THE RELATION BETWEEN CHEMICAL COMPOSITION AND REFRACTIVE INDEX IN THE BIOTITES

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Abstract

It is suggested that the relation between the chemical composition and the refractive index of the biotites should be considered from the point of view of the substitution of the metal atoms in the structural formula. The influence of Fe'', Fe''', Ti'''' and probably also Ti''', Mn'', Zr'''', Cr''', etc., upon the refractive index must be taken into account. This is illustrated by plotting the values of total iron against γ for a large number of biotites analyzed during recent years.

The present work is the outcome of an investigation of the biotite system to ascertain how far the refractive index of a biotite is an indication of its chemical composition. As a result of this investigation it is believed that previous workers on this subject have over-simplified the matter and that the relationship is a much more complicated one than has been supposed. In A. N. Winchell's (1) studies on the biotite system, the various biotites are calculated into molecules for the purpose of plotting their composition against their refractive indices. In these molecules Winchell omits lime, calculates ferric iron as ferrous, MnO and TiO_2 as FeO, F as OH, and Na_2O as equivalent to K_2O. After a study of the reliable analyses of biotite reported during recent years, the author believes that these complex minerals cannot be treated in such a simple manner but that the influence on the refractive index of several of the oxides present in the biotite must be taken into account.

It is suggested that the biotites should not be studied as molecules in relation to their refractive indices, but that we should consider them from the point of view of the substitution of the various atoms in the structural formula. We may first consider which atoms are likely to play a part in influencing the refractive index of the biotites. We may feel fairly certain that Fe'', Fe''' and Ti, when substituted for Mg in increasing amounts, are liable to raise the refractive index. The parts played by Mn, Zr and Cr are more difficult to assess owing to the fact that few biotites contain appreciable amounts of these elements or at least, especially in the case of the two latter, the amounts present are seldom sought after. The author disagrees with Winchell and Jakob in their statements that biotites do not contain lime, since many reliable analysts report small amounts of CaO. However, again in the case of Ca we have very little data from which to draw any conclusions as to its effect, if any, on the refractive index. As regards fluorine, the substitution of the hydroxyl group by this element very probably brings about a lowering of the refractive index, since, if we may argue from analogy, minerals which have a high fluorine content have a low refractive index (cf. fluorite and calcite, sellaite and magnesite).

There is the further probability that elements in a higher state of oxidation exert a greater influence on the refractive index than those at a lower state. Two of Larsen's (2) biotites from the San Juan Region, Colorado, may be compared with two analyzed by Tsuboi (3), as follows.

	Fe_2O_3	FeO	Total FeO	TiO_2	γ
Larsen	17.13	1.85	17.27	3.63	1.720
Larsen	17.71	0.53	16.46	4.19	1.723
Tsuboi	0.27	19.46	19.70	4.07	1.646
Tsuboi	0.76	18.39	21.48	4.68	1.658

Tsuboi's biotites contain approximately the same amount of TiO_2 and have higher total iron than Larsen's, yet their refractive indices are very much lower. Fluorine is not reported in Tsuboi's analyses, but from the summation the amount, if any, present cannot be very great. Kunitz (4) has shown that the oxidation of FeO in biotite raises the refractive index N_g, for example from 1.667 to 1.718 for a change from 6.51% Fe_2O_3 and 17.83% FeO in natural biotite to 24.89% Fe_2O_3 in the same mineral after heating. Kôzu and Yoshiki (5) have found that, on heating a biotite, the value of γ is raised from 1.655 to 1.703. Winchell (1*b*) believes that biotite as found contains some Fe_2O_3, but that those which "contain much Fe_2O_3 do so only as a result of oxidation of FeO in the crystal by natural processes." Whether this statement is correct or not, it is nevertheless a fact that petrologists, when dealing with biotites occurring in rocks, frequently find that they contain an appreciable amount of Fe_2O_3 and therefore the influence of this oxide on the refractive index must also be taken into account.

Titanium present in the form of Ti_2O_3 may have also a different effect upon the refractive index than when it is present as TiO_2. Jakob and Parga-Pondal (6) have found that biotites do contain Ti_2O_3, but, in the absence of sufficient data, the influence of this lower oxide on the refractive index cannot be ascertained at present.

Winchell states that "some variation between the indicated and actual optic properties must be expected" since his diagram makes no attempt to show the effect of the oxides of the various elements mentioned above on the optic properties. It is, however, believed that his method of representing the relation of chemical composition to optic properties in the biotites by means of a square diagram is wrong, since many of the titania-iron biotites have higher refractive indices than those given in the few reported analyses of siderophyllite. To illustrate this statement we may plot the refractive indices of several biotites against their iron content. The results will be seen in Fig. 1. The analyses used for this graph have been taken from the literature published during the last forty years. Some new analyses by the author are also included and also some hitherto unpublished analyses of biotites by Dr. S. R. Nockolds. In order to plot the iron content against refractive index (γ), the amount of Fe_2O_3 present must be neglected for the moment and the total iron plotted as FeO. The values of Fe_2O_3, FeO, total FeO, and TiO_2 for these biotites are given in Table 1, with also, in some cases the values of MnO and ZrO_2. Unless stated to the contrary, the values of MnO, ZrO_2 and Cr_2O_3 are less than 0.50%.

It can be seen from Fig. 1 that the biotites occupy two main fields. Those biotites which contain iron and titania are mainly grouped in field 1, while those containing iron, titania and MnO in excess of 0.50% lie in field 2. The points 12, 14, 15 and 16 are biotites whose analyses are given by von Eckermann, Jakob and Karvano and which contain rather less TiO_2 than most other biotites with the same amount of iron. Thus, the values of the refractive indices of these biotites are less than those of the biotites which occupy field 1. Points 1 and 41 represent biotites described by Nockolds and Chapman which contain more titania than other biotites with the same iron content, so that their refractive indices have higher values than the biotites of field 1. The position in Fig. 1 of Chapman's biotite (No. 42) cannot, however, be accounted for so easily. Grout's biotite No. 9 has a higher refractive index than would be expected from its iron and titania content, but contains 1.65% ZrO_2, which may account for its high refractive index. Prider's titaniferous-phlogopite (No. 59) will be seen to have a refractive index far ahead of other biotites with a higher iron content.

Nockolds' and Kranck's siderophyllites (Points 5 and 17), which contain very little or no titania, have much lower refractive indices than comparable iron-titania biotites in field 1. Nockolds' siderophyllite admittedly contains 2.03% fluorine, which might be expected to lower its refractive index. Fluorine is not reported in Kranck's siderophyllite, but, from the summation of the analysis, there can be very little if any there. On the other hand, Kranck's siderophyllite contains 9.12% Fe_2O_3 to 21.62% FeO which might be expected to raise the refractive index beyond that of a purely ferrous iron siderophyllite. It is very much to be regretted that the other analyses of siderophyllite from Pike's Peak (18) and Tanokamiyama, Japan (19) are not accompanied by statements of their refractive indices. Owing to the scantiness of the data it cannot definitely be established that siderophyllite has a lower refractive index

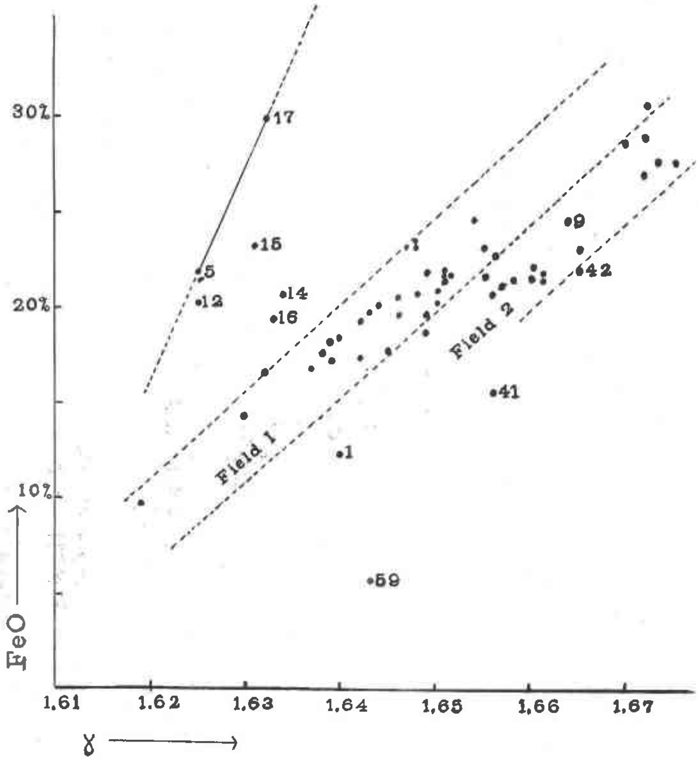

FIG. 1. Plot of total FeO against γ for the biotites. Numbers correspond to the biotites listed in Table 1.

Field 1 contains iron-titanium biotites.

Field 2 contains iron-titanium biotites which in most cases have more than 0.50% MnO.

than the titania-bearing biotites, but it would appear to be highly probable that this is the case.

Kunitz (20) has shown that the refractive index of biotite increases with increasing titania content when the amount of iron remains practically constant. He found that the relationship between increase in titania and increase in refractive index can be expressed by a straight line. From the graph given by Kunitz it appears that the amount by which the refractive index is raised for an increase of 1.0% TiO_2 is .01. This seems to be somewhat excessive as the following calculations will show.

It might be suppposed that if we knew the refractive index of a biotite containing iron, we could calculate from observed values the refractive index of a biotite containing the same amount of iron plus a certain

TABLE 1

No.	Author	γ	Fe_2O_3	FeO	Total FeO	TiO_2	
1	Nockolds	1.640	1.53	10.97	12.35	5.08	
2	Nockolds	1.645	3.41	14.86	17.93	3.54	
3	Nockolds	1.649	4.41	15.84	19.81	3.11	
4	Nockolds	1.655	7.04	16.91	23.25	3.12	
5	Nockolds[7]	1.625	0.79	20.98	21.69	0.21	
6	Grout[8]	1.630	7.44	7.72	14.42	1.67	
7	Grout[8]	1.640	4.05	14.80	18.44	2.23	
8	Grout[8]	1.655	3.03	23.23	25.96	3.32	
9	Grout[8]	1.664	1.14	23.75	24.78	2.73	$ZrO_2=1.65$
10	Grout[8]	1.648	8.63	12.96	20.72	4.34	
11	Grout[8]	1.639	.64	17.60	18.18	1.50	
12	Jakob[9]	1.625	5.03	15.84	20.37	1.95	
13	Jakob[9]	1.643	4.03	16.26	19.89	3.16	
14	Jakob[9]	1.634	4.08	16.85	20.52	2.71	
15	von Eckermann[10]	1.631	2.01	21.54	23.35	2.74	
16	Karvano[11]	1.633	3.28	16.38	19.33	2.45	
17	Kranck[12]	1.632	9.12	21.62	29.83	tr	
18	Deer[13]	1.656	3.22	19.94	22.84	3.48	
19	Deer[13]	1.652	2.48	19.07	21.30	3.63	
20	Deer[13]	1.650	2.90	18.30	20.91	3.99	
21	Tsuboi[14]	1.657	4.49	15.00	19.04	3.29	MnO=0.52
22	Tsuboi[14]	1.656	2.07	18.97	20.83	2.62	MnO=0.33
23	Tsuboi[14]	1.655	1.00	20.09	21.99	2.52	MnO=0.51
24	Tsuboi[14]	1.665	3.37	20.15	23.18	2.77	MnO=0.43
25	Tsuboi[14]	1.650	1.00	19.23	20.13	3.30	MnO=0.13
26	Tsuboi[15]	1.673	2.42	25.60	27.78	2.28	MnO=1.66
27	Tsuboi[15]	1.670	2.10	26.80	28.69	3.33	MnO=0.50
28	Tsuboi[15]	1.672	3.02	26.02	28.74	2.74	MnO=0.84
29	Tsuboi[3]	1.638	0.68	16.88	17.49	2.65	MnO=0.35
30	Tsuboi[3]	1.672	1.05	26.34	27.28	3.79	MnO=0.58
31	Tsuboi[3]	1.661	0.87	20.88	21.66	3.53	MnO=0.63
32	Tsuboi[3]	1.657	0.71	20.80	21.44	3.20	MnO=0.80
33	Tsuboi[3]	1.675	1.86	26.17	27.84	3.64	MnO=0.67
34	Tsuboi[3]	1.651	0.87	21.10	21.88	3.29	MnO=0.48
35	Tsuboi[3]	1.646	0.27	19.46	19.70	4.07	MnO=0.16
36	Tsuboi[3]	1.658	0.76	18.39	21.48	4.68	MnO=0.20
37	Tsuboi[3]	1.661	3.00	18.83	21.53	3.15	MnO=0.34
38	Tsuboi[3]	1.660	0.77	21.42	22.11	3.28	MnO=0.45
39	Tsuboi[3]	1.660	2.95	18.87	21.53	3.07	MnO=0.35
40	Tsuboi[3]	1.649	0.69	18.11	18.73	2.99	
41	Chapman[16]	1.656	nil	15.52	15.52	5.22	
42	Chapman[16]	1.665	2.33	20.88	22.98	4.17	
43	Chapman[16]	1.672	8.00	23.54	30.74	2.94	
44	Hall†	1.619	3.33	6.73	9.73	1.66	
45	Hall	1.632	2.59	14.40	16.73	2.95	
46	Hall†	1.637	2.79	14.26	16.77	3.90	
47	Hall†	1.639	2.78	14.84	17.34	2.20	
48	Hall	1.642	1.62	16.02	17.48	4.59	
49	Hall	1.642	2.73	17.08	19.54	3.74	
50	Hall	1.644	3.46	16.92	20.04	4.21	
51	Hall	1.646	1.42	19.27	20.55	4.99	
52	Hall†	1.647	3.16	20.34	23.18	4.01	
53	Hall	1.648	1.83	21.54	23.19	3.52	
54	Hall	1.648	2.39	20.99	23.14	4.31	
55	Hall	1.649	1.51	20.53	21.89	5.27	
56	Hall†	1.651	1.03	20.56	21.49	3.05	
57	Hall	1.651	2.60	19.17	21.51	3.68	
58	Hall†	1.654	3.05	22.06	24.81	5.40	
59	Prider[17]	1.643	2.18	3.73	5.69	8.97	

† Analyst: N. Sahlbom.

amount of titania. This may be expressed in the following way:—

Let x = the amount of Fe present.
y = the amount of Ti present
A = the influence of Fe on the refractive index (γ)
B = the influence of Ti on the refractive index (γ)

The refractive index may then be calculated from the equation

$$xA + yB = \gamma$$

We do not know what exactly is the influence of Fe (either as Fe'' or Fe''') on the refractive index, but we do know the refractive index of such a biotite as Nockolds' siderophyllite which contains practically no titania. This siderophyllite has the same amount of total FeO as biotite No. 55 (Table 1). The value of γ for the siderophyllite is 1.625 and for the biotite No. 55 is 1.649. No. 55 contains 5.27% TiO_2, so that the amount by which 1% of TiO_2 raises the refractive index is:—

$$\frac{1.649 - 1.625}{5.27} = .0046$$

The correctness of this value may be tested by calculating the refractive indices of various biotites given in Table 1. The line drawn between Nockolds' and Kranck's siderophyllites (Nos. 5 and 17) has been used for reading off the values of the refractive index for the various values of total FeO. The results of the calculations are given below:—

TABLE 2

Biotite	Total FeO	TiO_2	Observed γ	Calculated γ	Error
1	12.35	5.08	1.640	1.640	.000
2	17.93	3.54	1.645	1.636	−.009
7	18.44	2.23	1.640	1.632	−.008
14	20.52	2.71	1.634	1.636	+.002
15	23.35	2.74	1.631	1.640	+.009
16	19.33	2.45	1.633	1.634	+.001
19	21.30	3.63	1.652	1.640	−.012
29	17.49	2.65	1.638	1.634	−.004
32	21.44	3.20	1.657	1.638	−.019
46	16.77	3.90	1.637	1.639	+.002
48	17.48	4.59	1.642	1.643	+.001
54	23.14	4.31	1.648	1.647	−.001
57	21.51	3.68	1.651	1.642	−.009
58	24.81	5.40	1.654	1.652	−.002

It will be seen from Table 2 that in many cases the calculated value of γ agrees with the observed value of γ within small limits of error, but that at other times the discrepancy is somewhat large. If the value given by Kunitz had been taken, the error in most cases would have been still greater. It is understandable that there should be some differences between the calculated and observed values of γ since, in the first place, the data upon which the calculation is founded are rather scanty, and in the second place no allowance is made for the presence of Fe_2O_3, Ti_2O_3, MnO, etc., in the biotites. Grout (8) believes that many authors quote too low values for the refractive indices of their biotites. He himself was dealing with biotites several of which contained quite appreciable amounts of Fe_2O_3 and which, therefore, could not be compared with biotites from other areas containing less Fe_2O_3.

In conclusion it may be said that no sure information can be obtained as to the chemical composition of a biotite from its refractive index alone, since a biotite which is high in iron and low in titania may have the same refractive index as one which is low in iron and high in titania. Much work remains to be done upon the analyses of the end members of the biotite series together with careful determinations of their refractive indices.

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