_5(PO_4)_3(OH)$									.0040							.0012			4
									.0021										
$CaCO_3$									.0021					.0021					5
														.0184					
$MgCO_3$								.0021						.0021					6
								.02915						.0163					
$FeCO_3$						.0163								.0163					7
						.0201													
$Fe_{12}Si_8O_{20}(OH)_{16}$		.0134				.0201						.0134							8
		.4559										.2566							
$Mg_{12}Si_8O_{20}(OH)_{16}$		.0194						.02915				.0194							9
		.4365										.2372							
$Al_4Si_8O_{20}(OH)_4$		.0650	.01625									.01625							10
		.3715	.18575									.22095							
$K_2Al_4(Si_6Al_2)O_{20}(OH)_4$		.2136	.1068								.0356	.0712							11
		.1579	.07895									.14975							
$Na_2Al_4(Si_6Al_2)O_{20}(OH)_4$		.0600	.0300							.0100		.0200							12
		.0979	.04895									.12975							
$Al_4Si_4O_{10}(OH)_8$		.0979	.04895									.0979							13
												.03185 (excess H_2O)							

CO_2 is assigned to an equivalent amount of MgO to form $MgCO_3$. If excess CO_2 still remains this is assigned to (FeO+MnO) in the ratio 1:1 to form $FeCO_3$ (Table 1, line 7).

(FeO+MnO) remaining after forming $FeCO_3$ is assigned to combined SiO_2 and H_2O+ in the molecular ratio 3:2:2 to form $Fe_{12}Si_8O_{20}(OH)_{16}$ (Table 1, line 8) and MgO remaining after forming $MgCO_3$ likewise to form $Mg_{12}Si_8O_{20}(OH)_{16}$ (Table 1, line 9).

The next stage involves the distribution of Al_2O_3 and remaining combined SiO_2 between Al_2O_3, $Al_4Si_8O_{20}(OH)_4$ and a trio of "normative formulae," $Al_4Si_4O_{10}(OH)_8$, $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$ and $Na_2Al_4(Si_6Al_2)O_{20}(OH_4)$. The molecular Al_2O_3: SiO_2 ratio in this trio of formulae is 1:2. If the molecular ratio Al_2O_3:remaining combined SiO_2 is less than 1:2 these constituents are distributed between $Al_4Si_8O_{20}(OH)_4$ and the trio by solving the equations $X+Y=$available Al_2O_3 (molecular) and $4X+2Y=$remaining combined SiO_2 (molecular), where X is the molecular amount of Al_2O_3 in $Al_4Si_8O_{20}(OH)_4$ and Y is the molecular amount of Al_2O_3 in the trio of "normative formulae." If the molecular ratio Al_2O_3: remaining combined SiO_2 is greater than 1:2, combined SiO_2 is assigned to Al_2O_3 in the ratio 2:1 and the remaining Al_2O_3 reported as "excess Al_2O_3." In the example given in Table 1 the first alternative applies so $Al_4Si_8O_{20}(OH)_4$ is formed (Table 1, line 10).

K_2O is then assigned to Al_2O_3, combined SiO_2 and H_2O+ in the ratio 1:3:6:2 to form $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$ (Table 1, line 11) and Na_2O similarly assigned to form $Na_2Al_4(Si_6Al_2)O_{20}(OH)_4$ (Table 1, line 12). Remaining Al_2O_3 and combined SiO_2 with H_2O+ in the ratio 1:2:2 are then placed into $Al_4Si_4O_{10}(OH)_8$ (Table 1, line 13). Any H_2O remaining is reported as "excess H_2O."

Weight percentages of the different normative formulae are then calculated as follows.

FeS multiply the molecular proportion of S assigned to this molecule by 88 (Table 2, line 8)
FeS_2 multiply the molecular proportion of S assigned to this molecule by 60
$Ca_5(PO_4)_3(OH)$ multiply the molecular proportion of P_2O_5 assigned to this molecule by 335 (Table 2, line 12)
$CaSO_4 \cdot 2H_2O$ multiply the molecular proportion of SO_3 assigned to this molecule by 172
$CaCO_3$ multiply the molecular proportion of CO_2 assigned to this molecule by 100 (Table 2, line 9)
$MgCO_3$ multiply the molecular proportion of CO_2 assigned to this molecule by 84 (Table 2, line 10)
$FeCO_3$ multiply the molecular proportion of CO_2 assigned to this molecule by 116 (Table 2, line 11)
$Fe_{12}Si_8O_{20}(OH)_{16}$ multiply the molecular proportion of FeO assigned to this molecule by 124 (Table 2, line 5)
$Mg_{12}Si_8O_{20}(OH)_{16}$ multiply the molecular proportion of MgO assigned to this molecule by 92 (Table 2, line 6)
$Al_4Si_8O_{20}(OH)_4$ multiply the molecular proportion of Al_2O_3 assigned to this molecule by 360 (Table 2, line 4)
$K_2Al_4(Si_6Al_2)O_{20}(OH)_4$ multiply the molecular proportion of K_2O assigned to this molecule by 796 (Table 2, line 2)
$Na_2Al_4(Si_6Al_2)O_{20}(OH)_4$ multiply the molecular proportion of Na_2O assigned to this molecule by 764 (Table 2, line 3)
$Al_4Si_4O_{10}(OH)_8$ multiply the molecular proportion of Al_2O_3 assigned to this molecule by 258 (Table 2, line 7)

"Excess Fe_2O_3" molecular proportion is multiplied by 160 to convert to weight percentage (Table 2, line 13), "excess CaO" by 56, "excess Al_2O_3" by 102, and "excess H_2O" by 18 (Table 2, line 14).

TABLE 2. CONTENTS OF RECALCULATED NORMATIVE FORMULAE FOR THE ANALYSIS OF THE BERSHAM MUDSTONE GIVEN IN TABLE 1

Normative molecule		Weight percentage	Line no.
Free SiO_2		34.40	1
$K_2Al_4(Si_6Al_2)O_{20}(OH)_4$	.0356 ×796	28.34	2
$Na_2Al_4(Si_6Al_2)O_{20}(OH)_4$	.0100 ×764	7.64	3
$Al_4Si_8O_{20}(OH)_4$	.01625×360	5.85	4
$Fe_{12}Si_8O_{20}(OH)_{16}$	.0201 ×124	2.49	5
$Mg_{12}Si_8O_{20}(OH)_{16}$	.02915× 92	2.68	6
$Al_4Si_4O_{10}(OH)_8$	.04895×258	12.63	7
FeS	.0006 × 88	0.05	8
$CaCO_3$	.0021 ×100	0.21	9
$MgCO_3$	.0021 × 84	0.18	10
$FeCO_3$	.0163 ×116	1.89	11
$Ca_5(PO_4)_3OH$	.0012 ×335	0.40	12
excess Fe_2O_3	.0038 ×160	0.61	13
excess H_2O	.03185× 18	0.57	14
TiO_2		0.94	
C		0.40	
H_2O-		0.79	
Total		100.07	

RELATION OF NORMATIVE MOLECULES TO ACTUAL MINERALOGICAL COMPOSITION

The normative formulae into which the analytical data are recast do not correspond to the compositions of minerals actually present. The reasons for selecting the formulae used are discussed below.

Sulfides

The common sulfide mineral of argillaceous rocks is iron pyrite, FeS_2, but this only appears in the argillaceous norm if the determined ferric iron content of the rock is insufficient to form FeS with the S. Although FeS_2 may be primary in some rocks, there is considerable evidence that the first iron sulfide to form in sediments is the monosulfide (e.g. see Van Straaten, 1954). There are several ways in which FeS can be converted into FeS_2, and the actual nature of the reaction probably depends on the rate of sedimentation. If sedimentation is rapid, part, at least, of the FeS may be converted to FeS_2 by a reaction of the type $2FeS+3H_2O \rightarrow FeS_2+Fe(OH)_3+3H^{+}+e.$ with subsequent aging of the $Fe(OH)_3$ into Fe_2O_3. Where this has occurred there is no doubt that recasting the chemical data into FeS gives a closer approximation to the original mineralogical composition of the sediment. If the iron bearing mineral relationships are to be used for elucidating the physico-chemical conditions of sedimentation, it is advantageous to recast in this way. If sedimentation is slow, the conversion may take the form, $FeS+HS \rightarrow FeS_2+H^+$ or $FeS+8H^+ + SO_4 \rightarrow FeS_2+4H_2O$, according to the pH-Eh conditions of sedimentation. If either reaction has occurred, the S should be recast into FeS_2 for a close approximation to the mineralogical composition at the time the sediment was accumulating. This of course can be readily achieved. Each 1% FeS is equivalent to 0.68% FeS_2+0.45% Fe_2O_3. Clearly, if it is desired to recast the chemical data in terms of the minerals now existing in the rocks, this conversion should always be made, but if the object is to obtain some insight into the physico-chemical conditions of sedimentation, a decision whether or not to make this conversion must be taken for each case and must depend on the estimated rate of sedimentation. In the author's view it is wiser to leave the sulfide as FeS unless definite evidence exists of its conversion to FeS_2 before burial (e.g. insufficient ferric iron available to form FeS with the available S), but the problem is involved and will be discussed more fully elsewhere.

Phosphate and sulfate

The phosphate normative formula chosen, $Ca_5(PO_4)_3OH$, is the theoretical formula for hydroxyapatite. F is rarely determined in analyses of argillaceous rocks, but when data on this element are available, F should be combined with CaO and P_2O_5 to form $Ca_5(PO_4)_3F$. Collophane, which may be present in some rocks, may contain CO_3^{2-} in place of some of the OH^-. Since the normative phosphate content is determined by the P_2O_5 content, the difference between normative phosphate and the actual content of phosphate minerals should be insignificant. To the extent that collophane is present carbonates might be over-estimated in the norm, but since the phosphorus content of most argillaceous rocks is low the error will rarely, if ever, be serious. Some attention has been paid to the possible occurrence of ferric phosphate. From the thermodynamic data (Garrels, 1960, p. 230) it appears unlikely that this compound could exist as a primary component of many argillaceous rocks, and no serious error is involved in ignoring it.

When a sulfate mineral is present in argillaceous rocks in sufficient amount to make the SO_3 content significant, it is more likely to be gypsum ($CaSO_4 \cdot 2H_2O$) than anhydrite ($CaSO_4$). If anhydrite is known to be present, the $CaSO_4 \cdot 2H_2O$ figure can be converted to $CaSO_4$ by multiplying by the factor 0.79, the conversion resulting in the liberation of 0.21% H_2O for each 1% $CaSO_4 \cdot 2H_2O$.

Carbonates

The carbonate formulae selected probably require no justification. The carbonate minerals occurring in argillaceous rocks are calcite, dolomite and siderite. If $CaCO_3$ is the only carbonate normative molecule, this can be equated to calcite, but where $MgCO_3$ appears in addition, the possibility of dolomite being present must be considered. Natural inorganically produced calcites are low in Mg (Goldsmith, 1959), but the calcitic parts of marine organisms may contain significant amounts of this element, and unless the molecular amount of $MgCO_3$ is greater than 40% of that of $CaCO_3$, it cannot be assumed that dolomite is necessarily present. Such highly magnesian calcites are metastable, and if the $MgCO_3$ content is such that the presence of dolomite is indicated, $MgCO_3$ may safely be combined with an equal molecular proportion of $CaCO_3$ to form dolomite, the excess $CaCO_3$ being assigned to calcite. Natural dolomites may deviate from pure $CaMg(CO_3)_2$, but the contents of normative $CaCO_3$ and $MgCO_3$ are small enough in most argillaceous rocks for this deviation to be ignored. Small amounts of $FeCO_3$ may also be contained in calcite, but if the $FeCO_3$ molecular content is greater than 10% of the $CaCO_3$ molecular content, it is an indication of the presence of siderite. Natural siderites usually contain Mg and Ca in addition to Fe^{2+}, and in some natural siderites the molar percentages of $MgCO_3$ are approximately equal to those of $CaCO_3$ (Taylor, 1949, p. 49). Where normative $FeCO_3$ exceeds the combined normative $CaCO_3$ and $MgCO_3$, the three carbonate molecules may be combined into siderite. If a rock contains both calcite and siderite, the scheme of recalculation adopted here may assign too much Mg and too little Fe to the carbonates. The total carbonate content will be little affected, but the Mg:Fe ratio in the normative $(Mg,Fe)_{12}Si_8O_{20}(OH)_{16}$ will not truly represent the Mg:Fe ratio of the clay mineral fraction of the rock.

Silica and silicates

The free silica content may be safely equated to the quartz content of the rock since the chemical methods are designed to determine SiO_2 in this form.

The common clay minerals of argillaceous rocks are illite, chlorite, kaolinite and, more particularly in young rocks, montmorillonite. Of these only kaolinite has a normative formula, *viz.* $Al_4Si_4O_{10}(OH)_8$.

(*a*) Illite.

Illite is a group name embracing fine-grained muscovite, paragonite hydromuscovite, phengite, etc. $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$ is the theoretical, formula for muscovite and $Na_2Al_4(Si_6Al_2)O_{20}(OH)_4$ that of paragonite. The other illites resemble muscovite modified by various replacements. K^+ may be replaced by Na^+ or $(H_3O)^+$, 6-fold co-ordinated Al^{3+} may be replaced by Mg^{2+}, Fe^{2+} or Fe^{3+} with compensating replacement of Al^{3+} in

4-fold co-ordination by Si^{4+}, or Al^{3+} in 4-fold co-ordination may be replaced by Si^{4+} with the charge balance maintained by omission of K^+ from the interlayer sites. Ignoring for the moment the presence of Fe^{3+} a general formula for such illites may be written:

$$(H_3O)^+_\alpha(K, Na)_x Al_{4-y}(Fe, Mg)_y Si_{(6+z)} Al_{(2-z)} O_{20}(OH)_4,$$

where $\alpha = 2 + y - x - z$ for a charge-balanced structure. Simple algebraic calculations show that in terms of the normative formulae this is equivalent to

$$\frac{x}{2}(K, Na)_2Al_4(Si_6Al_2)O_{20}(OH)_4 + \left(\frac{z}{2} + \frac{y}{12}\right) Al_4Si_8O_{20}(OH)_4 + \frac{y}{12}(Fe, Mg)_{12}Si_8O_{20}(OH)_{16}$$
$$+ \left(\frac{3}{4}(2 - z - x) - \frac{y}{3}\right) Al_4Si_4O_{10}(OH)_8 + \left(\frac{15y}{6} - \frac{\alpha}{2}\right) H_2O.$$

For an illite of the formula

$$(H_3O)^+_{0.76}(K, Na)_{1.07}(Mg, Fe)_{0.76}Al_{3.27}(Si_{6.80}Al_{1.20})O_{20}(OH)_4,^1$$

(compare Grim *et al.* 1937, p. 823, Table 3, No. 2) the equivalent amounts of normative formulae are:

0.535	$(K, Na)_2Al_4(Si^6Al_2)O_{20}(OH)_4$	
0.463	$Al_4Si_8O_{20}(OH)_4$	
0.063	$(Mg,Fe)_{12}Si_8O_{20}(OH)_{16}$	for each formula unit of the illite.
−0.156	$Al_4Si_4O_{10}(OH)_8$	

Treating (K, Na) as K and (Mg, Fe) as Mg for simplicity 1.82 gms. illite ≡ 1.00 gms. $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$ + 0.78 gms. $Al_4Si_8O_{20}(OH)_4$ + 0.16 gms. $Mg_{12}Si_8O_{20}(OH)_{16}$ + 0.06 gms. H_2O − 0.18 gms. $Al_4Si_4O_{10}(OH)_8$. Other examples could be given for hydromuscovites, phengites, etc., illustrating a general relationship that, if an illitic mineral is present in the rock, it will be expressed essentially as $(K,Na)_2Al_4(Si_6Al_2)O_{20}(OH)_4 + Al_4Si_8O_{20}(OH)_4$ with lesser effects on the contents of $(Mg,Fe)_{12}Si_8O_{20}(OH)_{16}$ and $Al_4Si_4O_{10}(OH)_8$.

(*b*) Chlorite.

It is unlikely that the chlorite in sedimentary rocks is Al-free. Weaver (1958, p. 256) has suggested that most chlorites in sediments are trioctahedral and, if this is so, the chlorite compositions could also be represented in terms of the formulae used in these calculations. Thus if the magnesian component of the chlorite is $Mg_{(12-\beta)}Al_{2\beta}Si_{(8-\beta)}O_{20}(OH)_{16}$ it may be derived from

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[1] Consideration of this formula in the light of possible replacements suggests that the H_2O content of this illite may have been slightly underestimated. For this reason an equivalent amount of excess H_2O is not quoted. The effect on the subsequent figures is insignificant.

$$\frac{(12-\beta)}{12}\,Mg_{12}Si_8O_{20}(OH)_{16} + \frac{13\beta}{12}\,Al_4Si_4O_{10}(OH)_8 - \frac{7\beta}{12}\,Al_4Si_8O_{20}(OH)_4 - \frac{15\beta}{6}\,H_2O.$$

Taking a reasonable value for β (*e.g.* 2) 1.204 gms. aluminous chlorite $\equiv$1.000 gms. $Mg_{12}Si_8O_{20}(OH)_{16}$+1.215 gms. $Al_4Si_4O_{10}(OH)_8$−0.913 gms. $Al_4Si_8O_{20}(OH)_4$−0.098 gms. H_2O. For the Fe^{2+} component the figures are slightly lower. Thus, ignoring for the moment the possible presence of Fe^{3+} proxying for Al^{3+} in the chlorites, equating the chlorite content in the rock to normative $(Mg,Fe)_{12}Si_8O_{20}(OH)_{16}$ would result in this content being underestimated by 0.15–0.20% for each 1% $(Mg,Fe)_{12}Si_8O_{20}(OH)_{16}$ reported, if all the Mg^{2+} and Fe^{2+} in the silicates were contained in this mineral.

(*c*) Montmorillonite.

There is very little information on the composition of normal sedimentary montmorillonites (Weaver, 1959, p. 180), but soil montmorillonites are commonly rich in aluminum. Nevertheless their compositions depart markedly from the normative formula $Al_4Si_8O_{20}(OH)_4$. A general formula can be written in the form $Al_{(4-y)}(Fe,Mg)_ySi_{(8-x)}Al_xO_{20}(OH)$, where $x+y \simeq 0.7$ (to account for the net negative charge on the montmorillonite lattice) and some Fe^{3+} may be replacing Al. In terms of the normative formulae this formula is equivalent to

$$\frac{(12+y-6x)}{12}\,Al_4Si_8O_{20}(OH)_4 + \frac{y}{12}\,(Fe,Mg)_{12}Si_8O_{20}(OH)_{16}$$
$$+\left(2y-\frac{x}{2}\right)H_2O - (4y-9x)Al_4Si_4O_{10}(OH)_8,$$

if the excess negative charge is balanced by $(H_3O)^+$ ions. For a beidellitic montmorillonoid with $x=0.47$ and $y=0.23$ each 1% of this mineral in a rock would appear in the list of normative formulae as 0.77% $Al_4Si_8O_{20}(OH)_4$, 0.19% $Al_4Si_4O_{10}(OH)_8$, 0.03% $(Fe,Mg)_{12}Si_8O_{20}(OH)_{16}$ and 0.01% excess H_2O.

(*d*)Other possibilities.

Similar mathematical relationships between the normative formulae and other less common clay minerals, *e.g.* vermiculite, chamosite, etc., may be deduced should a particular investigation require this.

If "excess Al_2O_3" appears in the list of normative formulae, $Al_4Si_8O_{20}(OH)_4$ cannot appear. It may indicate the presence of a hydrated alumina mineral in the analysed rock but, more commonly, it will merely indicate that the chlorite present is aluminous. Thus if a chlorite of composition $Mg_{10}Al_4Si_6O_{20}(OH)_{16}$ is present in a rock, it could, under certain conditions, appear in the list of normative formulae as $Mg_{12}Si_8O_{20}(OH)_{16}$, excess Al_2O_3 and excess water. Each 1.20% of the chlorite would be equivalent to 1.00% $Mg_{12}Si_8O_{20}(OH)_{16}$+0.26% Al_2O_3+0.04% H_2O–0.10% $Al_4Si_4O_{10}(OH)_8$.

The "excess Fe_2O_3" in the list of normative formulae may be present either in the form of iron oxide minerals or as Fe^{3+} proxying for Al in clay mineral structures. If the latter is the case, the calculated content of normative $Al_4Si_4O_{10}(OH)_8$ will be too low by 3.59%, normative $Al_4Si_8O_{20}(OH)_4$ will be too high by 2.25% and excess H_2O too high by 0.34% for each 1% excess Fe_2O_3 representing Fe^{3+} proxying for Al.

The bulk of the Ti of argillaceous rocks is probably present in the form of finely divided rutile or anatase, both TiO_2 minerals, so this oxide is best reported as free TiO_2. Feldspar may be present in argillaceous rocks but does not appear amongst normative formulae. It can be related to the normative formulae through the expression:

$$2(K, Na)AlSi_3O_8 \equiv (K, Na)_2Al_4(Si_6Al_2)O_{20}(OH)_4 + Al_4Si_8O_{20}(OH)_4 + 4H_2O - 2Al_4Si_4O_{10}(OH)_8.$$

Each 1% $KAlSi_3O_8$ in the rock will be equivalent to 1.43% $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$+1.29(5)% $Al_4Si_8O_{20}(OH)_4$+0.13% H_2O−1.85(5)% $Al_4Si_4O_{10}(OH)_8$. Each 1% $NaAlSi_3O_8$ will be equivalent to 1.46% $Na_2Al_4(Si_6Al_2)O_{20}(OH)_4$+1.37% $Al_4Si_8O_{20}(OH)_4$+0.14% H_2O−1.97% $Al_4Si_4O_{10}(OH)_8$. If much feldspar is present, it is clear that the mica-type formulae will be seriously over-estimated in the list of normative formulae as will the content of $Al_4Si_8O_{20}(OH)_4$, whereas $Al_4Si_4OH_{10}(OH)_8$ will be markedly under-estimated. This is a deficiency of this scheme of recalculation, but at present no way of avoiding the difficulty is apparent.

The Argillaceous Norm

The normative formulae used in the scheme of recalculation may be grouped into normative minerals to form the argillaceous norm for the purpose of comparing different argillaceous rocks. Normative $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$, $Na_2Al_4(Si_6Al_2)O_{20}(OH)_4$ and $Al_4Si_8O_{20}(OH)_4$ are grouped together into normative illite, $Fe_{12}Si_8O_{20}(OH)_{16}$ and $Mg_{12}Si_8O_{20}(OH)_{16}$ together into normative chlorite and $Al_4Si_4O_{10}(OH)_8$ is returned as normative kaolinite. Normative free SiO_2 is returned as normative quartz. If normative $CaCO_3$ exceeds normative $MgCO_3$ in molecular proportions, normative $MgCO_3$ is combined with an equal molecular proportion of normative $CaCO_3$ and returned as normative dolomite, the excess normative $CaCO_3$ being returned as normative calcite. If normative $FeCO_3$ is present, the molecular proportion of normative $MgCO_3$ must equal that of normative $CaCO_3$, and initially the two latter normative molecules are combined. If normative $FeCO_3$ exceeds normative $CaCO_3$

$+MgCO_3$, the whole carbonate content is returned as normative siderite. If normative $FeCO_3$ is less than normative $CaCO_3+MgCO_3$, the normative $FeCO_3$ is combined with an equal molecular proportion of normative $CaCO_3+MgCO_3$ and returned as normative siderite, the excess $CaCO_3+MgCO_3$ being assigned to normative dolomite. Normative FeS and normative FeS_2 are combined to form normative iron sulfide, and normative $Ca_5(PO_4)_3OH$ is returned as normative apatite. The other normative formulae are returned without combination. Thus for the example recalculated (Tables 1 and 2) the argillaceous norm is given in Table 3.

TABLE 3. ARGILLACEOUS NORM FOR THE BERSHAM MUDSTONE, THE ANALYSIS OF WHICH IS GIVEN IN TABLE 1

Normative minerals	Weight percentage
Quartz	34.40
Illite	41.83
Chlorite	5.17
Kaolinite	12.63
Siderite	2.28
Iron sulfide	0.05
Apatite	0.40
Fe_2O_3	0.61
H_2O (total)	1.36
TiO_2	0.94
C	0.40
Total	100.07

The grouping of the normative formulae into normative minerals is based on two generalizations.

(1) The principal trioctahedral clay minerals in argillaceous rocks are chlorites, so the total content of trioctahedral normative silicate formulae is assigned to chlorite.

(2) Of the dioctahedral normative silicate formulae those based on the mica sandwich are assigned to illite and that based on the kaolinite sheet to kaolinite.

In the absence of evidence of the actual composition of the clay minerals in the rock chosen as an example, no real comparison can be made between the actual clay mineral composition of the rock and the normative clay mineral composition. However, *x*-ray diffractometry has demonstrated the presence of quartz, illite, kaolinite and minor chlorite in this rock, and this information permits an estimate of the maximum differences that can exist between the actual and normative clay mineral compositions. Obviously all the $(Mg,Fe)_{12}Si_8O_{20}(OH)_{16}$ cannot be assigned to the illite, since chlorite occurs in the rock, and probably the minimum content of chlorite that could be detected is not less than 3.00%. The probable maximum amount of $(Mg,Fe)_{12}Si_8O_{20}(OH)_{16}$ that could be present in the illite can be estimated by assuming only 3% chlorite present of the most highly aluminous variety, *viz.* $(Mg,Fe)_8Al_8Si_4O_{20}(OH)_{16}$. If, further, the illite carries no $(H_3O)^+$, the probable contents of the different clay minerals would be 33.66% illite, 24.25% kaolinite and 3.00% chlorite. To the extent that $(H_3O)^+$ is present in the illite the content of this mineral would be increased and that of kaolinite reduced, *e.g.* if 0.7 ions of $(H_3O)^+$ are present in the interlayer positions for each 20 oxygens and 4(OH), the above figures must be revised to 41.58% illite, 16.51% kaolinite and 3.00% chlorite. If the "excess Fe_2O_3" is in the clay minerals, the kaolinite content must be increased by 2.19% and the illite content reduced by 1.37%. Thus the extreme possible clay mineral composition in this direction is 32.29% illite, 26.44% kaolinite and 3.00% chlorite.

The other extreme is to consider the illite free from Fe^{2+} and Mg. If all the $(Fe,Mg)_{12}Si_8O_{20}(OH)_{16}$ is assigned to the chlorite, this cannot be as aluminous as $(Fe,Mg)_8Al_8Si_4O_{20}(OH)_{16}$, for the content of kaolinite would then be too small for it to be detected by *x*-ray methods. A more reasonable composition would be $(Mg,Fe)_{10}Al_4Si_6O_{20}(OH)_{16}$, in which case the clay mineral composition would be 46.0% illite, 7.13% kaolinite and 6.1% chlorite or, if it is assumed that the "excess Fe_2O_3" represents Fe^{3+} in the clay minerals, 44.6% illite, 9.32% kaolinite and 6.1% chlorite, (with a correction in the excess H_2O figure).

Where illites have been analysed from argillaceous sedimentary rocks they usually contain both (Fe^{2+},Mg) and $(H_3O)^+$ ions, and it appears more likely that some of the $(Fe,Mg)_{12}Si_8O_{20}(OH)_{16}$ is in illite, but with sufficient in the chlorite for this latter mineral to be present in greater amount than 3%. Thus the true illite content in these rocks is likely to be appreciably above that of the first extreme considered but less than the second, and the content of normative illite appears a very reasonable approximation to the actual content of this mineral. This is also true for the contents of chlorite and kaolinite.

The argillaceous norm affords a good basis for the comparison of analyses of different argillaceous rocks. The contents of quartz and TiO_2 indicate the magnitude of abrasion product contribution to the sediment, contents of illite, chlorite and kaolinite the total clay mineral contribution and the remainder the chemical additions to the sediment. Among the clay minerals normative chlorite reflects the content of trioctahedral clay minerals, normative kaolinite the content of kaolinite-type dioctahedrals and normative illite the content of mica-type dioctahedral clay minerals. Study of the chemical addition fraction permits rapid reference of the rock to the sulfide, carbonate or oxide facies of deposition. The argillaceous norm does not correspond exactly to the actual mineralogical composition of the rock in the majority of cases, any more than the igneous norm does, but it does appear to illustrate the principal features of the rock on which classification and comparison may be based, features which are not always apparent by direct inspection of the analytical data.

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