

**BULLETIN NO. 305. SERIES E, CHEMISTRY
AND PHYSICS, 49. DEPARTMENT OF THE
INTERIOR UNITED STATES GEOLOGICAL
SURVEY. THE ANALYSIS OF SILICATE
AND CARBONATE ROCKS**

Published @ 2017 Trieste Publishing Pty Ltd

ISBN 9780649052097

Bulletin No. 305. Series E, Chemistry and Physics, 49. Department of the Interior United States Geological Survey. The Analysis of Silicate and Carbonate Rocks by W. F. Hillebrand

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Cover @ 2017

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DEPARTMENT OF THE INTERIOR
UNITED STATES GEOLOGICAL SURVEY

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THE ANALYSIS OF
SILICATE AND CARBONATE ROCKS

Wm. Francis BY
W. F. HILLEBRAND



WASHINGTON
GOVERNMENT PRINTING OFFICE
1907

SILICATE ROCK ANALYSIS.

PART I.—INTRODUCTION.

1. IMPORTANCE OF COMPLETE AND THOROUGH ANALYSES.

The composition of the ultimate ingredients of the earth's crust—the different mineral species which are there found and of many of which its rocks are made up—was the favorite theme of the great workers in chemistry of the earlier half of the nineteenth century, and for the painstaking care and accuracy of Berzelius, Wöhler, and others the mineralogists and geologists of to-day have reason to be thankful. Considering the limited facilities at their disposal in the way of laboratory equipment and quality of reagents, the general excellence of their work is little short of marvelous. As an outgrowth of and closely associated with the analysis of minerals came that of the more or less complex mixtures of them—the rocks—to aid whose study by the petrographer and geologist a host of chemists have for many decades annually turned out hundreds of analyses of all grades of quality and completeness. With the growth and extraordinary development of the so-called organic chemistry inorganic chemistry gradually fell into a sort of disfavor. In many, even the best, European laboratories the course in mineral analysis, while maintained as a part of the curriculum of study, became but a prelude to the ever expanding study of the carbon compounds, which, multiplying rapidly and offering an easy and convenient field for original research and possible profit, proved more tempting to young chemists than the often worked over and apparently exhausted inorganic field. For one student devoting his time to higher research on inorganic lines fifty perhaps were engaged in erecting the present enormous structure of carbon chemistry. The instruction afforded the student in mineral analysis was confined to the ordinary separations of the commoner ingredients occurring in appreciable quantities, with little regard to supposed traces and with still less attempt to find out if the tabulated list really comprised all that the mineral or rock contained.

With the introduction of improved methods of examination by the petrographer, especially as applied to thin rock sections, and the use

of heavy solutions, whereby, on the one hand, the qualitative mineral composition of a rock could be preliminarily ascertained with considerable certainty, and on the other chemical examination of the more or less perfectly separated ingredients was rendered possible, a great help and incentive was afforded to the few chemists engaged in rock analysis. The microscope often obviated in part the necessity for tedious and time-wasting qualitative tests, and the heavy solutions, by permitting the concentration and separation of certain components, facilitated the detection of elements whose existence had long been overlooked.

Meanwhile, in the progress of chemistry new methods and reagents for qualitative detection and quantitative separation and estimation were gradually being devised and discovered. The belief that some well-established methods were adequate was shown to be unwarranted; some had to be discarded altogether; others were still utilizable after modification. In the light thus shed it became possible to explain many hitherto incomprehensible variations in the composition of some rock species or types, as shown in earlier analyses, and in not a few cases it appeared that the failure to report the presence of one or more elements had obscured relations and differences which more thorough examination showed to exist (see p. 17). Consequently there arose a feeling of distrust of much of the older work in the minds of those chemists and petrographers who were best fitted to judge of its probable qualities. This, and the incompleteness of nearly all the earlier work (and much of that of to-day, unfortunately), as shown by the largely increased list of those elements now known to enter into the normal composition of rocks, are rendering the old material less and less available to meet the increasing demands of the petrographer.⁶

And yet these demands on his part are, with few exceptions, by no means so exacting as they should be. Frequently the analysis is intrusted to a student without other experience than that gained by the analysis of two or three artificial salts and as many comparatively simple natural minerals, and with a laboratory instructor as adviser whose experience in rock analysis may be little superior to his own. In other words, one of the most difficult tasks in practical analysis is expected to be solved by a tyro, and his results are complacently accepted and published broadcast without question. Even to those thoroughly familiar with the subject rock analysis is a complex and often trying problem. Although long practice may have enabled

⁶ Dr. Henry S. Washington, in Professional Papers Nos. 14 (Chemical analyses of igneous rocks published from 1884 to 1900, with a critical discussion of the character and use of analyses) and 25 (The superior analyses of igneous rocks from Roth's Tabellen, 1869 to 1884, arranged according to the quantitative system of classification) of the United States Geological Survey, has done a most important work in sifting the great mass of data accumulated in the thousands of analyses published since 1869. After a systematic critical examination he has assigned to each analysis a certain value on a scale of 5. Many of these values may be incorrect, but in most cases they undoubtedly give a fairly true measure of the weight to be attached to a particular analysis.

one to do certain parts of it almost mechanically, perplexing questions still arise which require trained judgment to properly meet and answer, and there is yet room for important work in some of the supposedly simplest quantitative determinations. If the results are to have any decided value for purposes of scientific interpretation and comparison, they must be the outcome of the work of one who is able to find his way through the intricacies of an analysis in which from fifteen to twenty-five components are to be separated and estimated with close approach to accuracy, and this a beginner can not hope to do. The conscientious chemist should have a live interest in this matter. He should work with a twofold purpose in view—that of lightening the labors of those who come after him by enabling them to use his work with less supplementary examination, and that of enhancing his own reputation by meriting encomiums on work that has stood the test of time.

How little understood may be the principles underlying the treatment of bodies so complex and the accurate separation and determination of their constituents, even when these are comparatively few in number, has been strikingly shown during the last five years in the work of several committees of chemists charged with the investigation of the methods employed in various lines of technical chemistry involving the analysis or assay of zinc ores, slags from the smelting of copper ores, argillaceous limestones, and cements. In all cases a most woful inability to obtain agreeing results is apparent, not only among those less experienced, but among those supposed to be most expert in each of the particular fields as well. Some improvement in silicate analysis has resulted from the investigations set on foot and the recommendations made by these committees, and further improvement may be expected, but the situation is yet anything but satisfactory. The art of analysis stands in great need of more thorough treatment in our educational institutions.

The petrographer, again, should seek to have his analyses made as complete as possible, and not, as is so often the case, be content with determinations of silica, alumina, the oxides of iron, lime, magnesia, the alkalis, and water. The latter course, it is true, is entirely justifiable at times, and may serve the immediate purposes of the analyses, but their incompleteness may, on the other hand, not only conceal points fruitful of suggestion to the attentive mind, but, what is of still greater importance, they may be actually misleading. Enough instances of totally inaccurate conclusions to be drawn from them have fallen under my own observation to fully justify this plea in favor of greater completeness in rock and mineral analysis made for purely scientific purposes.^a

^a For a further presentation of this subject from the view point of an experienced petrographer, see Washington, H. S., *Manual of the Chemical Analysis of Rocks*, 1904, pp. 8-17.

The importance of the points indicated in the foregoing paragraph is shown by the difference between the analyses given below. The specimens were taken and analyzed at widely separated times and by different persons, it is true, but they were unquestionably from the same rock mass, in which, however much the relative proportions of the different mineral constituents might vary within certain limits, there can be no reason to doubt the general distribution of all the elements shown by the second analysis.

Analyses of specimens taken from the same rock mass at different dates.

	Earlier analysis.	Later analysis. ^a		Earlier analysis.	Later analysis. ^a
SiO ₂	54.42	53.70	Li ₂ O.....	Trace.	Trace.
TiO ₂		1.92	H ₂ O below 110°.....		.80
Al ₂ O ₃	13.37	11.16	H ₂ O above 110°.....	c 2.76	2.61
Cr ₂ O ₃04	CO ₂	1.82	1.75
Fe ₂ O ₃	b 6.61	3.10	P ₂ O ₅06
FeO.....	b 3.52	1.21	SO ₂44
MnO.....		.04	F.....		.03
CaO.....	4.38	3.46	Cl.....		
SrO.....		.19			
BaO.....		.62	Less O for F.....	99.58	100.40
MgO.....	6.37	6.44			.19
K ₂ O.....	10.73	11.16			
Na ₂ O.....	1.60	1.67			100.21

^a A still more recent analysis of another of the series of rocks of which this is an example has shown that this "later analysis" is itself probably incomplete and incorrect in part—incomplete because of the probable presence of 0.2 per cent or more of ZrO₂, incorrect because of the error in Al₂O₃ resulting from having counted the ZrO₂ as Al₂O₃, and from the fact that titanium is not fully precipitable in presence of zirconium by Cooch's method (the one employed). This latter error involves both the TiO₂ and the Al₂O₃. (See p. 115.)

^b From the fact that repeated determinations of the iron oxides in this and related rocks from the same region show always a great preponderance of ferric oxide, it is not improbable that the figures given for the two oxides in the first analysis were accidentally transposed.

^c In the published analysis it does not appear whether this is total water or, as seems probable, only that remaining above 100°.

Another instance of similar kind is given below. Here, again, certain differences are explainable by natural variations in the proportions of the constituent minerals, but it can hardly be doubted that TiO₂, BaO, SrO, P₂O₅, and SO₂ were present in both specimens in approximately the same amounts. In the earlier analysis determinations of some supposedly unimportant constituents were purposely omitted, or made only qualitatively, with results that can not be otherwise than fatal to a full comprehension of the mineralogical nature of the rock.

Analyses of specimens taken from the same rock mass at different dates.

	Earlier analysis.	Later analysis.		Earlier analysis.	Later analysis.
SiO ₂	44.31	44.65	Na ₂ O.....	4.45	5.67
TiO ₂	Not est.	.95	Li ₂ O.....		Trace.
Al ₂ O ₃	17.20	13.87	H ₂ O below 110°.....	.77	.95
Fe ₂ O ₃	4.44	6.96	H ₂ O above 110°.....		2.10
FeO.....	3.73	2.94	H ₂ O by ignition.....	3.30	
MnO.....	.10	.17	CO ₂11
CaO.....	10.40	9.67	P ₂ O ₅		1.50
SrO.....		*.37	Cl.....		Trace.
BaO.....		.76	SO ₂61
MgO.....	6.37	5.15			
K ₂ O.....	3.64	4.49		99.11	99.92

* Not entirely free from CaO.

Prof. F. W. Clarke has shown that the combined percentages of titanic and phosphoric oxides in rocks of the earth's crust, averaged from hundreds of analyses, amount to 0.8 per cent. When the determination of these is neglected the error falls on the alumina. If the alumina is then used as a basis for calculating the feldspars, it is easy to see that a very large average error in the latter may result, amounting to several per cent of the rock.

In order to emphasize more strongly the importance of completeness in analysis, a few facts brought out by the hundreds of rock analyses made in this laboratory may be cited. It has been demonstrated most conclusively that barium and strontium are almost never-failing constituents of the igneous rocks of the United States and of many of their derivatives. The amounts are usually below 0.1 per cent for each of the oxides of those metals, but higher amounts are by no means uncommon. Furthermore, the weight of barium is almost without exception in excess of that of strontium; but a still more important point is that the igneous rocks of the Rocky Mountain region, so far as examined, show far higher average percentages of both metals than the rocks from the eastern and the more western portions of the United States. The following examples serve to illustrate certain types of Rocky Mountain igneous rocks: Of seven rocks forming a Colorado series, six held from 0.13 to 0.18 per cent of BaO, while in the seventh the percentage was 0.43. The SrO ranged from 0.07 to 0.13 per cent for six and was 0.28 for that one highest in BaO. Of thirteen geologically related rocks from Montana, embracing basic as well as acidic and intermediate types, the range of BaO was from 0.19 to 0.37 per cent, with an average of 0.30 per cent. Three others of the same series contained 0.10 per cent or less, while the seventeenth carried 0.76 per cent BaO. The SrO ranged from 0.37 per cent in the last instance to an average of 0.06 for the other sixteen. Certain peculiar rocks from Wyoming carry from 0.62 to 1.25 per cent BaO and from 0.02 to 0.33 per cent SrO. Surely this concentration of certain chemical elements in certain geographic zones has a significance which future geologists will be able to interpret if those of to-day are not.

Again, vanadium is an element which few chemists have ever thought of looking for in igneous rocks, though it has long been known to occur in magnetites and other iron ores. A. A. Hayes, in 1875, reported its occurrence in a great variety of rocks and ores. To quote from Thorpe's Dictionary of Chemistry: "It is said to be diffused with titanium through all primitive granite rocks (Dieulafait), and has been found by Deville in bauxite, rutile and many other minerals and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands." It is further reported to

comprise, as the pentoxide, up to 0.1 per cent of many French and Australian^a clays, 0.02 to 0.03 per cent of some basalts, 0.24 per cent of a coal of unknown origin, and 0.45 per cent of a coal from Peru. Still later examinations in this laboratory of about 100 rocks, chiefly igneous, covering nearly the whole continental territory of the United States, show not only its general qualitative and quantitative distribution, but that it predominates in the less siliceous igneous rocks and is absent, or nearly so, in those high in silica. In some of the more basic rocks it occurs in sufficient amount to affect seriously the figures for the oxides of iron unless separately estimated and allowed for (see β , p. 140), a matter of considerable importance, since the petrographer lays great stress on accuracy in their determinations.

The same investigation has also thrown some light on the distribution of molybdenum, which seems to be confined to the more siliceous rocks and to occur in quantities far below those commonly found for vanadium.

Finally, had it not been my practice of late years to look for sulphur in rocks, even when no sulphides were visible to the eye, its almost invariable presence in the form of sulphide and consequent connection with the long mystifying lack of agreement between results for ferrous iron obtained by the Mitscherlich and the hydrofluoric-acid methods might not have been suspected (see A, p. 131).

While strongly upholding the necessity for more thorough work, necessarily somewhat at the expense of quantity, it is far from my intention to demand that an amount of time altogether disproportionate to the immediate objects to be sought should be expended on every analysis. But it is maintained that, in general, the constituents which are likely to be present in sufficient amount to admit of determination in the weight of a sample usually taken for analysis—say 1 gram for SiO_2 , Al_2O_3 , etc., to 2 grams for certain other constituents—should be sought for, qualitatively at least, in the ordinary course of quantitative work, and their presence or absence noted among the results. If present in little more than traces, that knowledge alone may suffice, for it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0.02 or 0.06 per cent. In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present. Failure to do this may subject the analyst to unfavorable criticism when, at some future time, his work is reviewed and the omissions are discovered by new analyses.

Finally, whenever possible, a thorough microscopical examination of the rock in thin section should precede the chemical analysis. This

^a J. C. H. Mingaye has lately confirmed its wide distribution in Australian rocks, coals, etc. (Records Geol. Survey New South Wales, vol. 7, pt. 3, 1903, p. 213.)