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IN ROCK ANALYSIS

BY

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STOCKHOLM

KUNGL. BOKTRYCKERIET. P. A. NORSTEDT & SÖNER

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However much is written about the determination of ferrous iron in the analysis of silicates, sources of error are discovered every now and then in the methods used, with the result that older determinations of this substance are less reliable than the determinations of perhaps any other substance. Since HILLEBRAND and STOKES<sup>1</sup> pointed out the errors that arise in employing MITSCHERLICH's method, owing to the effect of ferric salts on pyrite that may happen to be present, scarcely any experienced analyst now uses any other than the hydrofluoric acid method. But even if the latter, carefully applied, leaves little to be desired with respect to the accuracy with which the analysis can be carried out, there always remains an uncertainty in the result, which considerably diminishes the value of the analysis.

HILLEBRAND<sup>2</sup> has already shown that the presence of vanadium not inconsiderably influences the determination of ferrous iron. But by determining the percentage of vanadium one can correct the value for the ferrous iron.

Another element that can also affect the determination of ferrous iron is titanium, and here the case is worse. Titanium is rarely absent from a silicate rock. In the analysis result it is always reported as titanium-dioxide, and it seems scarcely to have been suspected that it may possibly be present in the rock as titanium trioxide. Of the titanium that is present in silicate rocks only a small quantity

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<sup>1</sup> Z. für anorg. Ch. Vol. XXV (1900), p. 326.

<sup>2</sup> Bull. U. S. Geol. Survey, No. 176 (1900), p. 95.

may be said to occur as titanite. The greater part is contained in the ferromagnesian minerals.<sup>1</sup> How titanium is present in these is still an open question, but everything goes to prove that it occurs, at least in part (as ilmenite, biotite, etc.), in the triatomic stage. At present, however, we have no means of distinguishing  $Ti_2O_3$  from  $TiO_2$  in the presence of iron, and for the present, therefore, we must put up with the uncertainty that is incident to the determination of ferrous iron owing to the uncertainty of the degree of oxidation of the titanium.

But even apart from the disturbing influence that can be exercised by other ingredients in the rock, there are other circumstances that can cause entirely incorrect conceptions of the quantity of ferrous iron that actually occurs in the rock.

A number of irregularities in the determination of ferrous iron, which first seemed to be quite inexplicable, have since proved to be bound up with the state of division in the powder employed, and this in the unexpected way that the finer the powder was pulverized the lower was the figure for ferrous iron.

To illustrate this fact, the analysis of some powders of different degrees of fineness are quoted below. The method that has been employed is J. H. PRATT'S<sup>2</sup> simplified method, i. e. without the introduction of carbon dioxide. The fact is that it has proved, for quick work, that almost equally good results are obtained without, as with the employment of carbon dioxide.

$(H_4N)_2 Fe(SO_4)_2 + 6 H_2O$	Ferrous Iron		
	taken.	calculated.	found.
0,1276	0,0234	0,0230	— 0,0004
0,1432	0,0263	0,0259	— 0,0004
0,2634	0,0483	0,0474	— 0,0009
0,3592	0,0660	0,0654	— 0,0006

<sup>1</sup> See OSANN, Beiträge zur chem. Petrographie, II, Anhang (1905).

<sup>2</sup> Am. Jour. Sci., [3] Vol. XLVIII (1894), p. 149.

The determinations have been carried out as follows: into a 40 cc.-platinum crucible (with a close fitting cover) containing about 1 gram of rock powder, and a few small pieces of platinum wire to prevent bumping, was poured 5 cc. 10-normal sulphuric acid and then 5 to 10 cc. fuming hydrofluoric acid. The crucible was placed in a sand-bath, which was first heated so that the contents of the crucible boiled in 2—3 minutes and was kept boiling for 3—5 minutes. After rapid cooling with cold water the contents of the crucible were transferred to a platinum basin, diluted and titrated with  $\frac{1}{10}$  normal permanganate solution. Even when the grains of the powder used had the size of 0,25 mm., complete decomposition of the ferrous iron-bearing minerals was generally obtained.

A sample of Uppsala-granite containing 5,77 % of iron, calculated as ferric oxide, was crushed, without using steel implements, and pulverized in an agate mortar until the powder was so fine that when sifted through a sieve with meshes of 0,18 millimetres it left a residue of 6 % (A). A large part of this sample was fine-ground and carefully mixed (B), whereupon a part of this was ground still finer (C). As relative measures for the degree of fineness in the powder the percentage of hygroscopic moisture is appended:<sup>1</sup>

	Weight of sample dried at 105°.	Loss of weight at 105°.	Ferrous Iron found.
A. . . . .	0,9032	0,09	4,14
	0,9853	—	4,17
B. . . . .	0,7115	0,53	3,44
	0,7306	—	3,45
C. . . . .	0,7130	1,33	2,58
	0,7846	—	2,52

<sup>1</sup> At the Swedish Geological Survey's Laboratory all analyses of rocks are, as hitherto, calculated on materials dried at a temperature of 105° C. I hold that the analysis of air-dry samples, however to be desired, has no *raison d'être* as long as one has not agreed upon the fineness in the powder to be used in determining the water that passes away at 105° C. An analysis carried out on material pulverized according to the directions given

Another sample of the same granite was pulverized in a »diamond» steel mortar till the whole passed through a sieve with 35 meshes to the centimetre. Splinters of iron were removed with a weak magnet (the rock hardly contains a trace of magnetite or ilmenite), after which a portion of the sample was again pulverized in the agate mortar in the same way as with the preceding sample.

	Weight of sample dried at 105°.	Loss of weight at 105°.	Ferrous Iron found.
A. . . . .	1,0663	0,10	4,18
	0,9079	—	4,15
	1,0067	—	4,11
	0,8807	—	4,16
B. . . . .	0,7106	0,45	3,59
	0,7233	—	3,53
C. . . . .	0,7452	1,05	3,20
	0,6788	—	3,18

In order to obtain a material free from the finest dust, a large quantity of the same rock was pulverized and washed. For analysis a portion with grains of the size of 0,1—0,05 mm. (A) was used. Two samples of this (B and C) were pulverized, of which C had the fineness that is usually employed at the Survey's Laboratory in determinations of ferrous iron and alkalies. (These figures of course throw no light upon the percentage of ferrous iron in the rock itself.)

	Weight of sample dried at 105°.	Loss of weight at 105°.	Ferrous Iron found.
A. . . . .	0,9821	0,03	5,15
	0,9762	—	5,11
B. . . . .	0,9981	0,26	4,75
	1,0031	—	4,69
C. . . . .	0,9014	0,91	3,11
	0,9802	—	3,15

by WASHINGTON (Rock Analysis, p. 51) cannot, of course, give the same value for »water at 105°» as a powder produced according to DITTRICH (Gesteinsanalyse, p. 3).

These determinations show, with a clearness that seems to leave nothing to be desired, that the percentage of ferrous iron is diminished by pulverizing, and no other explanation can be given for this than that one of the minerals contained in the rock has been oxidized during the grinding. The rock here dealt with has no other minerals containing ferrous iron worth mentioning except biotite and hornblende. These were therefore isolated and analyzed separately.

**Biotite from Uppsala Granite.** Sp. gr. 3,08—3,11.

A sample with grains of the size of 0,5—0,26 mm. (A) and two samples of fine-ground material (B and C) were decomposed with 10-normal sulphuric acid in sealed pieces of the same glass tube filled with carbon dioxide.

	Weight of sample dried at 105°.	Loss of weight at 105°.	Ferrous Iron found.
A. . . . .	0,6181	0,03	20,33
B. <sup>1</sup> . . . . .	0,7597	1,11	17,54
C. <sup>1</sup> . . . . .	0,5702	2,03	17,38

**Hornblende from Uppsala Granite.** Sp. gr. 3,20—3,26.

The determinations were carried out according to PRATT'S method, partly on material with grains of the size of 0,18—0,26 mm. (A), partly on fine-ground material (B and C).

	Weight of sample dried at 105°.	Loss of weight at 105°.	Ferrous Iron found.
A. . . . .	0,3066	not determined	15,57
	0,3021	—	15,80
B. . . . .	0,3391	0,53	15,05
C. . . . .	0,3471	0,69	14,70

Both minerals were consequently oxidized by the grinding. As however the result as far as the hornblende is concerned cannot be considered fully conclusive and the

<sup>1</sup> These two determinations were carried out on different days and therefore the figures are not quite comparable for hygroscopic moisture.

scarcity of pure material prevented more determinations than mentioned above, I have attempted to substantiate the correctness of the conclusion drawn from the values already obtained by analyzing another material.

**Black Hornblende from Värmland.** (According to Dr. A. GAVELIN, somewhat combined with a light pyroxene.)

The mineral was analyzed partly in grains of 0,10—0,18 mm. (A), partly fine-ground (B).

	Weight of sample dried at 105°.	Loss of weight at 105°.	Ferrous Iron found.
A. . . . .	0,5122	0,16	22,59
	0,5208	—	22,63
	0,5084	—	22,55
B. . . . .	0,5129	0,45	21,37
	0,5202	—	21,62
	0,5305	—	21,34
	0,3652	—	21,45

These figures support those previously obtained. The sum of the oxidation shown in the isolated minerals is less, however, than we should have expected from the figures previously obtained for ferrous iron in the rock itself. But the inconsistency is easily explained if we attribute to mica the largest share in this oxidization. Mica is very difficult to pulverize by itself, but ground together with quartz it is comparatively easily brought to a high degree of fineness.

To decide whether this tendency to oxidize through grinding is also present in other minerals containing ferrous iron besides biotite and hornblende, a few more experiments have been carried out.

#### **Diallage from Ruotivare.**

The mineral was pulverized till it passed through a sieve with 35 meshes to the centimetre (A), and a part of this powder was fine-ground (B).

	Weight of sample dried at 105°.	Loss of weight at 105°.	Ferrous Iron found.
A. . . . .	0,5046	0,04	8,40
	0,5169	—	8,48
B. . . . .	0,5029	0,36	8,15
	0,4731	—	8,13

**Peridotite from Flisby**, Småland, was treated in the same way. The minerals containing ferrous iron are here principally augite and olivine.

	Weight of sample dried at 105°.	Loss at 105°.	Ferrous Iron found.
A. . . . .	0,8996	0,30	6,07
	0,8297	—	6,06
B. . . . .	0,7047	1,14	5,45
	0,7308	—	5,66

#### **Wehrlite from Ruotivare.**

	Weight of sample dried at 105°.	Loss at 105°.	Ferrous Iron found.
A. . . . .	0,5284	0,06	11,36
	0,5350	—	11,35
B. . . . .	0,5231	0,49	11,13
	0,5327	—	11,06

In this analysis a little of the ores remained undissolved in the coarser powder. The percentage of ferrous iron is therefore somewhat too low, but in spite of that it is higher than in the fine-ground powder.

In all the minerals and rocks now examined an oxidation of the ferrous iron has been noticed in the pulverization, and probably the case is the same with most minerals that contain ferrous iron. At all events what has been stated seems to me to be a sufficient proof that whenever the percentage of ferrous iron is to be determined in rocks the powder should be as coarse as the method of decomposition permits. Of analyses hitherto published the majority may be said to be subject, more or less, to the inaccuracy indicated. All the authors who have dealt in recent years

with the analysis of rocks lay stress on the necessity of having the material as finely pulverized as possible when determining the percentage of ferrous iron. Thus HILLEBRAND<sup>1</sup> speaks of »specially ground powder», WASHINGTON<sup>2</sup> says, »Whatever be the method employed for the determination of ferrous iron, it is imperative that the rock-powder be in an extremely fine state of division», and DITTRICH<sup>3</sup> enjoins that the sample shall be ground so fine »dass sich das Pulver vollkommen in die Poren der Haut einreiben lässt». Such a degree of fineness in the powder, however, is, as has been shown in the preceding, far from necessary for the decomposition of the ferrous iron-bearing minerals in rocks, and even if an occasional grain of ore remains undissolved, the fault that arises from this is in most cases less than that occasioned by oxidation during grinding. In any case that size of grain is to be preferred in the powder which gives the highest percentage of ferrous iron. Hence it follows also that MITSCHERLICH's method must be entirely discarded in determining the ferrous iron in silicate rocks. It is true that this has been advocated before, for other reasons, by HILLEBRAND and STOKES, but it seems none the less necessary to repeat it, since the method is included as lately as 1905 in DITTRICH's »Gesteinsanalyse». The only method at present practicable is to decompose with hydrofluoric acid and sulphuric acid (preferably, of course, in a carbon dioxide atmosphere) using as coarse a powder as the rock to be analyzed permits.

To illustrate the magnitude of the faults made by using fine-powdered material in determining ferrous iron, I append the determinations of iron in a series of »hällflint»-gneisses from the Utö district (from a work by Dr. P. J. HOLMQUIST, not yet published). These analysis were made

<sup>1</sup> Bull. U. S. Geol. Survey No. 178 (1900), p. 92.

<sup>2</sup> The chemical Anal. of Rocks (1904), p. 123.

<sup>3</sup> Gesteinsanalyse p. 3.

shortly before the observations described, and have since been corrected in consequence of them.

	Earlier determination (fine-ground powder).		Later do. (coarser powder).	
	Fe <sub>2</sub> O <sub>3</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	FeO
1.	0,50	0,48	0,31	0,65
2.	1,40	0,84	0,43	1,71
3.	0,75	0,67	0,42	0,96
4.	1,11	1,26	0,41	1,89
5.	1,08	1,63	0,37	2,27
6.	2,03	2,07	1,28	2,75
7.	0,52	1,74	0,18	2,04



