

A CHEMICAL CONTRIBUTION TOWARD THE  
COMPOSITION, STRUCTURE AND ORIGIN OF THE  
CRYSTALLINE ROCKS OF SOUTH-EAST MISSOURI

by

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INTRODUCTION.

The so called Iron Mountain region of south eastern Missouri, containing, as it does, extensive deposits of valuable minerals and building stones, presents a most interesting field for the geologist. The entire region covers an area about seventy miles square, and within this area are all the massive crystalline rocks of Missouri. They occur in irregular masses and isolated hills. Most of these crystalline rocks are granites or porphyries with an occasional occurrence of a basic dike.

Some work has been done on the geology of this region, but, as far as can be ascertained, there has been no attempt to make a complete study of the chemical composition of the crystalline rocks. Little has been done chemically beyond determining the silica, and thereby classifying them as acidic or basic. Erasmus Haworth, in his paper on the "Crystalline Rocks of Missouri" (1), gives four complete analyses by Melville, and a few partial ones by others.

It is the purpose of a study undertaken by Mr. J. A. Gibson, of which this present paper is a part, to obtain complete data on the chemical composition of the rocks of this region, and to trace, if possible, a relationship between their chemical composition and their structure.

(1) Mo. Geol. Survey, Vol. 8, Annual Report 1894.

SOURCE OF ROCKS.

The rocks used in this series of analyses were found in Madison County, Missouri, about one fourth of a mile north of Fredericktown. The land belongs to the Madison Lead and Land Company, and is located in section six of township thirty three north, range seven east. The exact spot from which they were taken is a few hundred yards below the crossing of the Saint Louis, Iron Mountain, and Southern Railroad and the Little Saint Francois River. At this place there is a contact of limestone with the crystalline rocks. Haworth describes this contact as follows: stating that "Over the surface of the porphyry is spread a layer of crystalline fragments and rounded boulders of various sizes. The sandstone with planes of false bedding distinctly marked and inclined at a high angle, pitch away from the central porphyritic elevation". Further than this he does not consider the nature of the crystalline rocks. (1)

It was found that the rock near the top of the ledge is porphyry, which changes into a coarse red granite at the water line. A comparison of the accompanying photographs with the plate shown in Haworth's paper (2) proves them to be photographs of the same spot. Every feature of the landscape

(1). Mo. Geol. Surv. Vol. 8, p 103.

(2). " " " " ", plate XI.



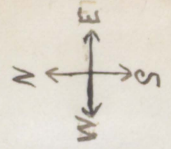


shown by Haworth was positively identified before our photographs were made.

A reference to the accompanying sketch map will show the features which are of interest in connection with this series of rocks. It will be seen that the river makes a U-shaped bend, and that the series of rocks under investigation was taken on an east-west line across the point of land so formed. (1)

The first specimen in this series was taken from the granite at the water line on the eastern side of this point of land. At various places along a line running west from this spot seventeen specimens were taken. The rock changes from a granite to a porphyry. Specimen five, taken about twenty eight <sup>feet</sup> up the face of the cliff from one, and about twenty feet above the water line, is porphyry. From here to the location of specimen fifteen the rock is various grades of porphyritic granite and granitic porphyry. Specimen fifteen is a coarse red granite like one. Specimen seventeen is a porphyry (somewhat granitic), and was found about twenty feet below the level of fifteen, and about twenty seven feet west of it. Sixteen is granitic porphyry and was found between fifteen and seventeen.

(1). In making this map no attempt has been made to draw any part of it to scale except the east-west line of specimens.



-5-

St. L., I. M. & S. R. R.

Public Road

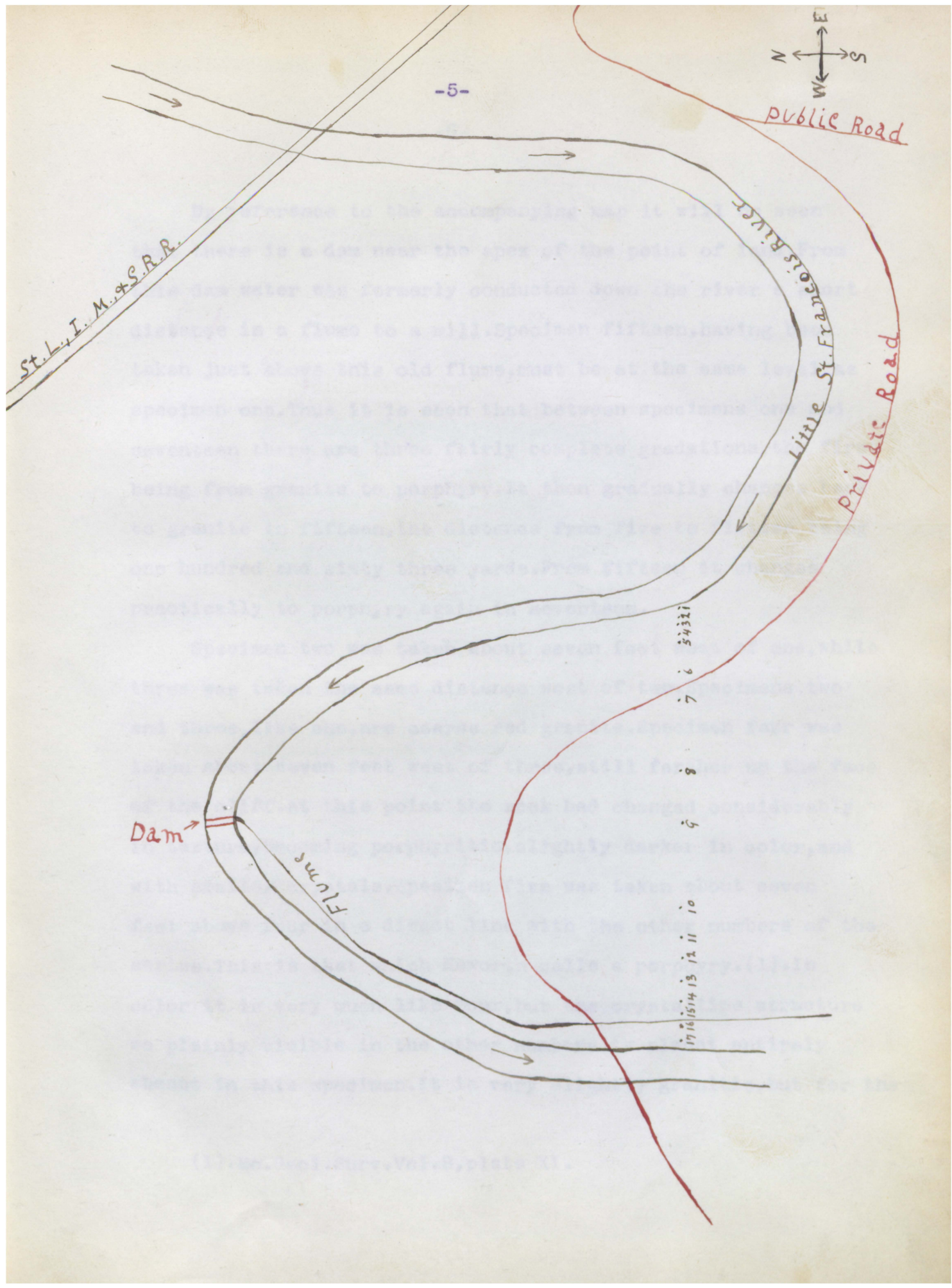
Private Road

Little St. Francis River

Dam

Flume

17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1

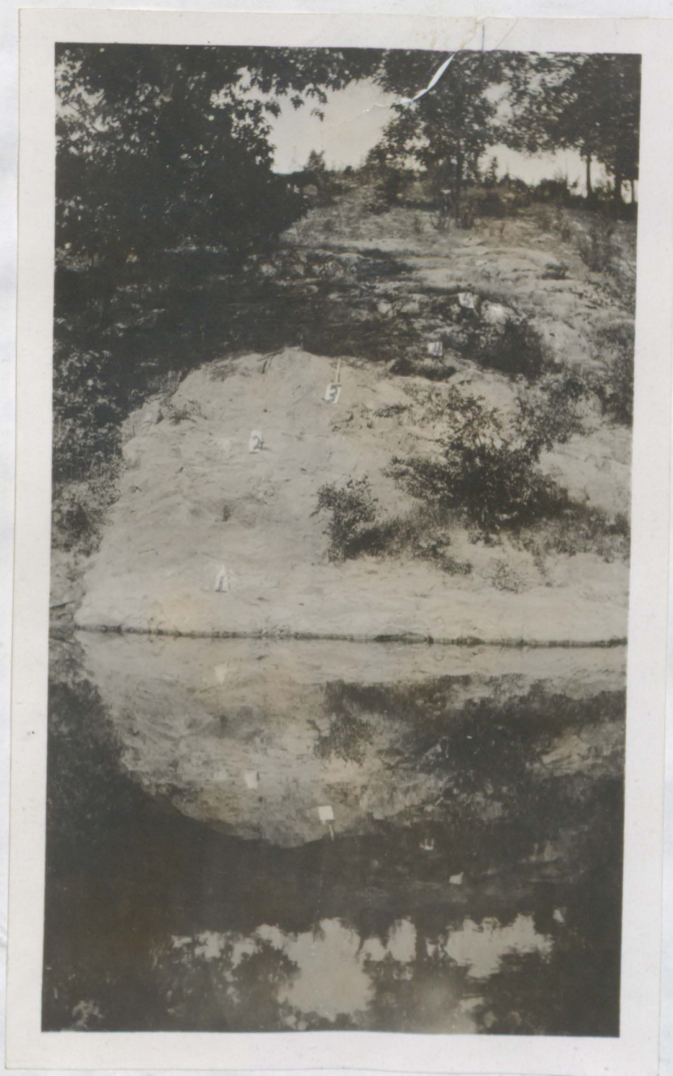


By reference to the accompanying map it will be seen that there is a dam near the apex of the point of land. From this dam water was formerly conducted down the river a short distance in a flume to a mill. Specimen fifteen, having been taken just above this old flume, must be at the same level as specimen one. Thus it is seen that between specimens one and seventeen there are three fairly complete gradations, the first being from granite to porphyry. It then gradually changes back to granite in fifteen, the distance from five to fifteen being one hundred and sixty three yards. From fifteen it changes practically to porphyry again in seventeen.

Specimen two was taken about seven feet west of one, while three was taken the same distance west of two. Specimens two and three, like one, are coarse red granite. Specimen four was taken about seven feet west of three, still farther up the face of the cliff. At this point the rock had changed considerably in texture, becoming porphyritic, slightly darker in color, and with smaller crystals. Specimen five was taken about seven feet above four in a direct line with the other numbers of the series. This is that which Haworth calls a porphyry. (1). In color it is very much like four, but the crystalline structure so plainly visible in the other numbers is almost entirely absent in this specimen. It is very slightly granitic, but for the

(1). Mo. Geol. Surv. Vol. 8, plate XI.







purposes of the present work it is justifiable to call it a porphyry. At no point in this series is there a break, but a steady gradation from the coarse red granite of one, two and three to a porphyry in five, within a total distance of about twenty eight feet. Reference to the accompanying photograph will show this first series of five numbers, the exact location of each specimen being marked by a white spot in the picture.

There<sup>is</sup> a shallow soil covering the rock in several places between the location of specimen one and that of seventeen, but there is undoubtedly no break whatever in the rock within this space.

In the present paper the first series of specimens, only, will be dealt with. The other twelve numbers will be dealt with in subsequent papers.

#### PREPARATION OF SAMPLES.

To obtain each sample a large quantity of the rock was taken out, broken into small pieces on a clean surface of the same kind of rock, and then sampled down to ten or fifteen pounds. These specimens were then packed and shipped to the laboratory. Here they were further sampled to about six hundred gram samples. Then these samples of six hundred grams each

were further broken up in a large iron mortar by direct blows of the pestle until they would pass through a ten mesh sieve. During this process the mortar was carefully covered by a cloth to prevent loss by flying particles. After the sample had been made to pass through this sieve, it was placed in the jars of an Abbe ball mill and ground down so that it would pass through a one hundred mesh sieve. A total sample of about six hundred grams was thus prepared for each number of the series. After a thorough mixing the total amount was sampled down in the usual manner, and about twenty five grams of the sample taken as a sample for analysis. This sample was again carefully mixed, and stored in glass stoppered weighing bottles. By taking so large a sample the error due to the introduction of a small amount of iron from the mortar, or of silica from the balls and the jars of the mill was reduced to a minimum. The method used in pulverizing the samples makes serious contamination from the former source very improbable, while the very large percent of silica present in these rocks would make the slight error due to the latter source negligible.

METHODS OF ANALYSIS.

In carrying out this work the standards set by the chemists of the United States Geological Survey have been followed as far as possible.(1).It was found that,for the most part, the methods which they employ are,in harmony with their ideals of work,the best that have been devised for determining the constituents of rocks.The present paper will deal with only the major constituents,leaving the minor ones to be included in a subsequent paper.

In order to determine the freshness of a rock it is necessary to determine the water and carbon dioxide.(2). The water found in rocks may be either hygroscopic or combined. It is necessary for the petrographer to know these facts in connection with a rock in order to make all analyses strictly comparable.(3).Washington says "Carbon dioxide is often present but,as far as is now known with certainty,only when the rock

(1).Professional Paper No.14,U.S.Geol.Surv.;Bulletin No.305U.S.G.S.,pp11-38;Washington's Manual for the Chemical Analysis of Rocks,pp 1-73.

(2)Washington,pp12-13

(3).Bulletin No.305,U.S.G.S.,p 53;Washington,pp 12,17.

is not strictly fresh, as a component of the secondary minerals, calcite, dolomite, siderite and cancrinite. If it is present it should always be determined, as it serves to a certain extent to measure the freshness of the rock."

Hygroscopic water was determined by the method given by Washington (1). This method involves heating weighed samples of rock powder to three hundred and eighty three degrees absolute to constant weight in an air bath, in previously ignited and weighed platinum crucibles. (2). It may be that some of the more loosely combined water of crystallization of some zeolites and other hydrous minerals is also driven off at this temperature and included as hygroscopic water.

Carbon dioxide was tested for qualitatively by the method given by Hillebrand (3). This method involves the addition of dilute hydrochloric acid to some of the rock powder under conditions most favorable for the detection of small amounts of this constituent. The results of such tests show that our rocks are fresh. (4).

(1) Manual of Rock Anal. page 73.

(2). The absolute thermometer is used in this laboratory.

(3). Bulletin No. 305, U.S.G.S., page 150.

(4). See analyses on page 15.



The combined water was determined by the "loss on ignition" method given by Washington (1). Since the rock is fresh and the amount of ferrous oxide small this method can be used safely.

In determining the silica the weighed sample of the rock powder was decomposed by fusion with Baker's analyzed sodium carbonate. This method of decomposition is preferred by Hillebrand. (2). The fusion was then dissolved in dilute hydrochloric acid in a beaker and the precipitated silicic acid filtered off. The filtrate was then evaporated to dryness in platinum dishes. It was found to be necessary to add a few cubic centimeters of alcohol before evaporation to reduce the sodium manganate formed in the fusion. In some of our preliminary analyses this was not done, and, as a result, the platinum was very perceptibly attacked. This behavior is due to the fact that the sodium manganate oxidizes the hydrochloric acid liberating chlorine which, in turn, reacts with the platinum. From this point the method given by Hillebrand was followed exactly (3).

(1) Washington, page 74.

(2). Bulletin No. 305, U.S.G.S., page 71.

(3). Bulletin " " " " " " " " et. seq.; J. Am. Chem. Soc. Vol. 24, page 262; Technology Quarterly Vol. 3, page 61.

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

Calcium oxide was determined in the filtrate from the aluminum and iron precipitation by the oxalate method (2).

Magnesium oxide was determined by the phosphate method in the filtrate from the calcium precipitation. (3).

The alkalies, sodium and potassium, were determined in a separate portion of the rock powder by the J. Lawrence Smith method. We did not vary much from the method as given by Hillebrand, using the form of platinum crucible designed for this determination. (4). Washington and Hillebrand recommend the use of eight parts of pure calcium carbonate and one part of pure ammonium chloride to one part of the very finely ground rock powder, as a fusion mixture. By using these proportions

(1). Bulletin No. 305 U.S.G.S., pages 82, 86, 88, 90.

(2). " " " " , page 101; Washington , page 115.

(3). " " " " , " 105; " , " 119.

(4). " " " " , " 144; " , " 130.

of these constituents of the fusion mixture it was never possible to obtain a complete decomposition of the rock powder, even though the latter had been previously ground to pass through a two hundred mesh sieve, and very thoroughly mixed with the fusion mixture. By using nearly double the proportion of calcium carbonate and ammonium chloride recommended it was possible to get a complete decomposition, which Washington insists upon, the rock powder having been previously ground to pass through the one hundred mesh sieve. A comparison of the data obtained in determining sodium and potassium in portions of the rock powder in which complete decomposition was not obtained, with those in which such was obtained, showed conclusively that, in the former case, a considerable per cent of these constituents had been lost by the incomplete decomposition. (1) In this determination Baker's analyzed chemicals were used. In this, as in all other determinations in this work, Jena glassware was used. Platinum was used for evaporations of solutions.

(1). Mr. C. J. Boner, working in this laboratory on the analysis of shales, had this same experience. At our suggestion he used a larger proportion of the constituents of the fusion mixture with very satisfactory results. This would seem to show that it is necessary, when working with rocks containing a high per cent of silica, to use a larger proportion of the fusion mixture than Hillebrand suggests in order to get complete decomposition of the rock powder.

DATA

	Sample No.1.		Sample No.4.		Sample No.5.	
	Pct.	Mol.	Pct.	Mol.	Pct.	Mol.
Si O <sub>2</sub>	75.14	1.252	69.52	1.159	73.53	1.226
Al <sub>2</sub> O <sub>3</sub>	13.52	.135	15.08	.148	12.62	.124
Fe <sub>2</sub> O <sub>3</sub>	1.35	.009	1.31	.009	2.13	.013
Fe O	.84	.012	.97	.014	1.91	.027
Mg O	.12	.003	.27	.007	.28	.007
Ca O	.05	.001	1.40	.025	.87	.016
Na <sub>2</sub> O	5.00	.081	5.19	.084	4.26	.087
K <sub>2</sub> O	3.47	.037	4.00	.043	3.97	.042
H <sub>2</sub> O +	.42	.023	1.35	.075	.50	.028
H <sub>2</sub> O -	.12	.007	.23	.013	.11	.006
C O <sub>2</sub>	Trace		Trace		Trace	
Total	100.03		99.32		100.18	



Some question has arisen as to the accuracy of the old chloroplatinate method for potassium, and as to the relative accuracy of this method and of the newer cobalti-nitrite method (1). Although the former method was used in this research, experiments are now in progress in this laboratory to determine this point, and they will be published in a subsequent paper.

Ferrous oxide was determined by the method of Cooke as given by Hillebrand (2), the arrangement of the water bath being slightly modified to suit conditions in this laboratory.

#### DISCUSSION OF DATA.

A study of these data will show that, chemically, there is no fixed relation between the rocks of this series. Sample four is seen to have a lower per cent of silica and a higher per cent of alumina, lime, alkalies and water than either of the other samples. Sample four is lower in ferric oxide than either one or five. Ferrous oxide and magnesium oxide increase from the granite to porphyry, but not in the same ratio. Sample five, which is highest in iron oxides, is

(1). Am. J. Sci. Series 4, Vol. 24, p 433; J. Ind. & Eng. Chem. 1, 791.

(2). Bulletin No. 305, U.S.G.S., page 140.

Sample one.

	Mol.	Mag.	Orth.	Alb.	An.	Cor.	Hyper.	Quar.
SiO <sub>2</sub>	1.252		222	486	2		6	536
Al <sub>2</sub> O <sub>3</sub>	.133		37	81	1	14		
Fe <sub>2</sub> O <sub>3</sub>	.009	9						
FeO	.012	9					3	
MgO	.003						3	
CaO	.001				1			
Na <sub>2</sub> O	.081			81				
K <sub>2</sub> O	.037		37					

Formula	Mol.Wt.	Norm.	
SiO <sub>2</sub> -----	536 x 60 = Quartz=	32.16	Q
K <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .6SiO <sub>2</sub> ---	37 x 556= Orthoclase=	20.57	} F } Sal.
Na <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .6SiO <sub>2</sub> --	81 x 524 = Albite =	42.44	
CaO .Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub> --	1 x 278= Anorthite=	.28	
Al <sub>2</sub> O <sub>3</sub> -----	14 x 102= Corundum =	1.43	} Fem.
MgO.SiO <sub>2</sub> -----	3 x 100} =Hypersthene=	.70	
FeO.SiO <sub>2</sub> -----	3 x 132}		
FeO.Fe <sub>2</sub> O <sub>3</sub> -----	9 x 232 =Magnetite =	<u>2.09</u>	
		<u>99.67</u>	

Sample four.

	Mol.	Mag.	Orth.	Alb.	An.	Cor.	Hyper.	Qtz.	Diop.
SiO <sub>2</sub>	1.159		258	504	42		8	339	8
Al <sub>2</sub> O <sub>3</sub>	.148		43	84	21				
Fe <sub>2</sub> O <sub>3</sub>	.009	9							
FeO	.014	9					4		1
MgO	.007						4		3
CaO	.025				21				4
Na <sub>2</sub> O	.084			84					
K <sub>2</sub> O	.043		43						

Formula	Mol. Wt.	Norm.	
SiO <sub>2</sub> -----	339 x 60	= Quartz -----	20.34 Q
K <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .6SiO <sub>2</sub> -----	43 x 556	= Orthoclase ----	23.91
Na <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .6SiO <sub>2</sub> -----	84 x 524	= Albite -----	44.02
CaO.Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub> -----	21 x 278	= Anorthite -----	5.84
MgO.SiO <sub>2</sub> -----	4 x 100	} Hypersthene ---	.93
FeO.SiO <sub>2</sub> -----	4 x 132		
CaO.SiO <sub>2</sub> -----	4 x 116	} Diopside-----	.90
MgO.SiO <sub>2</sub> -----	3 x 100		
FeO.SiO <sub>2</sub> -----	1 x 132		
			<u>95.94</u>

} Sal.  
F  
} Feen.

Sample Five.



	Mol.	Mag.	Orth.	Alb.	An.	Cor.	Hyper.	Qtz.
SiO <sub>2</sub>	1.225		252	414	64		21	474
Al <sub>2</sub> O <sub>3</sub>	.143		42	69	16	16		
Fe <sub>2</sub> O <sub>3</sub>	.013	13						
FeO	.027	13					14	
MgO	.007						7	
CaO	.016				16			
Na <sub>2</sub> O	.069			69				
K <sub>2</sub> O	.042		42					

Formula	Mol.Wt.	Norm.
SiO <sub>2</sub> -----	474 x 60 = Quartz	-----= 28.44 Q
K <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .6SiO <sub>2</sub> -----	42 x 556 = Orthoclase	---= 23.35
Na <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .6SiO <sub>2</sub> -----	69 x 524 = Albite	-----= 36.16
CaO.Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub> -----	16 x 278 = Anorthite	----= 4.45
Al <sub>2</sub> O <sub>3</sub> -----	16 x 102 = Corundum	-----= 1.63
MgO.SiO <sub>2</sub> -----	7 x 100	} = Hypersthene = 2.55
FeO.SiO <sub>2</sub> -----	14 x 132	
FeO.Fe <sub>2</sub> O <sub>3</sub> -----	13 x 232 = Magnetite	----= 3.02
		99.60

} F } Sal.  
} Fem.



Sample one.

$$\frac{\text{Sal}}{\text{Fem}} = \frac{96.85}{2.79} > \frac{7}{1} \quad \text{Class 1. (Persalic).}$$

$$\frac{Q}{F} = \frac{32.16}{63.29} < \frac{3}{5} > \frac{1}{7} \quad \text{Order 4. (Quardofelic).}$$

$$\frac{\text{K}_2\text{O} + \text{Na}_2\text{O}}{\text{CaO}} = \frac{118}{1} > \frac{7}{1} \quad \text{Rang 1. (Peralkic).}$$

$$\frac{\text{K}_2\text{O}}{\text{Na}_2\text{O}} = \frac{37}{81} < \frac{3}{5} > \frac{1}{7} \quad \text{Subrang 4. (Dosodic).}$$

Sample four.

$$\frac{\text{Sal}}{\text{Fem}} = \frac{94.11}{3.92} > \frac{7}{1} \quad \text{Class 1. (Persalic).}$$

$$\frac{F}{Q} = \frac{73.77}{20.38} > \frac{5}{3} < \frac{2}{1} \quad \text{Order 4. (Quardofelic).}$$

$$\frac{\text{K}_2\text{O} + \text{Na}_2\text{O}}{\text{CaO}} = \frac{127}{25} > \frac{5}{3} < \frac{7}{1} \quad \text{Rang 2. (Domalkic).}$$

$$\frac{\text{K}_2\text{O}}{\text{Na}_2\text{O}} = \frac{43}{84} < \frac{3}{5} > \frac{1}{7} \quad \text{Subrang 4. (Dosodic).}$$

Sample five.

$$\frac{\text{Sal}}{\text{Fem}} = \frac{94.03}{5.57} > \frac{7}{1} \quad \text{Class 1. (Persalic).}$$

$$\frac{F}{Q} = \frac{63.96}{28.44} < \frac{7}{1} > \frac{5}{3} \quad \text{Order 4. (Quardofelic).}$$

$$\frac{\text{K}_2\text{O} + \text{Na}_2\text{O}}{\text{CaO}} = \frac{111}{16} < \frac{7}{1} > \frac{5}{3} \quad \text{Rang 2. (Domalkic).}$$

$$\frac{\text{K}_2\text{O}}{\text{Na}_2\text{O}} = \frac{42}{69} < \frac{5}{3} > \frac{3}{5} \quad \text{Subrang 3. (Sodipotassic).}$$

lowest in alumina. The three samples are not of the same chemical composition.

If the mineralogical composition of these rocks be considered, rather more interesting facts will be found, but yet very slight evidence of any fixed relation. Not having made a petrographical examination of these rocks, it is not possible to know their actual mineralogical composition or mode. However, it was possible to calculate the standard mineralogical composition or norm on the basis of these chemical data. (1). Following the method of calculation given by Cross, Iddings, Pirsson and Washington (2), the norm of these rocks was calculated. It is seen that the silic minerals greatly predominate over the femic in all three samples, and that the latter increase toward the porphyry. The sample lowest in alumina is highest in corundum, and the one highest in alumina has no corundum. Sample one, which is highest in total silica, is highest in quartz, and lowest in the feldspars. Sample four, which is lowest in total silica, is highest in the feldspars and lowest in quartz. Sample one was found to have the following classification: Class 1, Persalane; Order 4, Britannare; Rang 1, Liparase; Subrang 4, Kallerudose. Sample four was found to belong to the same class and order as sample one, but it belongs to Rang 2

(1). Cross, Iddings, Pirsson and Washington's Quantitative Classification of Igneous Rocks, page 147.

(2). Ibid., pages 186-203.

Toscanase;Subrang 4,Lassenose.Sample five was found to differ from the classification of four only in its subrang,the former belonging to Subrang 3,Toscanose.(1).

The chemical study of the crystalline rocks of Missouri was suggested to Mr.J.A.Gibson by Professor W.G.Brown.The work described in this present paper has been done under the supervision and direction of Mr.Gibson.Professor W.G.Brown has given many valuable suggestions which have aided much in carrying out the details of this work.The author wishes to take this opportunity of expressing his gratitude to these gentlemen for their kind assistance.

(1).Cross,Iddings,Pirsson and Washington,page 166.

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