A New Method of Decomposition for Refractory Minerals and its Application to the Determination of Ferrous Iron and Alkalies[*]

By Jun Ito

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The common ferrous minerals noted for their resistance to attack by a boiling mixture of hydrofluoric and sulfuric acids[1] are staurolite, tourmaline, axinite, kornerupine, sapphirine, ilmenite, chromite, spinels, columbite-tantalite and chrysoberyl. The determination of the ferrous oxide content in these minerals has long been a difficult problem in mineralogy as well as in analytical chemistry.

Among many attempts by analysts and mineralogists to solve this problem, the Mitscherlich method[2], involving decomposition with sulfuric acid in a heated sealed glass tube, and the Rowledge method[3], employing fusion with sodium metafluoborate in a sealed pyrex glass tube or a Vycor tube (Juulinen's modification)[4] or in a stream of carbon dioxide in a platinum boat[5] (Groves's modification), have been considered to be the best. None of these methods however, is simple. The sealing of the glass tubing, fusion under special conditions, continuous boiling of the titrant, etc. are all very time-consuming and are very likely sources of error unless done by well qualified analysts.

The writer noticed the strong resistivity of Teflon against hydrofluoric acid and sulfuric acid as well as its durability at a high temperature (260°C) and pressure and used it as a liner in a high temperature-pressure steel bomb. In this way, a new method of the decomposition of minerals in hydrofluoric acid and sulfuric acid at elevated temperatures and under fairly high pressures was established. This is very simple, less subject to error, and suprisingly efficient method for refractory minerals.

On the other hand, the recent developement of flame photometry has changed entirely the method of determination of alkalies, and the classical Laurence Smith decomposition has been largely replaced by simple acid decomposition, because the complete separation of the other elements has become unnecessary. For refractory minerals such as mentioned above, however, the Laurence Smith method has still been believed to be superior and indispensable. The writer's method offers a much simpler and more suitable way of decomposition with minimum contamination; also the results of an analysis of the alkalies in refractory materials should be more accurate than before. Using many pure minerals and standards available at Harvard Mineralogical Musem, the writer obtained the results given in the following section.

Experimental

Apparatus.—The electric furnace employed was of a vertical type, with chromel-alumel winding. It was operated at 110 V. AC, with Variac control.

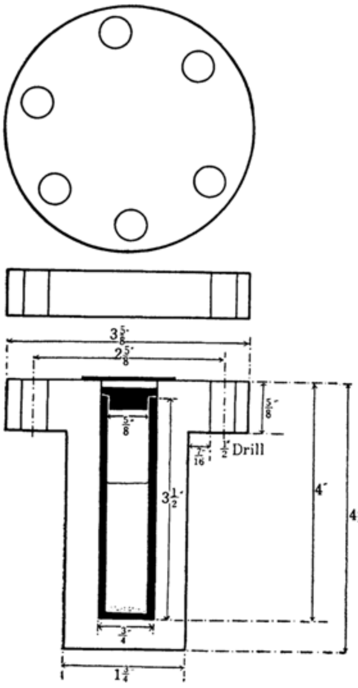

Fig. 1. Steel bomb and teflon liner.

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[*] This work was done while the writer was at the Department of Mineralogy, Harvard University, U. S. A.

1) J. H. Pratt, *Am. J. Sci.*, (3), 48, 149 (1894).

2) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Chemical Analysis", John Wiley, New York (1953), p. 911; Mitscherlich, *J. prakt. Chem.*, **81**, 116 (1860).

3) H. P. Rowledge, *S. Roy. Soc. W. Australia.* **20.** 169 (1934).

4) A. Juulinen, *Ann. Acad. Scient. Fennicaes*, **A III 47**, 19 (1956).

5) A. W. Groves, "Silicates Analysis", 2nd ed., London (1956), pp. 184-186.

Table I. Results of ferrous iron determination by both new and conventional methods in silicates

Sample	mg.	Heating time	FeO	Fe_2O_3	FeO, conventional
Tourmaline	200	2	11.70	nil	Insoluble
Newry, Maine	300	3	11.73		
Axinite, H. M. 86113	200	2	9.65	nil	Insoluble
Roseberry, Tasmania	300	3	9.72		
W-1 Diabase	300	3	8.92 (mean of 3 determinations)	—	8.97 (Recommended value 8.72)
Staurolite Fanning Co., Georgia, U. S. A.	300	3	12.56	1.20	Incomplete decomposition
Staurolite, Kootenay Lake, British Columbia	300	3	10.81	1.73	9.92
Kornerupine, H. M. 46934 Itrongahy, Madagascar	200	4	2.39	nil	1.47
Chrysoberyl, H. M. 96545 Tokowaja Lake, Urals	100	3	2.1	—	—
Garnet (Almandite), Davis, New Hampshire, U. S. A.	300	3	31.70	nil	31.37
Garnet (Almandite), North County, N. H., U. S. A.	300	3	21.42	nil	20.65

The temperature was measured with a thermometer.

The steel bomb (Fig. 1) was machined by Arthur and Harold Ames (Dunbar Lab., Harvard) from 316 stainless steel. The bomb was roasted in air for 24 hr. at 450°C to provide a protective oxide coating.

The Teflon liner (tetrafluoethylene) (Fig. 1) was machined by Dr. I. Barnes from 3/4 inch round Teflon stock. The rod was turned to 5/8 inch O. D. and bored with a 19/32 inch drill. The Teflon cap was turned to 5/8 inch O. D. on the upper end and 9/15 inch on the lower end. The Teflon gasket was cut from a 1/32 inch sheet of teflon. The length of the Teflon cup with cap in place was 3 1/2 inches. The bolts were Allen caps the screws 1/2 inch and 3 inch.

Reagents.

H_2SO_4	1 : 1
HF	48%
H_3BO_3	Saturated aqueous solution
$KMnO_4$	0.1 N Standard solution

Procedure.—1) Transfer 0.300 g. of the fine powdered sample to a Teflon liner. 2) Add 5 ml. sulfuric acid (1 : 1), 5 ml. hydrofuoric acid. 3) Stir well with a thin platinum spatula and then wash it with a few drops of pure water. 4) Cover the liner and place in the bomb. 5) Place the gasket and cover on the bomb. 6) Tighten the cover with bolts, using a vise and a rachet wrench. 7) Place the bomb in a preheated furnace at 240°C and leave for $3\sim4$ hr. 8) Take out, cool and open the bomb. 9) Pull out the teflon liner from the bomb using a thin needle. 10) a) For ferrous oxide determination, transfer the acid solution into a 500 ml. beaker filled with 300 ml. of distilled water and 10 ml. of saturated boric acid, then titarte with potassium permanganate standard solution. b) For alkali determination, transfer the acid solution into a platinum basin and heat until all the hydrofluoric acid is driven off, then follow the regular procedure for flame photometric determination.

Results

Diabase standard W-1[6] was analyzed for ferrous oxide (Table I) to check on the accuracy of the method. The results seem to be a little higher (0.1%) than the average analysis. The average value is not necessarily the true value, especially in terms of ferrous oxide determination with conventional methods, but a slight reduction of ferric iron to ferrous iron by pyrite ferrous sulfide could be suspected. Pyrite partly decomposed with this procedure.

Tourmaline from Newry, Maine, U. S. A., Axinite from Tasmania and Kornerupine from Madagascar were analyzed totally using the new method. The calculated formulae from the chemical analysis indicates that the iron present in these minerals is divalent, replacing magnesium manganese in the structure. Axinite definitely does not contain alkalies.

The iron in kornerupine and chrysoberyl is divalent; this explains their bluish color.

Fig. 2. shows that contamination of the iron by the steel of the bomb is remarkably low. Aparently the hydro fluoric acid and sulfuric acid were kept inside of Teflon liner well.

The blank consumption of potassium permanganate solution increases with the time of heating. For ferrous oxide determination, therefore, the heating should be limited to 4 hr. (Fig. 3) if possible.

Among the refractory minerals mentioned above, only tourmaline and kornerupine contain appreciable amounts of alkalies. The

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[6] H. W. Fairbairn and others, "A Cooperative Investigation of Precision and Accuracy in Chemical, Spectrochemical and Modal Analysis of Silicate Rock", U. S. Geological Survey Bulletin 980 (Analysis of Diabase W-1), (1953).

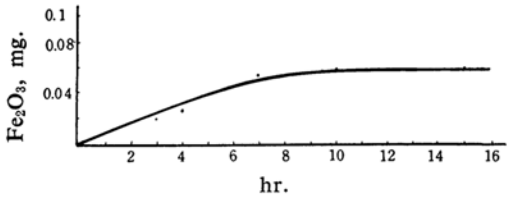

Fig. 2. Iron contamination during the decomposition with new method.

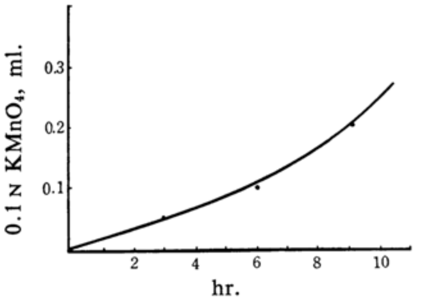

Fig. 3. Blank consumption of 0.1 N $KMnO_4$ after the heating of solution of H_2SO_4+HF with 1 ml of 5 N $Fe_2(SO_4)_3$ solution.

TABLE II. RESULTS OF ALKALI DETERMINATION

Mineral	Element	Number of analyses	%
Tourmaline	Na_2O	3	1.78
Newry, Maine	K_2O	3	0.09
Axinite, Roseberry,	Na_2O	2	nil
Tasmania	K_2O	2	nil
Kornerupine,	Na_2O	3	0.30
Madagascar	K_2O	3	0.12
Blank alkalies	Na_2O	3	0.5 ppm in final 100 ml test solution
	K_2O	3	0.5 ppm in final 100 ml test solution

results of the alkali determination are shown in Table II. Blank values of contamination from the new procedure did not exceed the values obtained by the conventional procedure. Actually, the new method decomposed minerals more completely than the other method, and subsequent flame photometric determination was very easily carried out. Although none of the refractory oxide minerals which will be mentioned in the following section contain appreciable amount of alkalies, this method should be very suitable when their alkali content is in question.

Discussion

The principle of the method is somewhat similar to that of the Mitscherlich method, but the use of hydrofluoric acid inside a sealed vessel at an elevated temperature and pressure has never been attempted before for lack of a suitable liner such as Teflon.

As the results show, the reaction between minerals and acids under the stated conditions were carried out completely, and the difficulty of the ferrous ion and alkali determination of the refractory minerals was reduced.

The acid solution in a Teflon-lined bomb can be heated safely as long as the sample requires. Iron and alkali contamination are not detected, although consumption of the potassium permanganate standard solution gradually increases due to the very slight decomposition of the Teflon container. Also, there is no chance for any other contamination of the cation from outside.

Neither appreciable oxidation nor reduction occurred during the heating within a limited time, and the oxygen (air) contained in the partly-filled bomb does not significantly affect the results. The air can be replaced by nitrogen gas if desired.

The apparatus can be designed on a large industrial scale as well as on a microchemical scale, and there is no danger of breakage during the entire procedure because no glassware is involved.

In addition, the writer has extended these

TABLE III. DECOMPOSITION OF NON-SILICATES

Mineral	Heating time, hr.	FeO	Grade of decomposition
Magnetite, $FeOFe_2O_3$	4	29.9	Complete, Fe^3 hydrolyzed
Pyrite, FeS_2	5	—	Very incomplete
Ilmenite, $FeOTiO_2$	6	45.1	Complete, Ti^4 hydrolyzed
Chromite, $FeOCr_2O_3$	6	32.9	Complete, clean solution
Tantalite, $(FeMn)(TaCb)_2O_6$	8	7.9	Complete, Fe^3 hydrolyzed
Columbite	8	12.2	Complete, Fe^3 hydrolyzed
Baddeleyite, ZrO_2	12	—	Complete, clean solution
Rutile, TiO_2	16	—	Complete, clean solution
Corundum, Al_2O_3	4	—	Complete, small amount of Al salt precipitated
Zircon, $ZrSiO_4$	10	—	Only HF was used. Complete

experiments toward non-silicate minerals that are mostly oxides and the most difficult materials to dissolve in acids.

Chromite, ilmenite, baddeleyite, columbite-tantalite, rutile and corundum were readily decomposed by the same treatment, although pyrite and zircon were only partly decomposed.

Recently the writer has tried to decompose zircon ($ZrSiO_4$) in various ways and has finally found that it decomposes in the same vessel after 10 hr. of heating at 240°C, using hydrofluoric acid alone instead of a mixture of sulfuric acid and hydrofluoric acid.

The method is good not only for chemical analysis, but also various industrial uses may be found for it.

Finally, the use of strong alkalies instead of acids (Teflon is stable in alkalies too) should be studied.

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Department of Chemistry
College of General Education
The University of Tokyo
Meguro-ku, Tokyo