

INTERPRETATION OF CHEMICAL ANALYSES OF CLAYS

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ABSTRACT

As a means of distinguishing between the broad groups of clay minerals, chemical analysis may be a valuable supplement to other methods, but rarely will it remove the necessity for other methods, X-ray analysis in particular. The two- and three-layer clay minerals may be distinguished by the $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ ratio or SiO_2 · sesquioxide ratio, but these ratios do not provide criteria for dividing either class. Among the three-layer clays, which embrace montmorillonite, nontronite, and the diverse hydrous micas, non-exchangeable K is a better criterion. It seems probable that montmorillonite, as found in bentonite deposits, does not contain significant amounts of non-exchangeable K, whereas all known hydrous micas contain significant, although widely variable, amounts of non-exchangeable K.

The greatest value of chemical analysis inheres in the fact that by means of calculation the specific nature of the isomorphism may be determined. But the degree of confidence that can justifiably be placed in the calculated isomorphism depends on the purity of the sample analyzed. SiO_2 as impurity may be shown by an excess of calculated Si^{++++} ions, or by a deficiency of octahedral cations. It also affects the calculated isomorphism of the tetrahedral layers of the lattice by reducing its Al content.

On the other hand, Al_2O_3 as impurity affects the calculation in the opposite way; that is, it reduces the number of Si^{++++} ions per unit cell, while increasing both tetrahedral and octahedral Al^{+++} ions. Fe as impurity has essentially the same effect as Al.

In some samples it is possible to detect SiO_2 as impurity by means of calculation.

Introduction. The two-layer clay minerals, as typified by kaolinite, can be readily distinguished from the three-layer clays such as the montmorillonites and hydrous micas, by the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio as determined by analysis. But this ratio has only limited value: as a means of determining what specific mineral is present in a given sample, the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio can never be relied on as a certain criterion. This is true even when the specimen analyzed is completely free from impurity. The same ratio is characteristic of all four of the different members of the kaolin group of clay minerals, kaolinite, dickite, nacrite, and halloysite. In the case of montmorillonites from different sources, there is a rather wide variation in this ratio owing to the fact that the montmorillonites form an isomorphous series. It seems safe to say, therefore, that the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio, or even the SiO_2 · sesquioxide ratio, or the $\text{SiO}_2:(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{MgO})$ ratio is not a dependable criterion of clay-mineral species.

Isomorphism in Montmorillonite. In the montmorillonite group of clay minerals, chemical analysis may be used to determine the essential nature of isomorphism and in consequence to show the origin and location of the charge on the lattice. The isomorphous character of the members of this group of minerals can probably be shown in no other way. The fact that the specific nature of the isomorphism can be calculated from the analysis is what gives the greatest value to the analysis. The evidence is that the specific pattern of isomorphism occurring in montmorillonite from different sources is rather widely variable. The isomorphism may involve (1) substitution of Al for Si in tetrahedral positions in the lattice, (2) substitution of Fe for Al in octahedral coordination, (3) substitution of Mg for Al in octahedral positions, and (4) substitution of cations of various kinds

by other kinds of cations in interlayer positions. The variations in the substitution in (1), (2), and (3) are basically what give the greatest interest to a chemical analysis.

Accuracy of Analysis. The statement is often made that the chemical analysis must be accurate. Unfortunately, a reliable criterion for accuracy is not now available. Recently, Schlecht (1951) and Schlecht and Stevens (1951) reported analyses of two silicates by 34 specially chosen analysts. The results showed surprising discrepancies. With a sample of granite the different chemists reported variations in SiO_2 of 1.69 percent; with Al_2O_3 differences of 2.78 percent; with Fe_2O_3 a difference of 1.38 percent; with K_2O a difference of 3.41 percent; with Na_2O a difference of 1.24 percent. All these differences are expressed as percent of the sample and not as percent variation of the respective compounds. The summation of all constituents ranged from 99.58 to 100.39 which is commonly thought to indicate reasonable accuracy of analysis. Since the range of totals was distinctly less than that of the major constituents, it is certain that where a given constituent, SiO_2 for example, was high, one or more of the other constituents must have been low.

It is probable that different chemists would obtain an equally wide variation in analyzing a given clay sample. Such variation would almost certainly make rather large differences in calculated isomorphism and consequently in the distribution of charges in the lattice of montmorillonite. For this reason alone we are not justified in making dogmatic assertions about the specific isomorphism as calculated from a single analysis.

Impurities. There is still another reason for caution in the interpretation of chemical analysis of montmorillonite, namely, the sample as analyzed may not have been free from impurity. Evidence on this point is presented by Mr. Osthaus in the following paper in this bulletin, who shows that reasonably pure montmorillonite contains only minor amounts of non-exchangeable Ca, Na, and probably little, if any, non-exchangeable K. Therefore, if the sample is found to contain significant amounts of non-exchangeable Ca, Na, or K, this should be regarded as evidence that the sample is a mixture.

Exchangeable Mg. An altogether different kind of point may have significant influence on the calculated isomorphism in octahedral coordination: that is, a considerable part of the Mg may be present as interlayer cations, or exchangeable Mg (Kelley 1945). Recently Dr. Foster (1951) and still more recently Osthaus (see the following paper, herein) have fully confirmed this fact. Therefore, exchangeable Mg must be determined and due allowance for the same must be made in calculating the distribution of cations to lattice positions.

Method of Calculation. In calculating lattice positions for the constituents found by analysis, the first step is to convert the analytical data into molecular equivalents. This is done by dividing percentages of each constituent by its molecular weight. Molecular equivalents are then converted into cation equivalents.

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Table 1. Calculated isomorphism and charge per lattice unit (Na-saturated montmorillonite).

Analysis		Mol equivalents	Cation equivalents	Charge equivalents	Charges per 44 charges	Cations per unit cell		Distribution in lattice layers		Charges	
SiO ₂ ----	58.96%	.9817	Si .9817	3.9268	30.9042	Si	7.726	Tetrahedral	Si	7.726	-.274
Al ₂ O ₃ ----	22.04%	.2162	Al .4324	1.2972	10.2090	Al	3.403		Al	.274	
Fe ₂ O ₃ ----	4.06%	.0254	Fe .0508	.1524	1.1994	Fe	.400				
MgO-----	2.50%	.0620	Mg .0620	.1240	.9759	Mg	.488		8.000		
Na ₂ O----	2.80%	.0452	Na .0904	.0904	.7115	Na	.711				
				5.5908	44.0000			Octahedral	Al	3.129	
									Fe	.400	
									Mg	.488	-.437
										4.017	-.711
								Interlayer	Na	.711	+.711

The second step is to convert cation equivalents into charge equivalents. This is done by multiplying the values for each cation by its valence. The sum of the charge equivalents represent total charge equivalents per 100 grams of sample. An alternate method is to calculate the oxygen equivalents for each cation.

The third step in the calculation is to convert cation charge equivalents into actual charges of each cation per a specified number of total charges; in this case the unit cell is taken, which contains 20 oxygens and 4 OH⁻ or a total of 44 negative charges. Since these negative charges must be balanced by cations, the sum of the positive charges must also be 44.

The fourth step is to convert charges of each cation into ions by dividing each by its valence.

If oxygen equivalents are calculated, the remainder of the calculation is merely a matter of converting oxygen equivalents into cations per 22 oxygens, which of course, is the oxygen equivalent of 44 charges. The final results will be the same by both methods. Instead of equivalents, as used herein, "ratios" or "proportions" is preferred by certain workers. For the purpose at hand, these terms are interchangeable.

Finally, the ions are distributed into lattice positions. Si goes to tetrahedral positions of which there are eight per structural unit. If the calculated Si is greater than eight, this is positive proof that the sample contained SiO₂ as impurity. But a deficiency of Si (less than eight) is by no means proof that the sample was free from uncombined SiO₂. Nearly all montmorillonites that have been analyzed show upon calculation less than eight Si ions per lattice unit but the amount of uncombined SiO₂ may not be sufficient to raise the calculated Si above eight. Therefore, the presence of SiO₂ as impurity may escape detection by calculation.

The deficiency in Si is made up by placing Al in the tetrahedral coordination. The remaining Al, all Fe, and non-exchangeable Mg are placed in octahedral coordination. All exchangeable cations go to interlayer positions.

Table 1 is presented as an example of the calculation.

It should be pointed out that four assumptions underlie the aforementioned calculation: (1) The analysis was accurate; (2) The sample was free from impurities with the exception of minor amounts of TiO₂, MnO, etc., and that these were present in the sample in the form of oxides; usually the amounts of these oxides is so small as to affect the calculated results only fractionally whether or not they are included in the calculation; (3)

The unit structure contains 20 oxygen and 4 OH⁻ ions; and (4) All H₂O found by analysis was derived from OH ions attached solely to octahedral cations or was adsorbed water. Hence all H₂O found is disregarded in making the calculations. However, by simple modification of the method, it is entirely possible to include all water found. Brown and Norrish (1952) recently showed that with hydrous mica (H₃O⁺) ions may be calculated from the H₂O found.

Effect of Impurities. It is not certain what is the most common impurity in samples of montmorillonite. If the sample is merely hand selected, even with the aid of the petrographic microscope, significant amounts of impurities of various sorts may be entirely overlooked. The greater part of the impurity is likely to be some form of SiO₂. For this reason the effect on the calculation of SiO₂ as impurity will be considered.

Stated in general terms, SiO₂ as impurity has the following effects on the calculated results: (1) It increases the number of calculated Si ions in a unit quantity of the sample; (2) It decreases the calculated total octahedral cations; (3) It decreases the total charge per unit cell. The reason for these effects should be obvious. The Si ion has four charges whereas practically all other constituent ions have three or less charges. If the sample is contaminated with SiO₂, obviously the total number of Si ions per unit quantity will be increased proportionately. Hence, an undue portion of the total cation charge will be borne by Si and accordingly the charge of all other cations will be reduced. If the sample actually contains tetrahedral Al, the effect of SiO₂ will be to increase the calculated number of Si ions, and therefore to decrease the number of Al ions required to fill the remaining tetrahedral positions in the lattice, hence, to decrease the charge in these layers. (Tetrahedra have unbalanced charge only when and to the extent to which some trivalent ion like Al is in tetrahedral coordination.)

Thus, it follows that insofar as the tetrahedral layers of the lattice are concerned, the calculated isomorphism will be diminished by SiO₂ as impurity.

Silica also affects the calculation with respect to the octahedral layer of the lattice. Since SiO₂ as impurity increases the number of calculated Si⁺⁺⁺⁺ ions per unit of sample, its presence has the effect of reducing the calculated numbers of all other cations. This effect is further magnified by the fact that Si has a higher valency than the other cations. The net result is the total number of calculated Al⁺⁺⁺, Fe, and Mg⁺⁺ ions available

for octahedral coordination will be reduced by SiO_2 as impurity. Consequently, its presence in the sample increases the calculated charge on this layer of the structure.

Al and Fe as impurity have an effect opposite to that of SiO_2 , that is, they increase the number of trivalent cations required to supplement Si in tetrahedral coordination and, therefore, they increase the calculated tetrahedral charge. At the same time, Al or Fe as impurity increases the total octahedral cations and accordingly reduce the octahedral charge.

But SiO_2 , Al_2O_3 , and Fe_2O_3 as impurity have one effect in common; namely, each of them reduces the total calculated charge on the lattice. This may be looked upon as the result of diluting the sample.

Enough perhaps has been said about principles. The question arises at once: Are the aforementioned effects purely hypothetical, or do they find significant expression

in actual analyses of montmorillonite? In the following paper Mr. Osthaus shows that they are not purely hypothetical and that, in certain cases, they can be used as evidence of impurities in actual samples of montmorillonite.

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