THE FRACTIONAL ANALYSIS OF SILICATES.

BY F. W. CLARKE.

In the course of some investigations upon the constitution of the natural silicates, it was found that in most cases the empirical formulæ were capable of interpretation in various distinct ways, leading to different structural expressions of equal probability. In some instances there was available evidence by means of which it was possible to choose between alternative formulæ; the final decision resting sometimes upon the association of minerals in nature, and sometimes upon the alterations which they undergo. Such data, however, are not always readily available, and even at their best they only establish presumptions in place of giving satisfactory proof. It became necessary, therefore, to seek for new data of an experimental kind, which should be analogous to the data used by the organic chemist in fixing the constitution of carbon compounds, and by their means to put the problem upon a more satisfactory footing.

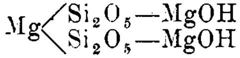
Two difficulties were evident from the start. First, the impossibility, in the present state of our knowledge, of measuring the molecular weights of the silicates; and secondly, the lack of plasticity in the material under investigation. The first difficulty is still unsurmountable; but the second is less formidable than it appeared at first, and the experiments presently to be described open up a feasible line of attack upon the outworks of the problem. The results are appearing in detail in a series of mineralogical papers by E. A. Schneider and myself; and only an outline of the chemical methods need be given in this communication. So far, the minerals studied belong mainly to the mica and chlorite groups, with a few other magnesian silicates like talc, serpentine and olivine, as accessories; and it remains to be ascertained whether the methods applicable to these compounds will fit other cases equally well. Theoretically, the outlook is favorable, but difficulties may exist which cannot be foreseen.

Of the minerals heretofore examined, all but one, olivine, contain water. This may represent water of crystallization, acid hydrogen, or hydroxyl in union with basic atoms, and the first problem is to discriminate between these several possibilities. To begin with, the relative stability of the water in each molecule gives a clue to its character; water of crystallization being easily expelled at comparatively low temperatures, and water of constitution being more tenaciously retained. In each case, therefore, the temperature of dehydration was roughly ascertained: every mineral being heated to constant weight first at 100°, then at 250°–300°, and finally at a full red heat. Whenever ferrous iron was present, the total water was also determined directly and so the errors due to possible oxidation during ignition were avoided. Studied in this way the vermiculite micas kerrite, jefferisite, and protovermiculite gave exceedingly suggestive results, each mineral corresponding to an ordinary mica, plus three molecules of water of crystallization, and with the alkaline metals of the original mineral equivalently replaced by hydrogen. Furthermore, the crystalline water fell sharply into two parts; two molecules being expelled at 100°, and the third being given off below 250°. Thus a mica having the composition $Al(SiO_4)_3Mg_3KH_2$ would yield by hydrous alteration a vermiculite represented by the formula $Al(SiO_4)_3Mg_3H_3+3H_2O$, to which latter compound kerrite approximately corresponds. In the true micas and chlorites the water does not seem to break up into separate fractions upon mere heating, and, being stable up to or near redness, is to be regarded as constitutional.

Up to this point the work done presents no particular novelty, and involves no new modes of procedure. The fractional determinations of water, however, have a direct bearing upon subsequent experiments, and clear the ground for work of a more troublesome kind. Having evidence before us regarding the amount of hydroxyl in a given silicate molecule, the next problem is to determine its distribution and character. It may be united with silicon, representing unreplaced hydrogen of the original silicic acid, it may be combined with magnesium in a univalent group $-Mg-OH$, or it may be linked with aluminum as $=Al-OH$ or

$—Al=(OH)_2$. In its broadest aspect, the problem is still far from complete solution, but at one point it has been attacked with some success, as follows:

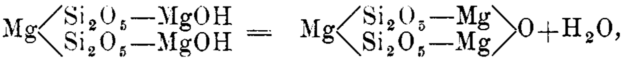
All of the silicates above mentioned as studied by us, except talc, are easily decomposable by aqueous hydrochloric acid. By dry hydrochloric acid gas, however, they are differently affected, and the differences seem to be due to the character of the hydroxyl. Each silicate in turn was weighed out in a platinum boat, and heated to constant weight at a temperature of about 400° in a stream of the thoroughly dried gas. The temperature, it must be noted, is one at which the water of constitution was still retained by the minerals. Olivine, which *contains no hydroxyl*, was practically unattacked, although the aqueous acid decomposes it with great ease. Talc, the true micas, and the vermiculites, were not acted upon, or at most very trivially. Serpentine and the chlorides, however, were strongly affected; and from them, after the reaction, water extracted considerable amounts of magnesium chloride, in which the magnesia was estimated. In serpentine and ripidolite about one-third of the magnesia was thus removable; or, in other words, the magnesia was separated into two fractions which presumably were differently combined. In these minerals the group —Mg—OH is almost necessarily assumed in any attempt to interpret their structure; and the amount of magnesia taken out as chloride was roughly proportioned to the quantity required by the simplest theory. That is, it seems probable that —Mg—OH in a silicate is converted by dry hydrochloric acid into a chlorhydrin group, —MgCl, the latter, by subsequent action of the gas being split off altogether as chloride, $MgCl_2$. This is the simplest explanation of the phenomena; although the nature of the reaction is by no means proved, and a good deal of investigation into it is still necessary. At all events, as regards the magnesian silicates of the groups studied, the new reaction appears to be a legitimate test for —Mg—OH, even though it may not be strictly quantitative. When action takes place, the group is almost certainly present; when there is little or no action, its absence may fairly be assumed.

In the case of talc, $Mg_3H_2Si_4O_{12}$, the foregoing principle finds ready application. For this mineral two constitutional formulæ have been proposed ; one, $Mg_3H_2(SiO_3)_4$, regards it as an acid metasilicate; the other,  $\mathrm{Mg}\left\langle\begin{matrix}\mathrm{Si_2O_5-MgOH}\\ \mathrm{Si_2O_5-MgOH}\end{matrix}\right.$ represents it as a basic salt of the acid $H_2Si_2O_5$. Now talc is practically unattacked by hydrochloric acid either wet or dry, and so a presumption is established in favor of the metasilicate formula. The group —Mg—OH is apparently not present. This view, fortunately, is maintained by other evidence, which also serves to illustrate another principle in fractional analysis.

When talc is sharply and quickly ignited, so as to produce complete dehydration, silica is set free. That silica may then be dissolved out by boiling with an aqueous solution of sodium carbonate, and estimated. One-fourth of the total silica of the mineral was thus liberated, its quantitative determination varying only 0.21 per cent. from the exact amount required. This decomposition represents a splitting up of talc in accordance with the following equation :

$$Mg_3H_2Si_4O_{12} = 3\,MgSiO_3 + SiO_2 + H_2O,$$

which is reconcilable only with the metasilicate formula. If the pyrosilicate formula were correct, the expulsion of water would be indicated thus :



$$\mathrm{Mg}\left\langle\begin{matrix}\mathrm{Si_2O_5-MgOH}\\ \mathrm{Si_2O_5-MgOH}\end{matrix}\right. = \mathrm{Mg}\left\langle\begin{matrix}\mathrm{Si_2O_5-Mg}\\ \mathrm{Si_2O_5-Mg}\end{matrix}\right\rangle \mathrm{O} + \mathrm{H_2O},$$

and it is not easy to see how silica could be split off. In short, the separation of the silica into two fractions, and the evidence furnished by the stability of the talc towards acids, prove that the hydrogen of the mineral is acid hydrogen, and establish the constitution of the species. Of all the possible formulæ for talc, the metasilicate formula alone satisfies the experimental conditions.

It has already been stated that the silicates under discussion, with the exception of talc, are readily decomposable by aqueous hydrochloric acid. Upon ignition, however, most of them split up into soluble and insoluble portions, which can be separately investigated. Serpentine, for example, splits up into soluble olivine and insoluble enstatite ; water, of course, being eliminated. This particular case of decomposition by heat has long been known ; but among the chlorites and the clintonite micas are found some new applications of the principle. Four examples, closely related, may be cited here, namely, three chlorites of similar type, and xanthophyllite, variety walnewite, from Siberia.

The method of investigation was as follows : Each mineral, of which a sample had been previously analyzed, was strongly ignited in powder over a blast. The operation was performed in a covered platinum crucible, and the ignition lasted for several hours. The material was next digested with strong hydrochloric acid, the mixture was evaporated to dryness, the residue treated with weak acid, and finally filtered off. There remained in the filter, of course, the insoluble portions of the minerals, plus the silica which had been liberated from the soluble parts. This silica was then removed by boiling with sodium carbonate solution, and the undissolved remainder was washed, weighed and separately analyzed. In each of the four cases it proved to have the composition of spinel, $MgAl_2O_4$, and in quantity it bore a definite relation to the formulæ of the original minerals. The latter were as follows, with their empirical formulæ subjoined:

A. Ripidolite (clinochlore), from West Chester, Pa.
B. Clinochlore, from Slatoust, Urals.
C. Leuchtenbergite, from Slatoust, Urals.
D. Walnewite, from near Slatoust.

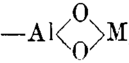
A. $Al_{38}Mg_{86}H_{140}(SiO_4)_{50}O_{113}$.
B. $Al_{38}Mg_{87}H_{143}(SiO_4)_{52}O_{113}$.
C. $Al_{42}Mg_{86}H_{143}(SiO_4)_{50}O_{121}$.
D. $Al_{86}Ca_{24}Mg_{52}H_{50}(SiO_4)_{28}O_{174}$.

Upson dehydration these become :

A. $Al_{38}Mg_{86}(SiO_4)_{50}O_{43}$.
B. $Al_{38}Mg_{87}(SiO_4)_{52}O_{42}$.
C. $Al_{42}Mg_{86}(SiO_4)_{50}O_{49}$.
D. $Al_{86}Mg_{52}Ca_{24}(SiO_4)_{28}O_{149}$.

Here we have, throughout, an excess of oxygen over the group SiO_4 ; and to that excess the amount of spinel formed by ignition is almost quantitatively proportional.

That a decomposition of this sort furnishes strong evidence relative to the constitution of the minerals in question, is clear without argument. Since, however, it is the purpose of the present paper merely to give a brief indication of methods in fractional analysis, an elaborate theoretical discussion would be out of place in it. The data, in all their relations, are being fully considered elsewhere*, and only a short notice of their bearing is needed here. In the chlorites the group —Mg—OH is certainly present; and the three examples here given all reduce to the general formula $Mg_2 (SiO_4)_2 R'_4$, in which R' is partly H, partly MgOH, and partly AlO_2H_2. The juxtaposition of the two latter groups serves to explain the formation of spinel upon ignition; while the soluble portions of the decomposed material appear to be mixtures of olivine and magnesian garnet, minerals which are common sources of chlorites in nature. Quite recently, Tschermak has sought to show that these particular chlorites are mixtures of amesite and serpentine. But serpentine, when ignited, yields insoluble enstatite, while the three chlorites studied give only spinel in the residue undissolved by hydrochloric acid. The inference is that the chlorites contain no serpentine molecules, and Tschemrak's view becomes untenable.

In the case of the walnewite, the spinel reaction has peculiar interest. In that mineral, the most basic known member of the clintonite group, there is good reason for assuming the existence of a univalent group  $—Al\langle{}^{O}_{O}\rangle Mg$, or—Mg—O—Al=O, each form of expression having its own theoretical advantages. The walnewite itself appears to be a mixture of isomorphous molecules, among which the compound $(AlO_2Mg)_4SiO_4$ is predominant. Such a compound might easily split up into olivine and spinel, $Mg_2SiO_4 + 2MgAl_2O_4$, and the quantity of spinel actually formed when walnewite is decomposed by heat, is almost exactly the amount required by theory. Two of the groups $—AlO_2Mg$, coalesce, with removal of one atom of magnesium, to form spinel, while the

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magnesium thus eliminated goes into the soluble olivine. The fact that the clintonite micas are almost invariably associated with spinel in nature, and frequently also with members of the olivine group, is very suggestive in this connection. The evidence of natural association and the evidence from the laboratory converge to one set of conclusions.

In the light of the foregoing statements the term "fractional analysis" practically defines itself. It is really an attempt at rational, as distinguished from empirical analysis; and it brings into the mineralogical laboratory the methods of the organic chemist. As yet, little more than a beginning has been made, but the field is promising and should yield a rich crop of valuable data. The researches are still in progress; and the results will be made public as rapidly as may be possible.

POST-MORTEM DIFFUSION OF ARSENIC, THE RESULT OF EMBALMING.

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James H. B———, a painter by trade, died on the morning of September 15th, 1891, after an illness, diagnosed by the attending physician as remittent fever.

Two hours after death the undertaker thrust an injecting needle into the abdomen of the deceased and injected a quantity of embalming fluid. The needle passed also above the diaphragm and the fluid was found on the autopsy to partly fill the thorax as well as the abdomen. This fluid contained about 100 grains arsenious oxide and ten grains zinc sulphate to the fluid ounce.

Coroner John Mathews took charge of the case because of rumors of foul play and ordered an autopsy. This was performed September 16th, by Dr. G. A. Lyons, twenty-four hours after the embalming. Parts of the viscera were removed. There was extensive peritonitis and there were pathological conditions that confirmed the