MINERALOGICAL MAGAZINE, DECEMBER 1980, VOL. 43, PP. 985-8

The structural role of Fe^{3+} in biotites from the Euganean Hills, Italy

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SUMMARY. Plots of partition coefficient (mineral/matrix) against ionic radius of the elements in seventeen biotites from trachytes and rhyolites of the Euganean Hills do not show differences in the type of diagram between the biotites with tetrahedral sites completely filled by Si and Al, and those in which filling is only possible with the intervention of Fe^{3+} (or Ti^{4+}) since these sites are incompletely filled by Si and Al. This behaviour seems to exclude, for the latter, the presence of Fe^{3+} (or Ti^{4+}) in the tetrahedral site. Similar indications are given by structural analysis. The possibility of existence of $[(OH)_4]^{4-}$ groups or, more probably, vacancies in these sites is therefore suggested. The consequences that these results would have on the possibility of correct calculation of the crystallo-chemical formula are discussed.

PLOTTING the partition coefficients between phenocryst pyroxenes and groundmass, Onuma *et al.* (1968) produced diagrams which revealed the dominant role of phenocryst crystal structure in determining the partition coefficient patterns between the phenocryst and its lava matrix. The later data of Higuchi and Nagasawa (1969), Higuchi *et al.* (1970), Jensen (1973), Matsui *et al.* (1977), and De Pieri and Quareni (1978) confirmed the occurrence in these diagrams of families of subparallel curves, having approximately the same general slope and peaking in the same points, probably indicating the optimum ionic radius for a cation in a given structural site.

As regards the biotites, the data of Matsui *et al.* (1977) regarding major and trace elements indicate the presence of two peaks, one representing the site of the cations in sixfold coordination and the other the K site in approximately twelvefold coordination. The greater or lesser deviations from these curves, shown by Co^{2+} and Cr^{3+}, indicate the presence of effects due to the properties of the magmas.

De Pieri *et al.* (1978) have recently reported data on the chemistry of seventeen biotites from trachytes and alkali rhyolites from the Euganean Hills (northern Italy). The analytical results clearly show that there are notable differences between the compositions of the biotites of the trachytes and those of the alkali rhyolites. One of the most striking chemical features is that the trachyte biotites contain sufficient Al to fill the tetrahedral sites whereas the rhyolite biotites do not. The above-mentioned authors write: '. . . If these sites are filled, evidently another ion must enter such tetrahedral positions and . . . we have chosen Fe^{3+} instead of Ti for tetrahedral sites. . . .' Since data on groundmass and bulk rock compositions are available (Piccirillo *et al.*, 1979; De Pieri and Quareni, 1978) I have constructed partition coefficient (PC)-ionic radius (IR) diagrams for these biotites, with the aim of seeing whether the result is a similar pattern to that described by Matsui *et al.* (1977) and whether any suggestion on the filling of the tetrahedral sites may come from this method.

PC-IR diagrams. Partition coefficients calculated from the analytical data reported in the previously quoted works are listed in Table I. In samples 111, 119, 127, 71, 113, 115, 125, 52, and 38, Al was apportioned between the *T*- and *Y*-sites on the assumption that the *T*-sites were completely filled. Columns 3 and 4 of Table I show the partition coefficients for tetrahedral aluminium (Al^{IV}) and octahedral aluminium (Al^{VI}), thus divided. In the remaining samples, in which the total Al present was not sufficient to fill the eight *T*-sites, the Fe_2O_3 was similarly divided according to the data of the chemical formula between the tetrahedral and octahedral sites: columns 5 and 6 of Table I show the resulting partition coefficients for tetrahedral Fe^{3+} ($^{IV}Fe^{3+}$) and octahedral Fe^{3+} ($^{VI}Fe^{3+}$). Column 7 shows instead the partition coefficients calculated assuming that all the Fe^{3+} is in the *Y*-sites, independently of whether the *T*-site is filled or not. Since in fifteen of the seventeen samples studied, the quantity of Sr in the biotites was less than 5 ppm (the limit of detection of the method used for the determination of this element), the values of column 16 show the maximum values possible for the partition coefficients of strontium.

TABLE I. *Biotite/matrix partition coefficients of rocks of the Euganean Hills*

Sample	1 Si	2 Ti	3 ^{IV}Al	4 ^{VI}Al	5 ^{IV}Fe^{3+}	6 ^{VI}Fe^{3+}	7 *Fe^{3+}	8 Fe^{2+}	9 Mn	10 Mg	11 Ca	12 Ba	13 Na	14 K	15 Rb	16 Sr
111	0.51	16.0	0.99	0.06	—	—	6.01	13.9	6.8	51	0.23	6.30	0.19	1.82	1.54	< 0.08
119	0.54	12.5	0.88	0.02	—	—	3.19	16.7	6.5	63	0.11	7.66	0.18	1.61	1.81	< 0.03
127	0.53	15.4	0.88	0.01	—	—	3.88	38.8	13.5	85	0.49	6.23	0.19	1.61	1.44	< 0.03
71	0.56	11.8	0.88	0.01	—	—	1.82	17.2	4.5	87	0.20	7.17	0.18	1.80	1.99	0.06
113	0.58	11.5	0.82	0.04	—	—	0.82	16.6	4.5	34	0.10	7.20	0.18	1.72	1.47	< 0.02
115	0.56	9.8	0.87	0.01	—	—	2.38	8.8	2.4	38	0.13	6.26	0.17	1.71	1.90	0.07
116	0.54	12.9	0.89	—	0.04	1.30	1.33	11.1	5.2	49	0.12	14.40	0.19	1.63	1.46	< 0.10
125	0.54	13.6	0.84	0.03	—	—	0.80	29.4	10.3	68	0.23	13.34	0.17	1.59	1.21	< 0.12
145	0.54	15.5	0.87	—	1.44	0.80	2.24	18.4	10.0	260	0.22	8.02	0.21	1.68	1.55	< 0.06
52	0.53	15.1	0.86	0.02	—	—	3.08	27.8	38.0	86	0.50	5.65	0.18	1.71	1.56	< 0.02
114	0.50	25.1	0.97	—	0.33	4.12	4.44	49.7	15.0	194	0.95	17.82	0.17	1.88	1.80	< 0.19
126	0.52	20.7	0.93	—	1.88	6.84	8.73	21.5	19.3	330	0.04	20.70	0.18	1.72	2.50	< 0.16
51	0.51	20.8	0.89	—	2.20	5.26	7.47	30.8	13.2	461	0.14	14.75	0.18	1.62	2.83	< 0.28
39	0.50	21.9	0.89	—	2.91	6.56	9.48	28.2	21.2	120	0.14	14.48	0.18	1.70	3.75	< 0.71
60	0.50	22.7	0.96	—	1.66	9.48	11.14	29.3	34.5	331	0.13	11.81	0.16	1.91	4.79	< 0.26
124	0.49	23.6	0.99	—	2.30	2.96	5.25	41.9	31.3	220	0.08	9.73	0.21	1.92	3.62	< 0.45
38	0.50	28.0	0.99	0.02	—	—	12.59	43.4	41.0	342	0.08	14.57	0.18	1.70	1.88	< 1.00

* Partition coefficients calculated with total Fe^{3+} in sixfold coordination.

The values of Table I were plotted against the ionic radii of Whittaker and Muntus (1970). For the biotites in which Al was enough to fill the *Y*-sites, diagrams were obtained similar to those shown in fig. 1 for sample 119: it is possible to draw a family of subparallel curves, passing through the ions with the same valency, which show two peaks at 0.78 and 1.52 Å approximately, following a pattern identical to that illustrated by Jensen (1973) and Matsui *et al.* (1977), and corresponding to optimum ionic radius values for the octahedral and interlayer sites respectively.

For the biotites in which Fe^{3+} should intervene to fill the *T*-site, PC-IR diagrams like those in fig. 2 for sample 39 are obtained. The family of subparallel curves still shows the two peaks at the IR values shown previously, but the representative points of the PC of octahedral and tetrahedral Fe^{3+} (stars in fig. 2) do not fit the general trend described by the other elements. A curve passing through the representative points of the trivalent elements (dotted line in fig. 2), drawn subparallel to the curves described by the monovalent and bivalent elements, seems to indicate a new apex at a value of *c.*0.67 Å, which is not present in the diagrams of Jensen (1973) and Matsui *et al.* (1977), and which cannot be correlated with any site in the biotite structure. If instead the PC of Fe^{3+} is shown in these diagrams, presuming all the Fe^{3+} to be in the *Y*-site (column 7 of Table I), the trend of the curves returns to normality, in the sense that a curve subparallel to the others and without spurious apexes (dashed line of fig. 2) may be drawn through the representative points of the PC of the trivalent ions too.

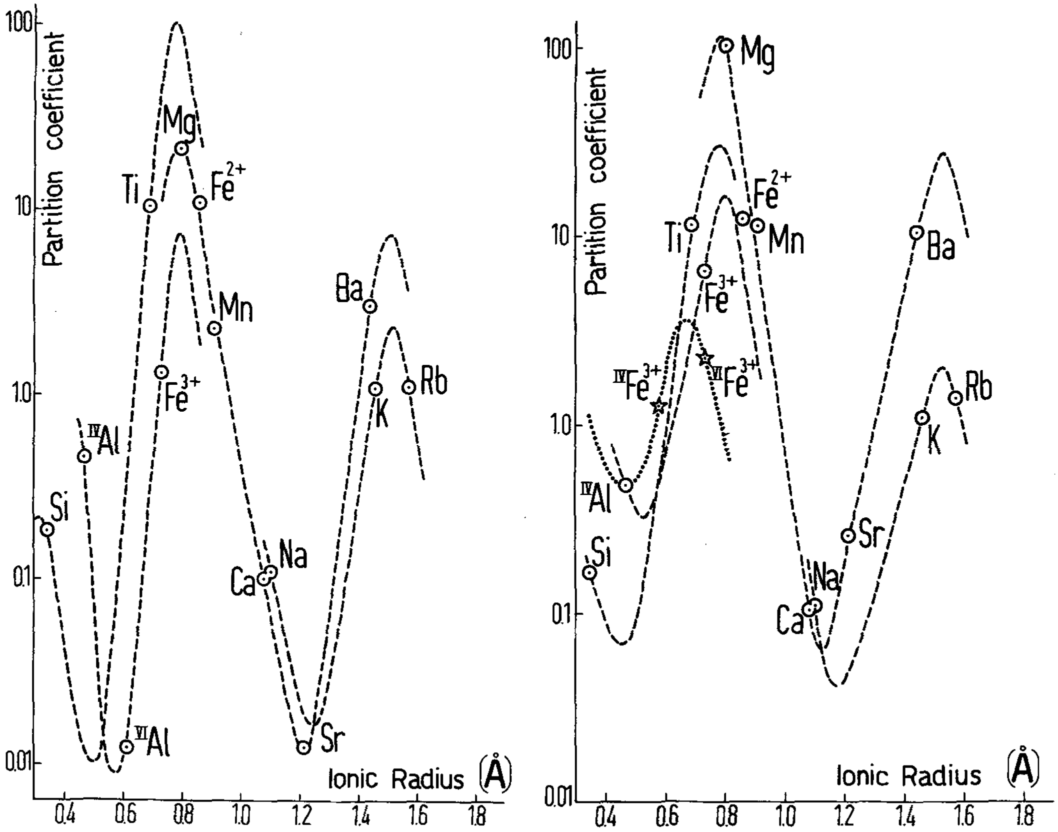
If it is assumed that Ti completes the occupancy of the eight *T*-sites and, if Ti^{4+} is apportioned between *T*- and *Y*-sites, we obtain partition coefficients for Ti^{4+} which, like those for Fe^{3+}, give rise to a spurious apex on the PC-IR diagram. The exact position of this apex cannot be determined because of the lack in the literature of the ionic radius of Ti^{4+} with tetrahedral coordination.

These results suggest that neither Fe^{3+} nor Ti^{4+} occupy those *T*-sites that are incompletely filled by Si and Al. If the indications obtained from the PC-IR diagrams are valid, we must conclude that vacancies exist in the *T*-sites of the structure of these biotites; otherwise substitutions of the $Si^{4+} \rightleftharpoons 4H^+$ type, i.e. the presence of $[(OH)]^{4-}$ groups which replace $[SiO_4]^{4-}$ tetrahedra, must be supposed; the last possibility, however, seems rather unlikely, owing to the notable deficiency of (OH) in most of these biotites.

Structural analysis. An attempt was made to define the true population of the *T*-sites by means of careful structural analysis. A 1*M* polymorph from sample 39 (De Pieri *et al.*, 1978) was selected for study, and the same crystal was analysed by electron microprobe (Table II).

The details and results of structural refinement (Mazzi, in prep.) are available upon request from the author. The results were inconclusive, but tended to support the hypothesis that Fe^{3+} and Ti^{4+} do not enter the *T*-site and that there are some vacancies in this site.

Moreover, from the bond length *T*–O no evidence was found for the presence of ions larger than Al^{3+} (like Fe^{3+} or Ti^{4+}), an occupancy (0.29 Al, 0.71 Si) in the *T*-site being estimated from the



FIGS. 1 and 2. FIG. 1 (*left*). Partition coefficient-ionic radius diagram for biotite 119. FIG. 2 (*right*). Similar diagram for biotite 39. The stars correspond to the PC of Fe^{3+} distributed between *T*- and *Y*-sites.

average bond length [1.654(2) Å]. (Estimated standard errors for interatomic distances are in parentheses and refer to the last decimal place.) The population 0.69 Si, 0.28 Al, 0.03 Fe^{3+} of the *T*-site, for instance, should increase the bond length *T*–O to about 1.661 Å. Lastly, no excesses or defects of electrons for the *T*-sites were observed in the difference-Fourier map. On the other hand, no indications could be obtained on the population of *Y*-sites M_1 and M_2 (and thus indirectly on the *T*-sites), both owing to the high number of substitutions they contain and owing to the presence of octahedral vacancies and the impossibility of splitting them between M_1 and M_2. The average bond lengths M_1–O and M_2–O are respectively 2.083(2) Å and 2.068(2) Å, while an average bond length *K*–O of 3.141(2) Å is obtained for the inter-layer site.

Conclusions. The following concluding comments can be drawn from the results shown here:

1. Within the limits of validity for this method of study, the partition coefficients *v.* ionic radii diagrams suggest the absence of both Fe^{3+} and Ti^{4+} in those *T*-sites that are incompletely populated by Si and Al in certain biotites from the Euganean Hills. If this is true, then vacancies exist in the *T*-sites in the structure of these biotites; an alternative hypothesis is less likely, viz. substitution of the $Si^{4+} \rightleftharpoons 4H^+$ type, i.e. the presence of $[(OH)]^{4-}$ groups replacing $[SiO_4]^{4-}$ tetrahedra.

2. Structural analysis cannot unequivocally establish whether the filling of the *T*-sites, incompletely populated by Si and Al, is due to Fe^{3+} (or Ti^{4+}), or $4H^+$, or whether it is not completed, thus causing tetrahedral vacancies. However, strong doubts arise on the possibility of the filling of the *T*-sites by Fe^{3+} (or Ti^{4+}) both through analysis of the scattering factors and of the tetrahedral bond lengths; no sure indication on the existence of tetrahedral vacancies was obtained.

3. If the indications of the PC-IR diagrams are valid, we must conclude that Fe^{3+} (or Ti^{4+}) is lacking in the *T*-sites. This result is relevant to the presentation of the structural formulae of biotites, since it casts doubt on the customary procedure

TABLE II. *Wet-chemical and electron-microprobe analyses of biotite 39*

	1	2
SiO_2	37.09	35.5
TiO_2	4.82	4.06
Al_2O_3	12.93	11.5
Fe_2O_3	7.10	—
FeO	10.73	*17.9
MnO	1.06	1.07
MgO	13.26	15.2
CaO	0.04	0.02
BaO	0.14	n.d.
Na_2O	0.83	0.71
K_2O	8.56	8.77
Rb_2O	0.08	n.d.
H_2O^+	4.09	—
P_2O_5	0.09	n.d.
Total	100.82	94.73

* Total Fe as FeO.
n.d. = not determined.

[1] Wet-chemical analysis (from De Pieri *et al.*, 1978).

[2] Electron-microprobe analysis (mean of six different points).

of filling the eight tetrahedral sites with Fe^{3+} and/or Ti^{4+} if there is insufficient Si^{4+} and Al^{3+}.

The doubt thus arises that there may be vacancies in the *T*-sites even in those biotites in which the analytical results show quantities of Al sufficient for this requirement. It may then be suggested that structural analysis is necessary for the correct partition of Al between the *T*- and *Y*-sites. The quantity of Al^{3+} lodged in the *T*-site may be a function more of the temperature than of the vacancies left unfilled by Si^{4+}.

Acknowledgements. Structural analysis was carried out by Professor F. Mazzi, to whom my warmest thanks go. I am also indebted to him for his critical reading of the manuscript. I also owe particular thanks to Professor E. M. Piccirillo for his helpful suggestions and discussions. This work was carried out with the financial support of the Comitato Nazionale delle Ricerche (C.T. 78.00322.05).

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[*Manuscript received 9 November 1979;
revised 17 March 1980*]