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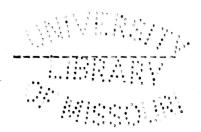
Form 26

A CONTRIBUTION TOWARD THE CHEMICAL COMPOSITION OF THE CRYSTALLINE ROCKS OF SOUTH-EAST MISSOURI

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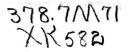


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INTRODUCTION

The study of the chemical composition of the crystalline rocks of South-East Missouri was undertaken a few years ago by Prof.J.A.Gibson. Prof.Gibson, assisted by Mr.W.J. Bray, collected several samples of granites near Fredericktown, in Madison County. These samples were taken from a single series or one outcropping of granite. A complete description of the rocks used in this series of analyses, the topography of the region where they were collected, and the methods of collecting and preparging the samples is given in the first nine pages of Mr. Bray's unpublished paper (A copy of this paper can be found in the University Library). Sample one is a coarse grained granite and the grain of each sample grows finer to number five which Dr. Erasmus Haworth calls porphyry. (1). The purpose of the present work is to determine completely the chemical composition of his samples one, two, three, four and five, and whether there is any difference in the chemical composition of these samples corresponding to the change in texture. Mr. Bray determined the major constituents of samples one, four, and five. The present paper, therefore, will deal with both the major and the minor constituents of samples one, two, three, four, and five. I have accepted from Mr. Bray's paper the determinations of silica, alumina, lime, magnesia, the alkalis, water, and the oxides of iron, after making the necessary corrections for the minor constituents. A complete analysis of an igneous rock is necessary for its exact chemical classification. (2).

METHODS OF ANALYSIS

In carrying out this work the methods used by the chemists of the United States Geological Survey were followed as closely as possible. (3).

- (1). Mo. Geol. Survey. Vol. 8, p. 103.
- (2). United States Geological Survey, Bull. No. 422, pp. 18-20.
- (3). Bull. No. 422.

In determining the silica the rock powder was decomposed by fusion with Baker's analized sodium bicarbonate. (1)

I first tried the normal sodium carbonate which is preferred by Hillebrand (2); but I had trouble in getting a complete fusion with the normal salt. I then tried the bicarbonate with good results. By using the bicarbonate, I got a complete fusion with a good Bunsen burner and without the use of a blast flame. When the fusion could be made without the use of the blast, I found that the platinum crucibles did not lose so much in weight.

My results confirm those obtained by C. Holthof (3) who, while experimenting in Bunsen's Laboratory, discovered that the bicarbonate could be used as a flux for the fusion of silicates without loss or danger from splattering, and at a much lower temperature than with the normal salt. Holthof used only a good burner without the blast.

The use of the bicarbonate was first suggested to me by Prof. J.A. Gibson. A few years ago some of Prof. Gibson's students, Mr. R.L. Prim and Mr. W.J.Bray, discovered that they could get a complete fusion with the bicarbonate as a flux when they could not with the normal carbonate. Mr. O.E.Sheppard, while working with silicate rocks in Prof. Brown's Laboratory, had trouble in getting a complete fusion with the normal carbonate. At my suggestion he tried the bicarbonate with good results.

^{(1).} Bull. No. 422, p. 90.

^{(2). &}quot; " pp. 83-98.

^{(3).} Zeitschrift fur Analytische Chemie Vol. 23, p. 499.

The hydroxides of iron, aluminum, vanadium, titanium, and zirconium were precipitated from the filtrates of the silica by redistilled ammonium hydroxide. The precipitate was filtered off, dissolved and reprecipitated, and finally ignited and weighed as the oxides. This residue was then dissolved by fusion with pyrosulphate, the fusion being dissolved in dilute sulphuric acid. The iron was then titrated by using a standardized potassium permanganate solution. (1).

Calcium oxide was determined by the oxalate method in the usual manner in the filtrates from which the iron and the aluminum had been removed. (2).

Only a trace of strontium could be found by the ether alcohol method. (3).

Magnesium oxide was determined in the filtrates from the calcium precipitation by the phosphate method. (4).

The titanium was determined in two ways. First by using the solution which has served for the titration of the total iron; second, by direct evaporation of the silica of the rock powder with hydrofluoric acid and sulphuric acid. Care must be taken to get rid of all the fluorine and the fluorides on account of their bleaching properties. I found that the two methods checked very well. The titanium oxide was then determined by the colorimetric method using a Schreiner colorimeter. (5)

- (1). Bull. No. 422, pp. 107-111.
- (2). " " p. 118.
- (3). " " p. 119.
- (4). " " p. 123.
- (5). " " pp. 128, 130.

A new sample of the rock powder was treated with hydrofluoric acid and sulphuric acid. The hydrofluoric acid was completely driven off by repeated evaporations with sulphuric acid. The residue was then treated with dilute sulphuric acid, filtered and the filtrate boiled with a known quantity of a standard silver nitrate solution and a little ammonium persulphate to bring out the pink color. This solution was then diluted to an exact volume and the color compared with that of the same volume of a standard solution by the use of a Schreiner colorimeter. (1).

A separate portion of the rock powder was fused with sodium carbojate and a little sodium nitrate for the determination of barium and zirconium. The method given by Hillebrand was followed exactly. (2).

Vanadium and chromium were determined in a separate sample of the rock powder according to Hillebrand's own method. (3). Chromium was tested for colorimetrically and vanadium was determined by titrating with a standard solution of potassium permanganate. No chromium was found, but vanadium was in sufficient quantities to be easily determined.

- (1). Bull. No. 422, p. 116.
- (2). " pp. 138, 140.
- (3). " p. 150.

Ferrous iron was determined by the method given by Cook. The apparatus was slightly simplified to suit the conditions in the laboratory. (1).

The alkali s, sodium and potassium were determined in a separate portion of the rock powder by the J. Lawrence Smith method. (2). The only variation made was the one recommended by Mr. W.J. Bray, that is the doubling of the quantity of fusion mixture to one part of the rock powder. A complete fusion can be obtained by thus doubling the fusion salts.

Hygroscopic moisture was determined by the method given by Washington. (3). This method involves heating the weighed samples of rock powder to one hundred degrees Centigrade to constant weight in an air bath, in previously heated platinum crucibles.

The combined water or total volatile matter was determined by heating weighed samples of the rock powder in previously heated and weighed Jena hard glass test tubes in a combustion furnace until constant weight was obtained.

Carbon dioxide was determined quantitatively according to Hillebrand's direct method. (4).

The regular method of determining phosphorous was used but no trace could be found. (5).

- (1). Bull. No. 422, p. 168.
- (2). " p. 171.
- (3). Manual of Rock Anal. p. 73.
- (4). Bull. No. 422, p. 179.
- (5). " p. 144.

DATA

Sample 1. Sample 2. Sample 3. Sample 4. Sample 5.

	Pct.	Pct.	Pct.	Pct.	Pct.
sio_2	75.14	72.69	74.45	69.52	73.53
A1203	12.88	15.36	10.84	13.67	12.48
Fe ₂ 0 ₃	1.35	1.14	3.26	1.31	2.13
FeO	.84	•54	.62	.97	1.91
${\tt TiO}_2$.19	.32	.19	.70	•34
ZrO2	.27	.21	.24	.24	.19
V203	.18	.19	.14	.37	.20
MnO	.02	.04	.03	.07	.02
MgO	.12	.11	.07	.27	.28
CaO	.05	1.04	.94	1.40	.87
B aO	.18	,04	.05	.04	.04
Na20	5.00	4.50	4.35	5.19	4.26
K20	3.47	3.43	3.46	4.00	3.97
H ₂ 0	.42	.41	.19	1.35	.50
H20-	.12	.30	.24	.23	.11
co2	trace	.24	.23	trace	trace
Sr0	17	trace	trace	11	τŧ
0 r 203	none	none	none	none	none
P205	Ħ	π	11	п	11
Total	100.23	100.56	100.30	99.43	160.24

DISCUSSION OF DATA

All reagents used to determine the results on page six were carefully tested. At least three determinations that checked within the limits of error were made for the calculation of the percentage of each constituent of each sample. Noticing the absence of phosphorous and the unusual high percentages of vanadium, a special test of the reagents used in these two determinations was made and the vanadium recalculated with special care to follow the exact method of Hillebrand.

From 1.530 analyses of granites (1) which represent all of the data accumulated by the chemists of the U.S.Survey down to January 1.1908, only 83 determinations were reported for vanadium. The average percentage of vanadium trioxide in these 83 rocks is .024. The large percentages of vanadium in these five samples is especially striking since Hillebrand shows (2) that vanadium is absent or nearly so in the highly siliceous rocks thus far examined. He also makes the statement that vanadium is widely distributed in the earth's crust and can be found in nearly all granites in small quantities. Thorpe's Dictionary of Chemistry states, "Vanadium is said to be diffused with titanium through all primitive granite rocks." It will be noticed from the data, page six of this paper. that the percentages of vanadium and titanium increase in the samples in the same order, namely three, one, two, five, and four, and in nearly the same ratio.

- (1).Bull.No.419, p 6.
- (2).Bull.No.422, p 148.

The facts in the preceeding paragraph might be of more interest to the geologist than to the chemist. It would also be interesting and of value to have a petrographical examination made. It is the plan of Prof.Gibson to have such an examination made and publish the results in connection with this paper and the data obtained by Mr. Bray.

The purpose of the analysis of the crystalline igneous rocks of South-East Missouri is to collect general information about their chemical composition, and, in this particular instance, to show whether there is a variation in chemical composition corresponding to the gradation from granite to porphyry. The analyses of the five samples which is completed in this paper does not show any regularity in the chemical composition. All five samples contain large percentages of silica. Samples one, two, three, and five lie within a range of three percent of each other, while sample four is three percent lower in silica than the lowest of these four. Sample four also contains larger percentages of calcium. sodium potassium, and moisture than any of the other samples. Although the results are interesting and of value, there is nothing in the data (page 6) to show any relationship between the chemical composition and the and the gradation from granite to porphyry; there being no regular increase or decrease of any of the chemical constituents from sample one to sample five.



The work described in this paper has been done under the supervision and direction of Prof. James A. Gibson. The author wishes to take this opportunity of expressing his gratitude to Prof. Gibson for his kind advice and assistance.

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