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CALCULATING FORMULAS FOR FINE GRAINED MINERALS ON THE BASIS OF CHEMICAL ANALYSIS

W. P. Kelley,
University of California, Berkeley 4, California.

Abstract

Data are presented showing that every element found by chemical analysis can be placed in a theoretically possible three layer lattice even when the sample is grossly impure. Therefore the fact that a possible lattice can be calculated is not proof of the mineralogical purity of the sample. The impurities may be in the form of admixtures, intergrowths or adsorbed.

Silica is likely to be the most abundant impurity of the fine grained minerals. It may occur as crystalline or amorphous forms, or as adsorbed silicate ions. Phosphate, Al, Fe or H ions may also be adsorbed. Brucite, chlorite, pyrophyllite, hydrargillite, any of the micas and possibly talc, kaolinite and halloysite may occur as occasional layers in the crystals of montmorillonite and other fine grained clays. All of these forms and kinds of impurity must be absent from the sample if complete confidence is to be placed in the calculated distribution of the ions in the lattice and in the formula that is derived from the same.

With minerals which contain tetrahedral Al ions, SiO_2, as impurity, affects the calculated values not only by increasing the number of calculated Si ions, but also by reducing the number of ions with octahedral coordination. If the total calculated octahedral ions is found to be less than 2.0 per half lattice unit, the probability is that the sample contained SiO_2 as impurity. Admixtures or intergrowths of brucite, chlorite and several other structurally related minerals affect the calculation by increasing the total octahedral cations. Since these kinds of impurities tend to cancel the effects of SiO_2 and since adsorbed ions also affect the results, the sample must be essentially free from all these kinds of impurity. Otherwise the calculated values have very little value.

Montmorillonite and glauconite probably comprise isomorphous series and the isomorphism may involve the proxying of Al ions for Si ions in tetrahedral positions of the lattice or the proxying of Fe, Mg or Ti ions for Al ions in octahedral positions. The interlayer positions may be occupied by any of various kinds of cations or some of them may be empty. The interlayer cations may or may not be exchangeable. It is not possible to determine base-exchange capacity or the exchangeable cations individually by calculation.

The numerical values obtained by calculation can be expressed by many different combinations of rational formulas. Therefore, the expression "end member formulas" for these minerals has no definite meaning. For a given sample, it can readily be shown that each of these combinations of formulas corresponds to the same overall chemical composition and this may closely approximate the analysis from which the formulas were calculated. But this agreement is an arithmetical necessity of the calculation, and therefore it has no significance.

The fact that the calculated negative charge on the lattice just balances the positive charge of the interlayer cations, is also an arithmetical necessity of the calculation. The balance merely indicates that no errors of calculation have been made. In no sense can it be regarded as evidence of purity of the sample. Neither can the balance be taken as evidence of the accuracy of the analysis.

Since the results of calculation on analysis of the fine grained minerals may be influenced significantly by impurities, admixed, intergrown or adsorbed, and since it may be impossible to secure definite proof that certain impurities were absent from the sample, it is suggested that the results should be treated cautiously and be given a qualitative rather than a quantitative interpretation.

INTRODUCTION

By means of calculation, several investigators (2, 8, 12, 15, 16) have attempted to determine just how the elements of certain fine grained minerals are distributed between tetrahedral, octahedral and interlayer, or so-called adsorbed, positions of the crystal lattice. In other words, the calculation is intended to show the nature of the isomorphism of the sample. The idea that these minerals belong to an isomorphous series is implicit in the assumptions on which the calculation rests.

As is well known, *x*-ray investigations have shown that montmorillonite and several other fine grained minerals are structurally similar to pyrophyllite and the micas. This means that they are made up of two tetrahedral planes of ions condensed with an octahedral plane, similar to that of hydrargillite or brucite, the combined three planes being considered the lattice layer. Such minerals are called three layer minerals. There is good reason for the assumption that in all these fine grained minerals, as in the silicates in general, each Si ion is surrounded by 4 O ions. From what is known about the distribution of electropositive ions in the micas, it is logical to assign Fe, Mg, and minor amounts of a few other cations to positions of octahedral coordination. On the other hand, Al ions may be either tetrahedral or octahedral, and various cations may occupy the positions formed by the hexagonal network of O ions on the surfaces of the lattice layer.

In all the better known three layer minerals, it is fairly certain that there are 8 tetrahedral, 6 octahedral, and 2 interlayer positions per lattice unit. All eight tetrahedral positions must be occupied by some electropositive ion, and all the octahedral positions may be filled, as in talc and biotite, or only 2 out of 3 positions, as in pyrophyllite and pure heptaphyllite muscovite. The interlayer positions may or may not be occupied, depending on the charges of the tetrahedral and octahedral cations.

Taking into consideration the charges of the different ions, the distribution, if accurately determined, indicates at once the centers from which the lattice charge originates. If the calculation locates the charge chiefly in octahedral positions, Marshall (12) and Ross and Hendricks (16) placed the mineral in the montmorillonite class; if in tetrahedral positions, the mineral, according to them, may be either beidellite, nontronite, or certain others.

Although neither Marshall nor Ross and Hendricks stated definitely that base-exchange capacity can be determined by calculation, it is clear from their discussion, as well as from that of Nagelschmidt (15) that they attached real significance to the fact that the calculated lattice charge balances the charges of the interlayer cations. Also, the reason why these minerals possess base-exchange property is thought to be made manifest by the calculation.

As is well known, different specimens of these minerals vary considerably in chemical composition. This has been explained on the basis of isomorphism. The problem then is to determine the distribution, in a lattice of the mica type, of the elements found by chemical analysis. This involves giving consideration to ion sizes, ion charges, and the numbers of tetrahedral, octahedral, and interlayer positions and O atoms per lattice unit.

There are several conditions that must be fulfilled before the results of the calculation can be accepted with complete confidence: (a) It must be known that the sample is composed of material of a given lattice type, (b) the purity of the sample must be assured, (c) the chemical analysis must be reasonably accurate. In addition, certain other facts must be known, as will be made clear as this discussion proceeds.

In view of the implications, as well as direct statements, in published reports on this subject, and the inherent difficulties met with in determining the purity of the fine grained minerals in general, it seemed desirable to consider rather critically (a) the effects of impurities of various kinds, and (b) the basic assumptions underlying the calculation.

TABLE 1. PERCENTAGE COMPOSITION OF SAMPLES[1]

Sample	2	3	16	M	14	R	S
SiO_2	51.29	54.60	50.64	59.47	49.4	50.30	49.56
Al_2O_3	15.53	18.17	15.73	19.11	10.2	15.96	15.08
Fe_2O_3	1.78	3.17	1.60	3.60	18.0	0.86	3.44
FeO					3.1		
TiO_2	0.23	0.13	0.08	0.66			0.40
P_2O_5				1.19			
CaO	3.24	2.49	3.34	0.21	0.6	1.24	1.08
MgO	4.34	2.02	5.37	3.51	3.5	6.53	7.84
K_2O				0.03	5.1	0.45	
Na_2O	0.35	0.15	0.25		1.4	1.19	
H_2O loss at 105°C	15.66	13.92	14.83	11.72	8.3	23.61	22.96
H_2O loss above 105°C	7.53	5.69	7.96				
Total	99.95	100.34	99.80	99.50	99.6	100.24	100.36
Exchangeable CaO	3.03	2.83	3.21	0.08[2]			

[1] Sample 2. Ca-saturated montmorillonite from bentonite, Otay, California; analyzed by J. B. Page.

Sample 3. Ca-saturated montmorillonite from bentonite, Osage, Wyoming; analyzed by J. B. Page.

Sample 16. Ca-saturated montmorillonite from bentonite, Newberry, California; analyzed by J. B. Page.

Samples 2, 3, and 16 were composed of particles 1μ or less in diameter, as measured by settling velocity.

Sample M. H-saturated montmorillonite ($<0.2\mu$) from bentonite. Reported by C. E. Marshall (12), p. 442.

Sample 14. Glauconite. Reported by Hendricks and Ross (8), p. 692.

Sample R. Montmorillonite from bentonite, Otay, California. Reported as Sample 3 by Ross and Shannon (17), p. 88.

Sample S. Montmorillonite from bentonite, Otay, California. Reported as Sample 4 by Ross and Shannon (17). Sample also contains 0.01 per cent MnO.

[2] Per cent H.

METHOD OF CALCULATION

Molal (M) values are first calculated for each electropositive ion found by analysis. The O equivalent of each is then determined by multiplying (M) Si and Ti by 2, (M) Al and Fe‴ by 1.5, (M) Fe″, Ca and Mg by 1, and (M) K, Na and H ions by 0.5. The sum of the O molal values thus obtained must necessarily just equal that found by calculating the percentages of O in the several oxides shown in the analysis and then converting the sum of the O percentages into mol equivalents, as was done by Marshall (12). The ratio of 11 to the sum of the O molal values is the factor by which the molal values of the other elements are multiplied in order to convert them into atoms per 11 O atoms, the equivalent of a half lattice unit. These calculated values are then assigned to positions corresponding to those of a three layer lattice of the mica type, due consideration being given to ion sizes.

Four tetrahedral positions are filled with electropositive ions in the following order: (a) Si, (b) P, (c) Al. The remaining Al and all Fe, Ti and Mg ions are assigned to octahedral positions, provided the total does not exceed 3. If the total exceeds 3 the excess of Mg is assigned to interlayer positions along with all the remaining cations.

It may be noted here that with all the better known three layer minerals, the octahedral positions could not be occupied by cations as large as Ca, Na or K without undue distortion of the lattice, and no other positions sufficiently large for these cations are available in the interior of the lattice framework. Consequently, Ca, Na, and K ions are placed in interlayer positions, as is customary with the micas.

This method is but a slight modification of Nagelschmidt's (15) and Harvey's (6) methods. In its main outlines, it agrees also with Marshall's (12) and Hendricks and Ross' (8). In fact, all these methods are based on the same general ideas; they differ merely in the details of the calculation and the consideration given to ion size.

With all methods, it is assumed that, with minor exceptions, the analysis was made on a pure specimen, and that it was accurate. As will be shown presently, it is possible to gain some indication as to whether or not SiO_2 was present as impurity in certain samples, but this is not always possible. However, there appears to be no means of determining by calculation whether certain other kinds of impurity were present or absent.

EFFECT OF IMPURITIES

SiO_2. The effect of SiO_2 can perhaps best be shown by calculations on known mixtures of SiO_2 and theoretically pure heptaphyllite muscovite, $K(Al)_2(Si_3Al)O_{10}(OH)_2$. Such data are reported in Table 2.

Here it is shown that the calculated atoms of K and Al (both tetrahedral and octahedral) and the lattice charge,* all slowly decrease as SiO_2 is added, and the number of Si atoms gradually increases, as would be expected. However, it is necessary to add SiO_2 to the extent of about one-third of the sample in order to bring the total calculated Si atoms above 4 per half lattice unit. On the other hand, the presence of SiO_2 is at once indicated by a reduction in the number of octahedral atoms below the normal 2.0.

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* Lattice charge is determined by subtracting the sum of the charges of all tetrahedral and octahedral cations from 22, the charge of 10 O ions and 2 (OH, F) ions.

TABLE 2. EFFECT OF SiO_2 ON CALCULATED LATTICE POSITIONS FOR MUSCOVITE

Sample	Interlayer	Octahedral	Tetrahedral		Total Octahedral Atoms	Charges	
	K	Al	Si	Al		Lattice	Interlayer cations
Pure muscovite by wt.	1.000	2.000	3.000	1.000	2.000	−1.000	+1.000
1 part SiO_2 +100 parts muscovite	0.988	1.994	3.030	0.970	1.994	−0.988	+0.988
5 parts SiO_2+100 parts muscovite	0.945	1.971	3.142	0.858	1.971	−0.945	+0.945
20 parts SiO_2+100 parts muscovite	0.806	1.903	3.486	0.514	1.903	−0.805	+0.806
40 parts SiO_2+100 parts muscovite	0.675	1.837	3.813	0.187	1.837	−0.676	+0.675

If applied to analyses of similar mixtures, the calculated values shown in Table 2 might easily be interpreted as indicating a hydrous mica. Thus there is strong reason why any sample showing less than 2.0 calculated octahedral cations per half lattice unit should at once be suspected of containing SiO_2 as impurity. In fact, to accept the results on any sample of the three layer minerals when the total octahedral atoms is less than 2.0, is to open wide the door to relatively large amounts of SiO_2 as impurity.

Contrary to what is likely to be anticipated, the results of Table 2 show that the presence of SiO_2 as impurity is not necessarily reflected by an excess of calculated Si ions, but rather by a deficiency of the ions which go into octahedral positions. This is an important point to which further reference will be made. With pyrophyllite and talc, SiO_2 as impurity is at once indicated by an excess of calculated Si atoms, but this is not true of minerals which contain Al in tetrahedral coordination.

In this connection it should be pointed out that Marshall avoided a deficiency of octahedral atoms by assigning Ca atoms to this layer in numbers sufficient to provide a total of 2.0 atoms per half lattice unit. Whatever excess of Ca remained was referred to as among the "cations per unit cell," whether exchangeable or nonexchangeable. Since each half lattice unit presumably contains 3 octahedral positions, if Ca ions can fit into some of them, why not into others? In a word, if any nonexchangeable Ca ions are assigned to octahedral positions, why not all of them?

Hendricks and Ross' remarks on this point should also be noted. In commenting on the means by which they provide equivalence between the calculated charge on the lattice and that of the interlayer cations, they state: "It is brought into agreement by change of Al between octahedral and tetrahedral coordination, Σ (the total) *being finally greater or less than 2.00.** In only 2 of the 42 analyses used in this study is the value of Σ below 2 and in most of them it is slightly, but significantly above 2." Again in referring to samples which gave a total of 1.94 octahedral atoms, they state: "While this is not an impossible situation, it is indicative of an unusual condition of formation and might be the result of lattice alteration." In view of the foregoing it might also have been due to SiO_2 as impurity in the sample.

TABLE 3. EFFECT OF SiO_2 ON THE CALCULATIONS FOR MONTMORILLONITE 3

Sample	Adsorbed		Octahedral				Tetrahedral		Total Octahedral Atoms	Charges	
	Ca	Na	Al	Fe'''	Ti	Mg	Si	Al		Lattice	Interlayer cations
As analyzed	0.195	0.021	1.540	0.174	0.007	0.220	3.979	0.021	1.941	−0.411	+0.411
Less 6% SiO_2	0.211	0.023	1.545	0.189	0.007	0.238	3.849	0.151	1.979	−0.446	+0.445
Less 8% SiO_2	0.217	0.024	1.545	0.194	0.008	0.245	3.799	0.201	1.992	−0.462	+0.458
Less 10% SiO_2	0.224	0.024	1.547	0.200	0.008	0.253	3.748	0.252	2.008	−0.473	+0.472

TABLE 4. CALCULATIONS ON MONTMORILLONITE 16 ASSUMING VARIOUS IMPURITIES

Sample	Adsorbed		Octahedral				Tetrahedral		Total Octahedral Atoms	Charges	
	Ca	Na	Al	Fe'''	Ti	Mg	Si	Al		Lattice	Interlayer cations
As analyzed	0.276	0.037	1.328	0.093	0.004	0.616	3.900	0.100	2.041	−0.589	+0.589
Less 1.60% Fe_2O_3	0.279	0.037	1.396		0.005	0.624	3.950	0.050	2.025	−0.594	+0.595
Less 0.02 mols Al	0.279	0.037	1.302	0.094	0.005	0.624	3.950	0.050	2.025	−0.594	+0.595
Less 0.0167 (M) Mg	0.278	0.037	1.365	0.093	0.005	0.543	3.928	0.072	2.006	−0.592	+0.593
Less 0.0223 (M) Si+ 0.0167 (M) Mg[1]	0.283	0.038	1.362	0.095	0.005	0.553	3.897	0.103	2.015	−0.606	+0.604
Less 0.01 (M) Si, 0.0067 (M) Al and 0.0167 (M) Mg[2]	0.281	0.038	1.355	0.095	0.005	0.550	3.931	0.069	2.005	−0.599	+0.600

[1] Equivalent to talc.

[2] Approximately equivalent to chlorite.

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* Italics by the writer.

Table 3 reports the calculations on a sample of montmorillonite with and without the elimination of certain amounts of SiO_2 from the analysis. The results show that, as SiO_2 was eliminated, the calculated values for all other cations gradually increased, as would be expected from the results shown in Table 2. It is necessary to eliminate SiO_2 to the extent of about 10 per cent of this sample in order to raise the total octahedral cations to 2.0. These data further confirm the idea that SiO_2 as impurity may be reflected by the number of octahedral cations rather than by an excess of tetrahedral Si ions. However, as will be shown later, this is not necessarily apparent.

Effect of Fe_2O_3 and Al_2O_3. As shown in Table 4, the elimination of Fe''', or an equivalent amount of Al, produces identical effects on the calculated values for all the other ions. This is merely a necessary consequence of the facts that both are trivalent and both occupy corresponding lattice positions. The amount of octahedral Fe''' and Al, being reduced by the elimination, the total octahedral cations was reduced accordingly. Thus the effect of Fe_2O_3 or Al_2O_3 as impurity is to produce changes in the calculated values exactly the opposite of those produced by SiO_2.

Effect of P_2O_5 and TiO_2. Marshall (12) reported analyses of samples of montmorillonite from a bentonite, which contained exceptional amounts of P_2O_5 and considerable TiO_2. He pointed out that, theoretically, P ions could occupy tetrahedral positions in the montmorillonite lattice. Neverless, montmorillonite has the power to adsorb phosphate ions from solutions, possibly by exchange with OH ions on the edges of the lattice.

As is well established, TiO_2 is often found as leucoxene in fine grained materials of volcanic origin. Moreover, Ti minerals are extremely insoluble and, therefore, it is improbable that Ti ions will become available for lattice positions during the alterations which volcanic materials must undergo in the formation of bentonite.

TABLE 5. MONTMORILLONITE M. CALCULATED LATTICE

Sample	Adsorbed			Octahedral				Tetrahedral			Total Octahedral Atoms	Charge	
	Ca	K	H	Al	Fe'''	Ti	Mg	Si	P	Al		Lattice	Interlayer cations
As analyzed	0.015	0.002	0.314	1.429	0.177	0.033	0.342	3.890	0.066	0.044	1.981	−0.344	+0.346
Less 5% SiO_2	0.015	0.002	0.334	1.425	0.188	0.035	0.363	3.789	0.070	0.141	2.011	−0.366	+0.366
Less TiO_2	0.015	0.002	0.316	1.461	0.178		0.344	3.913	0.066	0.021	1.983	−0.350	+0.348
Less P_2O_5	0.015	0.002	0.319	1.444	0.180	0.033	0.347	3.947		0.051	2.004	−0.353	+0.351
Less TiO_2 and P_2O_5	0.015	0.002	0.321	1.479	0.181		0.349	3.973		0.027	2.007	−0.355	+0.353

Hence, it is of interest to consider the effects of P_2O_5 and TiO_2 as impurities. The data presented in Table 5 illustrate this point. The analysis used was that reported by Marshall for extremely small particles ($<0.2\mu$) of montmorillonite. Larger particles from the same bentonite were also analyzed. Marshall pointed out that particles larger than 0.5μ contained an excess of SiO_2. As shown in Table 5, the particles even less than 0.2μ might also have contained SiO_2 as impurity, since the total calculated octahedral atoms of the sample as analyzed was somewhat less than 2.0. However, this might have been due to adsorbed or admixed phosphate, for the elimination of P_2O_5 affected the calculated results remarkably like the elimination of SiO_2, that is, it tended to increase the number of calculated octahedral atoms.

The same general kind of results were obtained by calculating Marshall's analysis of the sample 0.5μ–0.2μ, but with the samples coarser than 0.5μ the sum of the calculated Si and P atoms exceeded 4 per half lattice unit which, as indicated above, Marshall considers to be evidence of an excess of SiO_2.

It should be pointed out that Marshall's samples were electrodialyzed. Hence, they could hardly have contained soluble salts as impurities. What effect electrodialysis produces on adsorbed phosphate is not certain. Conceivably, it might remove the same. Hence, it is not certain that phosphate was adsorbed on this sample.

The analyses of the several sized particles as reported by Marshall indicate that this bentonite was extraordinarily heterogeneous. Silica was no doubt the most abundant impurity, but other impurities were also probably present, and, as indicated above, there is reason for doubt about the purity of even the smallest sized particles. As between particles $<0.2\mu$ and those from 0.2μ to 0.5μ, the ratios $SiO_2:Al_2O_3:Fe_2O_3:MgO$ were fairly constant, but this was far from true of the ratios $P_2O_5:CaO:TiO_2$. The writer is unable to avoid the conclusion that all these samples were more or less impure, and the same is thought to be true of samples 2, 3, 16 as reported in this paper.

Effect of Interleaving. In addition to admixtures, the crystals of these minerals might be intergrown with layers of chlorite, talc, brucite, hydrargillite, or possibly certain other minerals, as Gruner (5) suggested for vermiculite and Hendricks and Alexander (7) suggested for certain soil colloids. Therefore, it is appropriate to consider what effects would be produced by intergrowths of these substances. Such data are presented in Table 4. The effects on the calculation made on any of these samples will, of course, be the same whether the impurities were present as admixtures or were intergrown with the crystals as occasional layers.

It is of interest to note, first, that the elimination of any one of these substances, as well as of Fe_2O_3, produced one effect in common, namely a reduction in total octahedral atoms. The presence of only a very small amount of any one of these substances would account for the fact that the calculation on the original analysis gave results which indicated a certain percentage of octophyllite lattice units. (An excess above 2.0 of total calculated octahedral atoms must represent octophyllite units.) Secondly, the elimination of none of these substances greatly affected the calculated overall lattice charge. Other minor effects are apparent in the table.

Comparison of Table 4 with Tables 2 and 3 shows that the effects of SiO_2 as impurity might be largely cancelled by the presence of any one of several other kinds of impurity, whether present as admixtures or intergrown. Thus the fact that the total calculated octahedral atoms is exactly 2.0 per lattice unit is not positive proof that the sample was pure.

ADSORBED CATIONS

The foregoing calculations were made on the assumption that all the Mg, Al and Fe were present either as essential framework ions or else as constituents of some impurity. It is of interest to examine this assumption.

TABLE 6. CALCULATIONS ON DIFFERENT SAMPLES OF MONTMORILLONITE FROM THE SAME DEPOSIT OF BENTONITE

Sample	Adsorbed				Octahedral				Tetrahedral		Total Octahedral Atoms	Charge	
	Ca	K	Na	Mg	Al	Fe'''	Ti	Mg	Si	Al		Lattice	Interlayer cations
2	0.267		0.052		1.366	0.103	0.013	0.498	3.955	0.045	1.980	−0.590	+0.586
R	0.103	0.045	0.178		1.343	0.050		0.752	3.889	0.111	2.145	−0.428	+0.429
S	0.089				1.176	0.199	0.023	0.898	3.810	0.190	2.296	−0.177	+0.178
R Alternate	0.103	0.045	0.178	0.145	1.343	0.050		0.607	3.889	0.111	2.000	−0.718	+0.719
S Alternate	0.089			0.296	1.176	0.199	0.023	0.602	3.810	0.190	2.000	−0.769	+0.770

Table 6 reports the calculations on three different samples of montmorillonite, all of which were obtained from the same deposit of bentonite at Otay, California. Reference to Table 1 shows that the chief differences between these samples were in their Fe_2O_3 content and in the ratio of CaO to MgO. The fact that sample 2 contained much more CaO and correspondingly less MgO than samples R and S (17) was probably due chiefly to differences in the preliminary treatment of the samples. Number 2 was intentionally treated in such way as to bring about as complete

Ca saturation at *pH* 7 as possible, which means that readily exchangeable cations of all kinds were replaced by Ca ions. Soluble salts were also carefully removed. As separated from the original bentonite, sample 2 contained a substantial amount of exchangeable Mg. It is probable that samples R and S also contained exchangeable Mg. Attention is also called to the fact that K_2O and Na_2O were reported in sample R but not in sample S. In making the calculations on sample S, Mn was left out because the amount present would not affect the calculations significantly.

Mg Ions. The calculated values for samples R and S are reported on two bases, namely, (a) with all Mg ions in octahedral coordination, and (b) with a part of the Mg ions in interlayer or adsorbed positions. Since no information is available concerning the actual content of exchangeable Mg in these two samples, the assignment of Mg ions to adsorbed positions was purely arbitrary, as it must necessarily be with any sample whose content of exchangeable Mg is unknown. Conversely, *the assignment of all Mg ions to octahedral positions where the content of adsorbed Mg is unknown is almost equally arbitrary.* If we assume that all the Mg ions were in octahedral coordination in these two samples, then the lattice charge per half lattice unit would be -0.428 and -0.177, respectively, whereas, if amounts of Mg were adsorbed sufficient to provide exactly 2.0 octahedral cations, the respective charges would be -0.718 and -0.769. Thus we see that the position to which Mg is assigned may make great differences in the distribution of the charges.

Unfortunately, we have no accurate analytical method for differentiating sharply between exchangeable Mg ions and Mg ions located in octahedral positions. For example, when a finely pulverized sample of biotite is treated with a salt solution, as in the determination of the exchangeable bases, considerable Mg passes into solution. Kelley and Jenny (10) suggested that this is evidence of the partial decomposition of biotite. In addition, after as complete replacement as possible by Ca ions of all exchangeable cations held by montmorillonite, further treatment of the sample with ammonium salt solution commonly brings Mg into solution for a prolonged period. Moreover, upon electrodialyzing montmorillonite, Mg passes into the cathode cell of the apparatus for an indefinite period.

Therefore, it is not possible to draw a sharp line between interlayer Mg and octahedral Mg. Nevertheless, there is good evidence that many clays contain exchangeable Mg. Soil colloids commonly contain substantial amounts. As shown by Kelley and Liebig (11), treatment of montmorillonite with sea water results in the taking up of considerable Mg by exchange. Since the bentonites have probably been formed in saline solutions which contained more or less Mg, it is therefore to be expected that montmorillonite from bentonite will contain more or less adsorbed Mg.

Although mica with Mg ions in interlayer positions is not definitely known, it is not certain that nonexchangeable but adsorbed Mg could not occur in the three layer minerals just as Ca, Na and K are known to occur in the micas.

Fe and Al Ions. It is apparent that the differences in Fe_2O_3 in these samples of montmorillonite from Otay, California, are reflected in the calculated values as shown in Table 6. Even granting that the K_2O, Na_2O and TiO_2 found by analysis were present as impurities (for which substantial proof is entirely lacking) these samples still differ considerably.

As is well known, indefinite, but usually positive, amounts of Al, Fe and frequently Mn are brought into solution upon treating many samples and types of clay from different localities with neutral salt solutions. This is often explained on the ground that these cations were present in exchangeable form, that is adsorbed. As Marshall pointed out, the amount of such Al may equal one or two per cent of the sample. Since exchangeable monovalent and divalent cations can be readily replaced by trivalent cations by treating the sample with a dilute solution of $AlCl_3$ or $FeCl_3$, there seems to be no necessary reason why natural deposits of montmorillonite might not contain at least small amounts of adsorbed Al and Fe ions. These might be adsorbed not as trivalent ions but as divalent or monovalent ions. Hence, it is pertinent to consider the effect of adsorbed Al and Fe on these calculations.

In all the preceding calculations none of the Al or Fe was assigned to adsorbed positions. However, if any part of these elements should have been adsorbed, the effect on the calculated formula would have been quite analogous to what has already been shown for Mg ions. That is, the total octahedral atoms would be decreased and the lattice charge and that of the adsorbed cations would be increased. Hence, it is important to know definitely what part, if any, of the Al and Fe of the sample is adsorbed. Unfortunately, we have no accurate method for this determination. Mattson (14) found upon treating certain montmorillonitic soil colloids with $AlCl_3$ that substantial amounts of Al were adsorbed and at the same time the base exchange capacity decreased markedly. This latter might mean that adsorbed Al ions do not dissociate readily. Nevertheless, it is improbable that any considerable amount of Al or Fe ions will be adsorbed on the naturally occurring montmorillonite of strongly alkaline deposits.

H Ions. As is well known, the exchangeable metallic cations of colloids can be readily replaced by H ions. Any sample of montmorillonite which has been subjected to the sustained leaching action of rain water is likely to contain more or less adsorbed H ions. Certain deposits of bentonite are definitely acidic and the montmorillonite of these almost certainly contains adsorbed H ions and possibly adsorbed Al ions also. Other deposits are either approximately neutral or slightly alkaline. These may also contain more or less adsorbed H ions. It is important to stress here that the fact that the material is neutral or even slightly alkaline, does not necessarily preclude the possibility of adsorbed H ions. If present, adsorbed H ions certainly would serve to neutralize negative charges on the lattice, and to ignore the same would alter all the calculated values, since the O equivalent of the adsorbed H ions would be left out. Just as in the case of Al and Fe, we have no certain method of determining adsorbed H ions except by treating the sample with fairly strongly alkaline solutions. However, under the alkaline conditions of many bentonite deposits, it is unlikely that important amounts of adsorbed H ions are present.

GLAUCONITE

Table 7 reports the calculations on a sample of glauconite, the analysis of which was reported by Hendricks and Ross (8). These data show that the results of calculation on glauconite would be influenced by impurities very much as are those of montmorillonite. By assuming the presence of 1.60 per cent Fe_2O_3, or one layer of brucite or chlorite per 50, an equally possible lattice can be calculated for this sample. Calculations based on an assumed mixture of 1 part CaO and 100 parts of this sample as analyzed also gave a perfectly stable lattice. Thus it is shown that more than 1 per cent of $CaCO_3$ might be present in material of this kind with-

TABLE 7. GLAUCONITE 14. CALCULATED LATTICE

Sample	Adsorbed			Octahedral				Tetrahedral		Total Octahedral Atoms	Charge	
	Ca	K	Na	Al	Fe'''	Fe''	Mg	Si	Al		Lattice	Interlayer cations
As analyzed	0.048	0.476	0.198	0.499	0.991	0.189	0.382	3.618	0.382	2.061	−0.770	+0.770
Less 1.60% Fe_2O_3	0.048	0.482	0.201	0.553	0.915	0.192	0.386	3.662	0.338	2.046	−0.778	+0.778
Less 0.0167 (M) Mg	0.047	0.480	0.200	0.528	0.998	0.191	0.311	3.642	0.358	2.028	−0.776	+0.774
Less 0.01 (M) Si, 0.0067 (M) Al, and 0.0167 (M) Mg[1]	0.048	0.485	0.203	0.509	1.011	0.193	0.314	3.642	0.358	2.027	−0.784	+0.784
Plus 1 part CaO per 100	0.124	0.472	0.197	0.459	0.983	0.208	0.379	3.586	0.414	2.029	−0.914	+0.917

[1] Approximately equivalent to chlorite.

out its presence being revealed by the calculation. The effects produced by adding CaO assume special interest in the light of the fact that Hendricks and Ross calculated formulas for certain samples of glauconite which contained substantial amounts of CO_2.

The foregoing data show the general types of effects that would be produced by various kinds of impurities. If the amount of certain impurities exceeds a certain percentage, which percentage depends on the composition of the sample, an excess of SiO_2 will be found, or the total octahedral ions will be insufficient to provide a structurally stable lattice, or the sum of the adsorbed cations per half lattice unit will exceed 1. But within limits wide enough to embrace substantial amounts of impurities, it is quite possible to calculate lattices which theoretically would be perfectly stable. If mixtures of these kinds should be analyzed in the first place, none of these methods of calculation apparently affords a certain means of detecting the same. Moreover, the calculation cannot be used as a check on the accuracy of the analysis. In fact, theoretically possible lattices can be calculated on the basis of grossly inaccurate analyses.

It should be pointed out here that neither Marshall nor Hendricks and Ross employed lattice calculations as a means of establishing the purity of their samples. Nevertheless, the fact that definite places in the lattice were found for every element and definite formulas were proposed for certain samples, implies that the samples were thought to be pure, and it is certain that other scientists have assumed that this was evidence of purity.

PYROPHYLLITE MIXTURE

To show further that these calculations could lead to erroneous conclusions, not only as to the purity of the sample, but also as to the specific mineral present, the following calculations were made. The percentage composition of theoretically pure pyrophyllite was calculated. Then the percentage composition of a hypothetical mixture consisting of 100 parts pyrophyllite, 5 parts MgO, and 2.5 parts of CaO was calculated. Applying to this hypothetical analysis the same kind of calculations used above, results were obtained as reported in Table 8. These data show not only a

TABLE 8. HYPOTHETICAL MIXTURE OF PYROPHYLLITE, MgO, AND CaO
CALCULATED LATTICE

Adsorbed	Octahedral		Tetrahedral		Total Octahedral Atoms	Charges	
Ca	Al	Mg	Si	Al		Lattice	Interlayer cations
0.152	1.686	0.423	3.791	0.209	2.109	−0.305	+0.304

theoretically possible lattice with all the Ca as adsorbed ions, and all the Mg in octahedral coordination, but they also indicate that the analysis was that of a Ca-saturated montmorillonite or glauconite. An equally plausible lattice can be shown for this mixture by transferring Mg from octahedral to absorbed positions.

While, of course, no competent mineralogist is likely to mistake such a mixture for montmorillonite, these results show something of the treachery of this kind of calculation, particularly when applied to analyses taken from the literature.

END MEMBERS

Rational formulas corresponding to the preceding lattice values can readily be derived. Various combinations of theoretically possible formulas can be shown to be possible for a given sample. Four different combinations are given in Table 9 for the foregoing sample of glauconite. Many more could be shown. However, there are certain limits that cannot be exceeded. For example, the calculation definitely fixes the number of half lattice units containing tetrahedral Al at 38.5 per cent of the total in this sample, and the number containing 3 octahedral atoms must be 6.1 per cent. The latter may have been either neutral or charged, but since only divalent cations can occupy 3 octahedral positions in a given half lattice unit without imparting a positive charge to the octahedral layer, this may possibly impose a limit on the choice. In other respects rather wide choice is permissible. If this sample was a pure specimen, 23 per cent of the lattice units must have been electrically neutral, that is, they contained no interlayer cations.

Thus it follows that, insofar as this sample is concerned, the expression "end members," is essentially meaningless. This conclusion is consistent with Bragg's (1) view of the micas. He stated (p. 213): "It is almost impossible to give formulas of end members when so many types of replacement may take place. Mauguin's work showed that the concept of end members must be replaced by that of the number of atoms in certain groups within the cell. . . . The main point brought out by Mauguin's analysis is that the total number of oxygen atoms in the structural unit (in fluoriferous micas, of O and F atoms) is always *twelve* within the errors of analysis. Other constituents vary widely but this remains constant."

If the sample as analyzed was pure, it necessarily follows that the various kinds of lattice units were randomly distributed in all the small crystals present in this sample. Although K ions were the most abundant interlayer cations, about $\frac{1}{4}$ were Na ions with a still smaller number of Ca ions. How were these distributed and were they exchangeable?

TABLE 9. COMBINATIONS OF FORMULAS DERIVED FROM CALCULATED DATA FOR GLAUCONITE 14, TABLE 7

Per cent		I	Per cent		II
6.1	23.0	$(Mg)_3(Si)_4O_{10}(OH)_2$	6.1	23.0	$(Mg)_3(Si)_4O_{10}(OH)_2$
16.8		$(Fe''')_2(Si)_4O_{10}(OH)_2$	1.9		$(Fe''')_2(Si)_4O_{10}(OH)_2$
0.1		$(Al\ Fe''')(Si)_4O_{10}(OH)_2$	15.0		$(Al)_2(Si)_4O_{10}(OH)_2$
18.9	77.0	$*x(Fe'''Fe'')(Si)_4O_{10}(OH)_2$	18.9	77.0	$x(Fe'''Fe'')(Si)_4O_{10}(OH)_2$
19.9		$x(Fe'''Mg)(Si)_4O_{10}(OH)_2$	19.9		$x(Al\ Mg)(Si)_4O_{10}(OH)_2$
13.3		$x(Fe''')_2(Si_3Al)O_{10}(OH)_2$	38.2		$x(Fe''')_2(Si_3Al)O_{10}(OH)_2$
24.9		$x(Al)_2(Si_3Al)O_{10}(OH)_2$			
100.0			100.0		

		III			IV
7.5	23.0	$(Fe''')_2(Si)_4O_{10}(OH)_2$	22.9	23.0	$(Fe''')_2(Si)_4O_{10}(OH)_2$
15.5		$(Al)_2(Si)_4O_{10}(OH)_2$	0.1		$(Al\ Fe''')(Si)_4O_{10}(OH)_2$
6.1	77.0	$x(Mg)_3(Si_3Al)O_{10}(OH)_2$	6.1	77.0	$x(Fe'')_3(Si_3Al)O_{10}(OH)_2$
32.1		$x(Fe''')_2(Si_3Al)O_{10}(OH)_2$	7.2		$x(Fe''')_2(Si_3Al)O_{10}(OH)_2$
19.9		$x(Fe'''Mg)(Si)_4O_{10}(OH)_2$	24.9		$x(Al)_2(Si_3Al)O_{10}(OH)_2$
18.9		$x(Al\ Fe'')(Si)_4O_{10}(OH)_2$	38.2		$x(Fe'''Mg)(Si)_4O_{10}(OH)_2$
			6.0		$x(Fe'''Fe'')(Si)_4O_{10}(OH)_2$
100.0			100.0		

As Analyzed		As calculated from any set of the above formulas	
SiO_2	49.4	SiO_2	51.81
Al_2O_3	10.2	Al_2O_3	10.70
Fe_2O_3	18.0	Fe_2O_3	18.86
FeO	3.1	FeO	3.24
CaO	0.6	CaO	0.61
MgO	3.5	MgO	3.67
K_2O	5.1	K_2O	5.34
Na_2O	1.4	Na_2O	1.46
H_2O	8.3	H_2O	4.29
Total	99.6	Total	99.98

* x = Ca, 4.8; K, 47.6; Na, 19.8.

Socalled end members were also figured out for montmorillonite 16. Just as with the sample of glauconite, a considerable number of combinations of formulas is possible. With this sample, Ca ions were known to be the only exchangeable cations present, but the sample also contained nonexchangeable Ca and nonexchangeable Na. The last-named Ca ions might have been present as constituents of a substance corresponding to the brittle mica, margarite, and the Na ions as soda mica. Were these arranged randomly or in occasional layers? If the latter, then the crystals were interstratified, and hence not homogeneous. Thus it becomes apparent that various complications and essentially unanswerable questions arise when this question is examined closely.

Each combination of formulas listed in Table 9 contains every element found by analysis exclusive of H_2O. In the lower part of the table the original analysis of the sample and the chemical composition calculated from one of the combinations of formulas are shown. Each combination of formulas gives the same chemical composition. It will be noted that the calculated composition approximates the analysis. However, they differ somewhat. This is due mainly to differences in H_2O, but partly to the fact that the original total was 99.6 instead of 100. However, the ratio of $SiO_2:Al_2O_3:Fe_2O_3$, etc., is the same in both. If no errors of calculation have been made, this must be so, since the ratio of element to element is preserved throughout the calculation. Therefore, the fact that the calculated chemical composition approximates the original analysis has no significance; it is merely an arithmetical necessity and means nothing more than that no errors of calculation have been made.

It is also quite possible to derive rational formulas for known mixtures, such as the pyrophyllite mixture shown in Table 8. In fact, the calculated values, as listed in the foregoing tables, represent a sort of average formula for each sample. The rational formulas merely express the same results in terms of whole rather than fractional atoms. Therefore, the fact that rational formulas can be derived and that the calculated chemical composition approximates the analysis cannot in any sense be regarded as evidence of purity. Nor does it have any other significance.

That the calculated per cent of H_2O differs from the percentage found by analysis, might, of course, mean that the sample contained adsorbed H_2O. On the other hand, it might also mean that the sample contained some constituent, either admixed or intergrown, with a greater content of OH ions. These results suggest that exact knowledge as to the lattice OH ions of the sample could be used as a check on purity. Ross and Hendricks (16) pointed out that thermal analysis shows "that H_2O lost above 350°C is usually a close measure of the hydroxyl content." On the other hand, considerable variation has been found in the weight losses when samples of montmorillonite from different sources are heated from 300°C or even 400°C to 800°C. Furthermore, the temperature range over which adsorbed H_2O is driven off overlaps that of H_2O loss from lattice OH ions, as was reported by Kelley, Jenny and Brown (9). For this reason, thermal analysis is not an accurate means of determining lattice OH ions. As is well established, the socalled $+H_2O$ of montmorillonite from different sources often differs substantially. With samples 2, 3 and 16, Table 1, all of which were Ca-saturated, the H_2O given off above 105°C varied from 5.69 to 7.96 per cent.

General Discussion

Among the impurities most likely to be found in the fine grained minerals, SiO_2 is perhaps the most important. It may be present as crystalline quartz or cristobalite, as amorphous SiO_2, or as adsorbed silicate ions. *X*-ray analysis and optical methods can probably be depended on for evidence concerning crystalline forms of SiO_2, at least if the amount exceeds a low minimum, but amorphous SiO_2 and adsorbed silicate ions are more difficult to detect. That silicate ions are likely to be adsorbed by montmorillonite is suggested by the following. Bentonite deposits, the most abundant source of montmorillonite, are often alkaline, sometimes strongly so, as is the case with the Wyoming deposit from which sample No. 3 was obtained. This is just the condition in which SiO_2 is soluble. It is well established that upon treating a sample of montmorillonite with a soluble silicate, substantial amounts of silicate ions become adsorbed, possibly through exchange with OH ions on the edges of the lattice. Phosphate ions might also be similarly adsorbed. Such adsorbed ions are held rather tenaciously, and when present they will, of course, influence the total SiO_2 and P_2O_5 of the sample.

Amorphous Fe or Al oxide or hydroxide may also be present, although the amount in carefully prepared samples is not likely to be great.

As indicated already, interleaving is a possibility. Hydrargillite, chlorite, brucite, talc, pyrophyllite, the micas, kaolinite, and possibly other minerals might be present as occasional layers in the crystals of montmorillonite and other fine grained minerals. But whether the sample contains adsorbed, admixed or intergrown constituents, the effect on the calculations would be the same. If any of these kinds of substances is present in any of these forms, the crystals could not be said to be homogeneous.

Since montmorillonite has an expanding lattice, it would be expected that all the interlayer cations would be exchangeable, but many samples are known to contain small amounts of nonexchangeable Ca, Na and K. However, if the sample should contain an occasional layer with the composition of margarite, soda mica, muscovite or biotite, the adsorbed cations attached to these layers would probably not be exchangeable. The attractions of such interlayer cations might be shared between adjacent layers and thus prevent expansion along these interlattice planes. It is probable that such layers in materials like the fine grained minerals could not be detected on an ordinary *x*-ray powder diagram, by optical means or by thermal analysis. Interleaving would certainly have a bearing on the chemical composition, the calculated octahedral atoms, and the fact that nonexchangeable cations were present.

As pointed out already, Marshall (12) assigned Ca ions to octahedral positions and Caldwell and Marshall (2) assigned only exchangeable ions to interlayer positions. Accordingly, nonexchangeable Ca and K ions were placed in the gibbsite or brucite sheets of the lattice, that is in octahedral positions. In the opinion of the writer, this is very questionable. These ions are too large to occupy such positions and to assign them to octahedral positions makes it possible to calculate lattices for grossly impure samples, such as soil colloids almost certainly are.

The importance of definite information as to what ions are adsorbed can scarcely be overemphasized. This may apply to Si, P, Al, and Fe, but perhaps more particularly to Mg and H ions. Montmorillonite from certain bentonites is known to contain considerable replaceable Mg. It is not safe to assume, in the absence of evidence to the contrary, that all Mg ions occupy positions of octahedral coordination. Whether or not all interlayer Mg ions are readily exchangeable is not known definitely.

As indicated already, adsorbed H ions may not be completely exchangeable at *pH* 7. Apparently complete dissociation of all adsorbed H ions takes place only at relatively high *pH*. It has been found that montmorillonite is able to neutralize $Ca(OH)_2$ or $Ba(OH)_2$ at relatively high *pH* values. At the same time Ca or Ba ions become adsorbed. Therefore, the term "base saturation" can be defined only in terms of *pH*. It follows that the determination of adsorbed H ions involves considerable uncertainty. The same can be said, even more emphatically about the determination of adsorbed Al ions. We simply have no certain method for this determination. Therefore, it is difficult to distinguish sharply between Al as framework cations and as interlayer cations.

As shown in Table 6, different samples of montmorillonite from one and the same bentonite deposit may vary considerably in chemical composition. This variation is not confined to SiO_2 and the usual adsorbed cations; it also applies to Fe''' as well. This is difficult to harmonize with the idea that the samples were composed exclusively of one homogeneous mineral. Critical study is needed of different samples carefully selected from the same stratum and from different strata of a given deposit.

Reference has been made to the fact that Marshall's samples were electrodialyzed. While electrodialysis unquestionably has usefulness in the study of the clay minerals, it is very questionable when applied to substances to be used for lattice calculation. The reason is that under electrodialysis decomposition gradually takes place and the decomposition products are not dialyzed out at equal rates. Mattson (13) showed that the electrodialyzing material adjacent to the anode membrane may have different composition from that adjacent to the cathode membrane. Caldwell and Marshall found that the decomposition products pass through the membranes at widely different rates. The Hector clay underwent decomposition to an extreme degree.

The foregoing tables show that the calculated charge on the lattice is just balanced by that of the interlayer or socalled adsorbed cations. This was true in all cases, and the balance is not disturbed by eliminating any constituent whatever, by adding a foreign substance, or by the decision as to whether a given ion is located in framework or interlayer positions. Neither does balance depend on the accuracy of the analysis. The reason for this is found in the arithmetical necessities of the calculation itself. Since the ratios of the several electropositive ions to their O equivalents are preserved throughout the calculation, and the same ratios obtain in the substituted positions in the lattice, it is an arithmetical necessity that the sum of the charges of the electropositive ions will just equal the charges of the O ions. Therefore, the overall assemblage of ions, including O and OH ions, will be electrically neutral. If all cations are placed in framework positions of the lattice, irrespective of the size and charge of the individual ions, it will be electrically neutral, and if some of the cation are placed in interlayer positions, their total charge must necessarily just balance the charge on the lattice. The magnitude of the two respective charges will be affected by transfer of cations from interior to exterior positions, but the balance will not be affected. Hence we can say definitely that there is absolutely no significance to this balance. It merely shows that no arithmetical errors have been made in the calculation. This applies to the method of Marshall, Hendricks and Ross, and all others.*

A further consequence follows from the foregoing, namely, it is not possible to calculate base-exchange capacity from the chemical analysis. Neither is it possible to determine by calculation which ions are exchangeable and which are not. Consideration of ion sizes leads to the conclusion that certain kinds of ions must be on the exterior of the lattice layers, but this by no means proves that all of the interlayer cations are exchange-

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* In recent correspondence both Marshall and Ross stated that they recognize that there is no significance to this balance. Ross also pointed out that the total octahedral atoms should be at least 2 per half lattice unit.

able, or that others could not be adsorbed. For example, while Mg ions can readily fit into octahedral positions, they can also, in fact sometimes actually do occur as exchangeable Mg ions, and could then not be wholly in octahedral positions. There is no known method of determining what ions are exchangeable or the base-exchange capacity save by actual experiment.

It should be emphasized that the actual, as contrasted with the assumed, interlayer or socalled adsorbed cations must be known before high confidence can be placed in the results of lattice calculation. Since among the various samples which have been used by previous investigators for these calculations, the exchangeable cations have been determined in only a relatively few, and since many analyses were taken from published reports which gave no information concerning their adsorbed cations, the proposed formulas cannot be said to be well established. They simply rest on too many assumptions.

However, the idea of isomorphism in the fine grained minerals is not weakened by the foregoing data and discussion; it is only the quantitative aspects thereof that are brought into question. Qualitatively, no evidence whatever has been presented that isomorphism is not a real feature of these minerals. But it is necessary to have quantitatively accurate data on which to extablish a formula. As Ross and Hendricks (16) pointed out, isomorphism affords a logical explanation for the colloidal and base-exchange properties of the minerals. No other hypothesis yet proposed so well accounts for these properties.

However, it cannot be said that this hypothesis is fully in harmony with all the facts. While the charge on the lattice, occasioned by the lack of balance between the framework cations and the electronegative O and OH ions, is probably largely responsible for the fact that montmorillonite contains exchangeable cations, the extraordinary swelling properties of the Wyoming type of bentonite and the electron micrographs of the same suggest that other factors may also be involved.

If silicate ions should be adsorbed by montmorillonite, these might be either monovalent or polyvalent, and the base-exchange capacity of the material might be increased by this adsorption. If so the exchangeable bases would then not necessarily be located between lattice layers. This, of course, is purely speculative. It suggests the need for a study on the relation between base-exchange capacity and adsorption of silicate ions.

In view of the way the results of calculation are affected by certain kinds of impurities, it is possible that montmorillonite is purely heptaphyllitic, the amount of calculated octahedral atoms in excess of 2.0 being due to interleaving. However, it will probably be difficult either to prove or disprove this idea. The author fully recognizes that isomorphism as between heptaphyllite and octophyllite is a distinct possibility, but since the calculated octahedral atoms rarely exceed 2.0 by more than one or two tenths, it seems more reasonable to assume interleaving. The same conclusions would also apply to glauconite. Ross and Hendricks' (16) formula, $Na_{0.33}(Al_{1.67}Mg_{0.33})(Si_4)O_{10}(OH)_2$ for montmorillonite is in agreement with the idea that this mineral is a pure heptaphyllite.

As was indicated in the introduction to this paper, Marshall and Ross and Hendricks separated beidellite from montmorillonite on the basis of the ratio of the charge on the octahedral layer to that of the tetrahedral layer. As shown in Table 3 this ratio may be influenced considerably by the presence of SiO_2 as impurity. With sample 3 as analyzed, this ratio was about 10:1, whereas, the elimination of an amount of SiO_2 sufficient to provide 2.0 octahedral atoms per half lattice unit changed this ratio to about 1:1. This, of course, does not disprove that beidellite differs from montmorillonite in the way indicated, but it does suggest that samples of alleged beidellite should be carefully scrutinized with respect to impurities of all types. As bearing on this point as well as on interleaving in general, Grim and Rowland (4) state: "The thermal evidence indicates that many bentonites and other clays thought to be composed of a single clay mineral are actually mixtures of clay minerals probably closely intergrown."

It is scarcely necessary to say that the eliminations reported in the foregoing tables were *solely* for the purpose of showing how impurities would affect the calculated results. When calculating a formula for an actual sample, it is probably rarely justifiable to eliminate any constitutent. Unless positive evidence is at hand showing that a given kind of impurity was actually present in the sample, to neglect this or that constituent, as has been done by certain workers (8, 16) is purely arbitrary and can no more be justified than the elimination of any other constituent. K_2O and Na_2O, for example, could not exist as such in natural deposits of montmorillonite or glauconite. They must be combined either as soluble salts or as some alumino or ferrosilicate. Therefore, in the absence of Cl, SO_4, etc., if these cations are eliminated, corresponding amounts of Si and Al must also be subtracted, but to do this leads at once into pure speculation. However strong the evidence of interleaving may be, if the specific substance involved is unknown, there seems to be no satisfactory correction that can be introduced in the calculation.

As is well known, F ions frequently proxy for OH ions in the micas. Consequently, the content of OH ions is complementary to that of F ions. In some samples practically all OH ions are replaced by F ions. Several workers have reported F in the highly magnesian clay which Foshag and

Woodford (3) described from Hector, California. It is probable that careful analysis will reveal the presence of F in other clays. Hence, it is pertinent to consider the effects produced on the lattice calculations by F. All the aforementioned methods are based, essentially, on the assumption that each half lattice unit contains 10 O ions and 2 OH ions or 11 O atoms in the dehydrated material. When F is a constituent of the lattice, the dehydrated form will not contain exactly 11 O atoms.

The effect of F can perhaps be best brought out by considering the following theoretical formulas for muscovite, representing the greatest possible extremes in F content:

(a) $K(Al)_2(Si_3Al)O_{10}(OH)_2$
(b) $K(Al)_2(Si_3Al)O_{10}F_2$

Mere inspection shows that the proxying of F for OH does not alter the relations of other ions. The sum of the charges of K, Al and Si ions in each formula is 22, the equivalent of 11 O ions. The presence of F in the sample will, of course, modify the absolute percentages of SiO_2, Al_2O_3, etc., but the sum of the O equivalent of all the cations just equals the O+F ions present. The ratios of Si:Al:K is the same regardless of the F content and these ratios rather than the absolute percentages determine the calculated results. Therefore, the F content should be ignored in making the calculation. To subtract an amount of O equivalent to F, as was done by Caldwell and Marshall (2), results in erroneous values for every electropositive ion present.

Finally, it is generally admitted that montmorillonite and other fine grained minerals are among the most difficult with which the mineralogist has to deal. The growing importance now being attached to these minerals and the difficulties involved in their elucidation require the application of all possible methods of investigation and the best efforts of trained workers in this field. Nothing in the foregoing should be construed as indicating that these minerals are hopelessly complex, or as casting doubt on the possibility of arriving at a satisfactory understanding of the same through investigation. The whole purpose of this paper is to show some of the difficulties that must be overcome. Only by recognizing difficulties are they likely to be overcome.

Neither should it be assumed that lattice calculation is entirely useless. Undoubtedly, these calculations have already served to show at least one reason why montmorillonite has base-exchange property, and the calculations have contributed to a better understanding of why different samples differ in percentage composition. Nevertheless, the foregoing shows that the very nature of these materials places a limit on what can be accomplished by calculation. Its value depends on the purity of the sample. Supplemental to careful selection, the sample should be rigorously tested optically, *x*-rayed, and thermo-analyzed. In addition, examination with the electron microscope may be useful, and certainly careful chemical tests including base-exchange determinations are indispensable. After all these tests have been applied, a considerable margin of doubt may still remain. The chemical analysis may even then be susceptible of different interpretation. Therefore, in the opinion of the writer, the calculated values should be treated tentatively and be given a qualitative rather than a quantitative interpretation.

Conclusions

1. Theoretically possible lattices can be calculated from analyses of grossly impure specimens of minerals. In fact, possible lattices can be calculated for mixtures of wholly amorphous substances. Therefore, three consequences follow: (a) except in extreme cases, it is not possible to determine by calculation whether or not a sample is pure; (b) theoretically possible lattices can be calculated on the basis of highly inaccurate analyses; (c) unless definite information is available showing that the sample contains crystalline material of a given type, the calculation has no value.

2. If the total octahedral atoms, as calculated, are found to be less than 2.0 per half lattice unit, the sample probably contained either SiO_2 or P_2O_5 as impurity. If the total exceeds 2.0 by one or two tenths, it is possible that Al, Fe or Mg was present either as a constituent of some impurity, admixed or intergrown, or as adsorbed cations. However, since SiO_2 tends to decrease the calculated values, while Al, Fe and Mg increase the same, the sample might contain impurities even when the total is exactly 2.0.

3. The fact that the Si atoms, as calculated, do not exceed the total number of tetrahedral positions of the three layer minerals, is not proof that the sample was free from SiO_2 as impurity. With minerals which contain tetrahedral Al ions, an excess of SiO_2 manifests itself first by a reduction in the calculated octahedral atoms and only when the amount of SiO_2 is relatively great will an excess of Si atoms be indicated.

4. Unless it is known definitely that the sample contains no appreciable amount of adsorbed Mg, the assignment of all the Mg ions to octahedral positions is arbitrary, and may lead to erroneous conclusions regarding lattice charge, adsorbed cations and chemical formula.

5. Interleaving is a possibility in all the fine grained minerals. Since small amounts of nonexchangeable Ca, Na and K are often found in

samples of montmorillonite, it is suggested that these ions may be adsorbed on distinct layers of brittle mica, soda mica, muscovite or biotite.

6. Montmorillonite and other fine grained minerals may contain adsorbed H, Al or Fe ions, but the amount is not likely to be important in strongly alkaline deposits.

7. It can readily be shown that a considerable number and variety of combinations of formulas apply equally well to a given sample. Therefore the expression, "end members," as applied to the isomorphous minerals dealt with in this paper, is essentially meaningless. That the chemical composition, as calculated from the derived formulas, approximates the original analysis, has no significance.

8. The fact that the calculated lattice charge balances the charge of the interlayer cations has no significance. Like the agreement just referred to, it is an arithmetical necessity of the calculation itself and merely shows that no errors have been made in the calculation.

9. Base-exchange capacity or the individual exchangeable cations cannot be determined by calculation, not even when the sample is absolutely pure.

10. It is highly probable that the fine grained three layer minerals belong to isomorphous series, but the quantitative aspects of isomorphism can be determined by calculation only if the sample is free from important amounts of impurities, both admixed and intergrown, and at the same time all adsorbed ions are known.

11. There is absolutely no substitute for purity if reliable formulas are to be calculated.

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