Isomorphism as illustrated by certain varieties of Magnetite.

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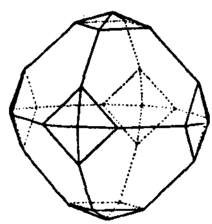
[Communicated by L. Fletcher, F.R.S., and read January 29, 1907.]

SOME years ago the writer received from St. Joseph du Lac in the County of Two Mountains, province of Quebec, Canada, a few small specimens of a black mineral which was identified as magnetite. Later, a more careful inspection of the fragments, which weighed from ten to fifteen grams each, showed that some of them were portions of crystals made up of an unusual combination, the octahedron {111} and a trapezohedron {311}. Further, chemical analysis showed that the composition was specially interesting, the mineral being titaniferous and containing, besides 3·24 per cent. of magnesia, a larger proportion of manganese than had been observed in the case of any magnetite previously examined. The crystals displayed no cleavage or parting, but a conchoidal to subconchoidal fracture. Hardness, about 6. Specific gravity (determined with the pycnometer), 4·913. Lustre, metallic and splendent: colour and streak, black. Strongly magnetic. The results of the chemical analysis were as follows:—



Magnetite from St. Joseph du Lac, Quebec: forms {111}, {311}.

		Atomic ratios of metals.	Atomic ratios of oxygen.
Ferric oxide	59·71	0·746	1·119
Titanium dioxide	5·32	0·066	0·132
Alumina	0·62	0·012	0·018
Ferrous oxide	22·70	0·315	0·315
Manganous oxide	8·46	0·119	0·119
Magnesia	3·24	0·081	0·081
Silica	0·16	—	—
	100·21	1·339	1·784

Then dividing respectively by 3 and 4 we get $\frac{1\cdot339}{3} = 0\cdot445$ and $\frac{1\cdot784}{4} = 0\cdot443$, the correct ratio for magnetite and other members of the spinel group. It is, of course, unlikely that the titanium exists in the mineral as dioxide; and if it be calculated as sesquioxide and the difference in the oxygen transferred to the iron the analysis becomes:—

			Atomic ratios of oxygen.	
Ferric oxide	65·01	...	1·219	1·357
Titanium sesquioxide ...	4·79	...	0·120	
Alumina	0·62	...	0·018	
Ferrous oxide	17·93	...	0·249	0·449
Manganous oxide ...	8·46	...	0·119	
Magnesia	3·24	...	0·081	
Silica	0·16			
	100·21			

Here the oxygen-ratio for protoxides and sesquioxides ($RO : R_2O_3$) is 0·449 : 1·357, or almost exactly 1 : 3 (1 : 3·022).

Another view with regard to the condition of the titanium in such minerals is that of Mosander, Knop, and others, viz. that it is present as $FeO.TiO_2$ or $FeTiO_3$, which replaces Fe_2O_3 isomorphously. Calculated on this basis the analysis would be:—

			Atomic ratios of oxygen.	
Fe_2O_3 ...	59·71	...	1·119	1·336
$FeTiO_3$ ...	10·11	...	0 199	
Al_2O_3 ...	0·62	...	0·018	
FeO ...	17·91	...	0·249	0·449
MnO ...	8·46	...	0·119	
MgO ...	3·24	...	0·081	
SiO_2 ...	0·16			
	100·21			

Here the ratio for RO to R_2O_3 (including $FeTiO_3$ with the latter) is also practically 1 : 3 (1 : 2·975). Knop[1], who made a study of octahedrons of titaniferous magnetite yielding on analysis 24·95 per cent. of TiO_2, favoured the last view as to constitution; for here if the titanium were calculated as Ti_2O_3 the ratio of $RO : R_2O_3$ was 1 : 1·165, while if $FeTiO_3$

[1] A. Knop, 'Ueber titansäurehaltigen Magneteisenstein.' Annalen der Chemie (Liebig), 1862, vol. cxxiii, pp. 348–53.

were regarded as replacing Fe_2O_3 the ratio became a normal spinel ratio. In all such cases, however, the question of the distribution of the oxygen is largely speculative, and the really significant ratio is that between the metals and oxygen as a whole. There is no probability whatever that in the case of the St. Joseph du Lac crystals the titanium is present in the form of intermixed rutile. Owing to the exceptionally large proportion of manganese the mineral may be regarded as intermediate between magnetite proper and jacobsite.

The form {311}, which is rare in magnetite, occurs also in spinel and other members of the group, including gahnite, franklinite, and chromite. It is very well developed in some of the spinel crystals from Amity and Monroe in New York State.

Since writing the above, the writer has paid a hurried visit to St. Joseph du Lac in the hope of discovering the exact locality from which the magnetite crystals were obtained. The person who had found them having died some time before, no definite information as to the exact spot was available, but some of the farmers of the district had long known of a massive magnetic ore occurring in connexion with crystalline limestone on Lot 71 of the Parish of Oka. This spot was visited and specimens of the ore obtained. They are black in colour and streak, less brilliant in lustre than the crystals described above and not quite so strongly magnetic. The specific gravity of a fragment was found to be 4·61, and a partial analysis proved that the mineral in addition to being titaniferous also contains considerable quantities of manganese and magnesia, the percentages of these three constituents being as follows:—

Titanium dioxide ...	6·94
Manganous oxide ...	3·90
Magnesia	5·58

The composition, in a general way, therefore, is similar to that of the crystals, and it is not unlikely that a more careful examination of the region would result in the discovery of the original locality.

The late Professor Penfield of Yale having called the writer's attention to the fact that magnetite crystals from Magnet Cove, Arkansas, also exhibited the combination {111}, {311} (with rhombic-dodecahedral faces in some cases), specimens from this locality, which have been for many years in the mineral collection of McGill University, have been submitted to chemical analysis in order to ascertain whether similarity of form was accompanied by closely related composition. The results, however, show that in the latter respect they differ decidedly from the

Canadian mineral. The Magnet Cove crystals lack the freshness and brilliancy of those from St. Joseph du Lac. Their hardness is about 6, and specific gravity 4·558. Lustre, metallic. Colour black and streak blackish-brown. Attracted by the magnet, though not so strongly as in the case of the mineral already described. The fine powder was not completely soluble in hydrochloric acid at ordinary pressures, but it dissolved completely on heating with hydrochloric acid in a sealed tube for several hours at a temperature of 150° C. The ferrous oxide was determined by decomposing in this way and titrating with potassium dichromate. The mineral was also completely decomposed by fusion with sodium disulphate. Quantitative analysis gave the following results:—

		Atomic ratios of metals.	Atomic ratios of oxygen.
Ferric oxide ...	59·01	0·739	1·106
Titanium dioxide ...	2·40	0·030	0·060
Alumina	10·37	0·203	0·304
Ferrous oxide ...	16·82	0·234	0·233
Manganous oxide ...	2·10	0·030	0·029
Magnesia	9·47	0·237	0·236
	100·17	1·473	1·968

Here, again, the ratio for metals to oxygen is the normal one, as will be seen by dividing respectively by 3 and 4: $\frac{1·473}{3} = 0·491$, and $\frac{1·968}{4} = 0·492$.

If, as in the last case, the titanium be calculated as Ti_2O_3 the analysis becomes:—

		Atomic ratios of oxygen.	
Ferric oxide ...	61·41	1·151	1·500
Titanium sesquioxide	2·16	0·045	
Alumina	10·37	0·304	
Ferrous oxide ...	14·66	0·204	0·469
Manganous oxide ...	2·10	0·029	
Magnesia	9·47	0·236	
	100·17		

Here the ratio for $RO : R_2O_3$ is 1 : 3·19 instead of 1 : 3, possibly indicating alteration and change in the distribution of oxygen between the ferrous and ferric iron. The alumina was determined by difference in the usual way and not directly. The large proportion of this constituent and of the magnesia indicate a mineral intermediate in composition between magnetite and spinel[1].

A third specimen of crystallized magnetite has also been examined, in order to ascertain whether its composition was exceptional. It came from Digby, Annapolis County, Nova Scotia, where it is said to occur in veins in the trap-rocks of the region. The crystals are about three-quarters of an inch in diameter and composed of two forms $\{111\}$ and $\{110\}$. In no case has the trapezohedron been observed. The specific gravity was found to be 5·067, and chemical analysis gave the following results :—

		Atomic ratios of metals.	Atomic ratios of oxygen.
Ferric oxide	70·64	0·883	1·324
Titanium dioxide	0·24	0·003	0·006
Ferrous oxide	26·13	0·363	0·363
Manganous oxide	trace	—	—
Magnesia	2·97	0·074	0·074
Silica	0·03	—	—
	100·01	1·323	1·767

Dividing by 3 and 4, we have $\frac{1{\cdot}323}{3} = 0{\cdot}441$ and $\frac{1{\cdot}767}{4} = 0{\cdot}441$, exactly the normal ratio for magnetite. As in the former cases, no lime was found, but magnesia was again present, no doubt replacing ferrous oxide.

The analyses given in this paper do not establish any definite relationship between crystalline form and chemical composition in magnetite, but are offered as a contribution to the study of isomorphism as occurring in this important species.

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[1] Many years ago Professor G. A. Koenig examined nodular masses of magnetite from Magnet Cove and found them to be titaniferous and also to contain a little vanadium ($V_2O_3 = 0{\cdot}17$). It was the writer's intention to examine the crystals for vanadium, but owing to want of time this has not been done. For Professor Koenig's analysis see Proc. Acad. Nat. Sci. Philadelphia, 1877, p. 293.