THE MODERN STUDY OF MINERALS[1]

HENRY S. WASHINGTON, *Geophysical Laboratory,*
Carnegie Institution of Washington

For an understanding of the modern conditions of mineralogy, or of any other science, it is well to cast a glance backward to see what our predecessors have or have not done; we may learn from their errors of omission or commission, or we may find that some things now regarded as novel were discovered many years ago. In his presidential address of 1922, Professor T. L. Walker[2] has traced "The Development of Mineralogical Methods," so that I need say little of this aspect of the matter. But the attention of mineralogists may be called to a book, little read nowadays but of perennial value, by William Whewell, D.D.[3] As Whewell was a mineralogist of note in his day, the native calcium oxalate being named after him, his chapter on the early history of mineralogy is of special interest to members of the Society.

Whewell, as does Herbert Spencer later, points out the three stages of a science. The first, which we may call the stage of infancy, is devoted to the collection of facts: a stage which in all sciences, as in the lives of human beings, persists through all the periods. Next, the stage of adolescence, is that in which the facts are correlated and the subject matter is classified. In the third stage, that of maturity, generalizations are drawn from the correlated facts and even, the crowning test of validity, verifiable predictions are made. The sciences may be likened to the gods of ancient Greece and Rome, for they do not grow old

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[1] Presidential address, presented at the fifth annual meeting of The Mineralogical Society of America, Ithaca, New York, December 31, 1924.

[2] T. L. Walker, *Am. Min.*, 8, 41, 1923. In my choice of subject I fear that I have trenched somewhat on my friend's theme, for which I trust that his pardon will be granted.

[3] W. Whewell, History of the Inductive Sciences, 2 vols., 1st ed., 1837; 3d. ed., 1882. For his account of Mineralogy see 3d., ed., vol. 2, 316–353 (1882).

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and decrepit but, once arrived at maturity, persist in the full strength of their powers, even increasing these from time to time. The gods themselves learn from experience.

It is of great interest to read in the pages of Whewell of the struggles of the early mineralogists to unravel the complex knot that confronted them, from the days when little or no distinction was made between a mineral and a rock, through the early studies of Steno, who first showed that the angles of rock crystal were constant, to the days of Romé de Lisle and Haüy, who laid the foundations of modern crystallography. The early attempts at classification of minerals are also instructive. First came the Natural History System of Mohs, about 1820, following the lines laid down by Werner, according to which minerals were classified by their external characters alone. About the same time Berzelius proposed his purely Chemical System, in which minerals were arranged according to the basic or electropositive elements, with little or no regard for the physical characters. When the phenomenon of isomorphous replacement was definitely formulated by Mitscherlich in 1822, although it had been first suggested by Fuchs in 1815 under the term "vicarious" elements,[4] Berzelius had to abandon his choice of the positive element and take refuge in the electronegative, from which position he was driven by the fact that isomorphism applies to the electronegative elements as well as to the electropositive. After a period of trials and uncertainty there gradually came into use the present system of classification, based on both the chemical and the crystallographic characters, with the optical and other physical characters as means of identification.

But the modern mineralogist is not, or should not be, satisfied with the discovery of new species, the determination of characters for identification, or the classification of minerals: were these the only aims the science could well be spoken of as a "fertiges Wissenschaft," a term applied to it by one of our most prominent mineralogists in conversation with me nearly forty years ago. The chief aims nowadays are broader and we strive to know how minerals are constituted, how they are formed, their relations to each other, to their conditions of formation and to the Earth, and so on. For such studies the determination of isolated facts

[4] It might be well to adopt this term, "vicarious," to indicate the replacement of one element by another, without any implication of isomorphism.

and characters is of little interest: what is of most interest and what is most needed is the correlation of the various characters. Such correlation may best be accomplished by cooperation between several workers, each one studying the mineral along the lines in which he is most proficient.

Another most important point, on which special stress is laid, is that the determinations of the different characters or constants should, one may even say must, be made on identical material. That is to say, the optical characters (as the refractive indices), the density, and the other physical characters should be determined on the same material that is used for the chemical analysis. Furthermore, whenever possible, a chemical analysis should be made of material of which the optical and other physical characters are determined, and vice versa. If the material is not identical the chemical and physical data cannot be correlated, and the value of either chemical or physical data is much enhanced if both kinds of data are determined on the same material. Mineralogical literature abounds in examples of uncorrelated determinations, and one can see in the compendia of Dana, Hintze, and Doelter many cases in which elaborate and probably very accurate determinations of, let us say, refractive indices for different wave lengths are reported but unaccompanied by a chemical analysis of the material used. It cannot be said that such determinations are wholly useless, but it is undeniable that much of their usefulness for the broader aspects of mineralogy (and physics), such as the study of the specific effects of the various elements on the physical constants, is lost by this neglect. This point was mostly overlooked among the earlier mineralogists, but at the present time its importance is becoming increasingly recognized.

Another important requisite is that the material studied be homogeneous. Otherwise, obviously, the chemical analysis may be made on material of one composition and the optical determinations on material of another, so that they would not be strictly correlatable. Lack of homogeneity may arise in two ways. The mineral may contain inclusions of foreign matter, sometimes easily visible to the naked eye or under the hand lens, in other cases discernible only by microscopic examination. Or the mineral may be free from inclusions but show a zonal structure from center to border, due to gradual change in composition with growth, brought about by the gradually changing composition of the surrounding medium.

The earlier mineralogists, to whom the modern methods of study of minerals in thin section were unknown, mostly ignored these sources of error, unless the inclusions were so prominent as obviously to invalidate the analysis. The modern worker, however, regards this matter of homogeneity as of prime importance, and it frequently happens that more time is spent in separating material of satisfactory purity and homogeneity, sometimes resulting in obtaining only a gram or less for analysis, than is devoted to the chemical analysis and the optical determinations. For crystallographic investigations lack of homogeneity is comparatively unimportant, especially if it be due to inclusions, although a zonal structure may cause notable error. For optical determinations inclusions are mostly negligible, but a zonal structure demands, of course, that determinations be made on each zone. Both kinds of inhomogeneity will, obviously, affect seriously determinations of density and the chemical analysis.

It should, therefore, be an invariable rule, before beginning the chemical analysis of a mineral, to study thin flakes with the microscope to detect the presence of inclusions and to test the zonal homogeneity by the determination of the refractive indices on many grains, an examination now readily and rapidly carried out with the liquids in common use. Many of the older analyses of minerals are rendered of little value because of the neglect of this precaution. This is especially true of opaque minerals, as modern study by metallographic methods has shown that in many cases material supposed to be homogeneous is really a mixture, so that a metallographic examination should always be made of an opaque mineral, especially one with metallic luster, before its chemical analysis is begun.

A few words may be said of some important differences between modern and the earlier methods of procedure in the study of minerals. For the crystallographic study the early mineralogist was fairly well equipped, inasmuch as the simple type of reflecting goniometer, invented by Wollaston in 1809, permitted reasonably accurate work, as is shown throughout Dana's System by his acceptance of many of the constants measured by Brooke and Miller, Breithaupt, von Rath, and even Wollaston himself in the case of calcite. There followed the more accurate horizontal, two-circle goniometer, and this has recently been more or less replaced by several types of two-circle and three-circle goniometers. The

modern results are more accurate than the old, but there is little difference in principle.

The differences in the determination of the optical characters, such as refractive indices, dispersion, and optic axial angle, show more change in method. In the olden days prisms had to be prepared with considerable labor and time, and I well remember the pride with which in 1889 Professor Fouqué showed me his collection of prisms of feldspar made for his classic studies of this group. Nowadays, the use of refractive index liquids permits of determinations on very small grains, with great ease, rapidity and sufficient accuracy. The modern refractometers should also be mentioned.

It is in the improvements and greater refinements of the chemical analysis of minerals, within the last fifty years or so, that the greatest strides have been made. Not only is the material now much more carefully selected, so as to be truly representative, but new methods have been introduced, which permit of much more accurate determinations, and the advance in apparatus and in purity of reagents is a most striking difference. The analyses, also, are now more complete, in that constituents, formerly neglected as being unsuspected to be present or of supposedly negligible importance, are now commonly determined, although many examples might be given of lamentable incompleteness even now. Up to the early eighties the alkalies and manganese generally and titanium always, were neglected in the analysis of specimens of such groups as the pyroxenes, amphiboles, and olivines: the mutually vicarious roles of hydroxyl and fluorine in topaz and other minerals, first discovered by Penfield, were not suspected, and many other errors of omission were committed, which nowdays would not be tolerated by a tyro in analysis. Also, the methods and the analytical facilities of those days were not quite what they are now: reagents were far from pure, there was no resistant pyrex or Jena glass, and so on. One gets an idea of the difficulties under which the analyst of the first half of the last century labored when one reads Faraday's Chemical Manipulations. Indeed, one wonders at the analytical skill of many of the early workers, who managed to determine the chemical composition of many minerals with means that the young student would now look on with contempt. For instance, it is said that Cossa, one of the best Italian mineralogical chemists about the middle of the last century,

congratulated himself because, for the analysis of a certain mineral, he had at his disposal a balance that weighed down to one *centigram*. A chemist would hardly congratulate himself on that today.

To return to the study of the general constitution of minerals, the possibility of isomorphous or vicarious replacement, or the presence of certain constituents in so-called "solid solution," has been mentioned. Such phenomena are of special importance in certain mineral groups, as the feldspars, the pyroxenes, the olivines, and the garnets, to mention only some of the more prominent. To study these properly, that is, to correlate the physical, especially the optical, properties, including density, with the chemical composition, the end-members must be studied and these should be chemically pure. In nature such end-members, as forsterite and fayalite in the olivines, are seldom or never found in a state of satisfactory purity. Thus, in even the purest natural fayalite a little magnesium replaces some iron, and conversely for forsterite. For this reason the Geophysical Laboratory, almost from its inception, began to make the more important rock-forming minerals synthetically, using the purest component ingredients, such as silica, alumina, lime, and magnesia. These "systems" were studied by physico-chemical methods, to determine the melting and inversion points of the crystalline phases, the composition and melting points of the eutectics, and so on. At the same time the optical characters, the density, and the other properties of the pure component substances and their compounds were determined. In this way and by these methods, often very laborious and their study extending over many months or even years, we have now a fairly complete and accurate knowledge of the physical characters of the end-members of some of the more important series of rock-forming minerals, a mass of data that is probably the most important contribution to mineralogy from the Geophysical Laboratory. Latterly, this has been supplemented by systematic study of many natural minerals, a study made quantitatively and accurately possible by the previously acquired knowledge of the chemically pure, artificially prepared end-members. We may thus evaluate with a fair degree of accuracy the specific effects of the different elements on the optical properties, refractive indices, dispersion, etc., the determinations being based on data that would not have the validity or authority that they

have were they based on the necessarily more or less impure end-members or the approximations to end-members that are furnished by nature.

Such end-members of series, and pure minerals in general are simply chemical compounds. Whewellite is calcium oxalate whether it is found in a coal bed or precipitated in a beaker: enstatite is magnesium metasilicate whether it forms part of a gabbro laccolith or is formed artificially in a platinum crucible heated in an electric furnace under exactly controlled conditions as to temperature, rate of cooling, etc. But in the former case of each the material is almost invariably contaminated, so that its optical characters, density, and melting point are seriously affected; whereas in the latter the composition of the substance is invariable and thus its physical characters are true and are reproducible.

These considerations lead to the thought that much too little attention is paid by chemists in papers and text-books to the statement of the crystallographic and the optical and other physical properties of the pure chemical compounds that are made in the laboratory. Most chemists are content, in the description of a new substance, to state that it crystallizes "in glistening needles," with no determination of the crystal system, or, if this be given, with no statement of the axial ratios or other crystallographic constants. There is scarcely ever any determination of the refractive indices or other data, the author contenting himself for the most part, with determination of the melting point (often very crude) and the density, done solely for purposes of identification. To give an example. The other day, on seeing some sublimed crystals of camphor in a bottle, the question arose as to its system of crystallization. The various standard text-books on organic chemistry, and even a well-known work on the identification of organic substances, gave no more information than that camphor crystallizes in "glistening prisms." Beilstein (Vol. III, p. 485) stated, on the basis of an observation in 1859, that it crystallizes in the hexagonal system. But, on turning to Groth's Chemische Krystallographie (Vol. 3, p. 687, 1910), written by a mineralogist, the system was found to be rhombohedral, and full crystallographic data were given. It would seem that modern mineralogists set a good example to their chemical brethren.

Finally, the latest method of studying minerals must be mentioned, that of study by the X-rays, according to the methods of Laue, the Braggs, and others. The utility of this has been shown recently in the Geophysical Laboratory, by work done on the pyroxene group, a work that serves also as an example of mutual cooperation, one of us (Merwin) doing the optical part, another the chemical, and a third the X-ray study. It would be unjust to my colleague, Dr. Wyckoff, to steal his thunder by giving here his results, but it may be said that his X-ray studies have shown clearly that certain minerals that for many years have been reckoned as pyroxenes can not belong to this group, their molecular structure being quite different.

Study of minerals along such lines is still in its infancy, but such examples as have come under my notice lead to the conviction that X-ray methods, especially when employed in conjunction with some of those longer known, are not only the most recent but among the most powerful methods of arriving at an understanding of what minerals, as well as artificial crystals, really are, how they are constituted, and how they are related.

It should again be said, in conclusion, that all determinations are to be made on identical material. The motto of Belgium may serve as a fitting summing up of my remarks—"L' Union fait la Force."

STUDIES IN THE MICA GROUP (ABSTRACT)[1]

A. N. Winchell, *University of Wisconsin*

In micas, as in other silicates, each crystal is an aggregate of several intergrown space-lattices which differ decidedly from each other in the size of their atoms. The oxygen space-lattice in mica includes F and H (as OH), but none of the other constituents. The formulas of micas omitting O, H and F, can be deduced from a study of a tabulation of the best analyses calculated into relative numbers of atoms (with the same omission) expressed as percentages.[2] From such a study it appears that micas are not orthosilicates, nor metasilicates, nor any other single type of silicates,

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[1] The complete article on the micas will appear in an early number of the American Journal of Science.

[2] This method is more accurate than the ordinary procedure because the determination of the precise percentages of F and H_2O is notoriously very difficult.