The Canadian Mineralogist
Vol. 37, pp. 1423-1429 (1999)

THE OXIDATION RATIO OF IRON IN COEXISTING BIOTITE AND HORNBLENDE FROM GRANITIC AND METAMORPHIC ROCKS: THE ROLE OF P, T AND $f(O_2)$

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ABSTRACT

Previously published and new data on the composition of coexisting biotite and hornblende from granitic and metamorphic rocks show that the degree of iron oxidation, R [= $Fe^{3+}/(Fe^{2+} + Fe^{3+})$], is different in these two minerals; the R of hornblende is greater. Granulite-facies minerals have the greatest difference in R, whereas in granitic rocks, those minerals show the least difference. The oxidation of biotite and hornblende under high-level conditions is accompanied by the crystallization of magnetite, and newly formed oxidized mafic minerals have a lower Fe/(Fe + Mg) and R than the original ones. Under mesozonal and catazonal conditions, the increase in pressure prevents the formation of magnetite, and oxidation is accompanied by a significant increase in R; these changes in the chemical composition of hornblende are supplemented by an increase in Al. Since the Al content of hornblende is known to be an indicator of pressure, such a correlation of R and Fe^{3+} content with aluminum content points to an increase of these parameters with a rise of pressure.

Keywords: biotite, hornblende, oxidation ratio, granitic rocks, metamorphic rocks, epizonal plutons, mesozonal plutons, catazonal plutons.

SOMMAIRE

Les données nouvelles et celles tirée de la littérature portant sur la composition de la biotite et celle de la hornblende coexistante des roches granitiques et métamorphiques montrent que le degré d'oxydation du fer, R [= $Fe^{3+}/(Fe^{2+} + Fe^{3+})$], est différent dans ces deux minéraux. La valeur de R est supérieure dans la hornblende. Les deux minéraux au faciès granulite font preuve de la plus grande différence en R, tandis que dans les roches granitiques, ces minéraux en montrent moins. Le taux d'oxydation de la biotite et de la hornblende dans un milieu épizonal est accompagné d'une cristallisation de la magnétite, et les minéraux mafiques oxydés néoformés possèdent un rapport Fe/(Fe + Mg) et un R plus faibles que les minéraux originaux. Dans un milieu mésozonal ou catazonal, l'augmentation de la pression entrave la formation de la magnétite, et l'oxydation est accompagnée d'une augmentation sensible de R; à ces changements de la composition chimique de la hornblende s'ajoute une augmentation dans sa teneur en Al. La corrélation entre la teneur en Al de la hornblende et la pression étant bien établie, une telle corrélation de R et de la teneur en Fe^{3+} avec la teneur en aluminium fait penser qu'il devrait y avoir une augmentation dans ces paramètres avec la pression.

(Traduit par la Rédaction)

Mots-clés: biotite, hornblende, degré d'oxydation, roches granitiques, roches métamorphiques, plutons épizonaux, plutons mésozonaux, plutons catazonaux.

INTRODUCTION

The distribution of Fe^{3+} and Fe^{2+} among minerals of igneous rocks is the key to solving such petrological problems as the redox state of the Earth's crust and the upper mantle (*e.g.*, Canil & O'Neil 1996, Wones & Gilbert 1982, Speer 1984), and the characterization of magmatic series in terms of their composition and degree of evolution (Lalonde & Bernard 1993). For instance, the differences between tholeiitic and calc-alkaline series, as was found long ago, depend on $P(H_2O)$ and $f(O_2)$. Accordingly, the rocks of both series are distinguished by the behavior of iron. The different partitioning of Fe among silicates and oxides in granitic rocks is controlled by $f(O_2)$ and explains many peculiarities of I- and S-type granites (Chappell & White 1974), the distinction of granites of the magnetite and ilmenite series (Ishihara 1977), and granitic rocks of the

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magnetite-free and magnetite-bearing facies (Fershtater *et al.* 1978, Fershtater 1987).

The aim of this paper is to document the main features of Fe^{3+} and Fe^{2+} distribution between coexisting biotite and hornblende in granitic and metamorphic rocks in order to assess the possibilities for geobarometry and estimates of oxygen fugacity.

BACKGROUND INFORMATION

In granitic rocks of the magnetite facies, more than 80% of the Fe is concentrated in magnetite, whereas in the magnetite-free facies, the mafic silicates contain all of the Fe. Accordingly, hornblende and biotite from granitic rocks of the magnetite facies have a relatively low Fe/(Fe + Mg) value, which is constant and independent of rock composition. In contrast, in rocks of the magnetite-free facies, this value in biotite and hornblende is higher, and increases with increasing SiO_2 content. Compositions of mafic minerals of the magnetite-free facies thus are similar to primary ones, whereas in rocks of the magnetite facies, these minerals form as a result of an oxidation stage of rock evolution, being accompanied by "exsolution" in the magnetite. The main reaction that connects the mineral assemblages of magnetite-free and magnetite facies is as follows:

$$\text{Fe-rich mafic mineral} + O_2 \rightarrow \text{Mg-rich mafic mineral} + \text{Mgt} \qquad (1)$$

in which the mafic mineral is amphibole or biotite.

The left-hand side of this reaction represents the minerals from magnetite-free facies, whereas the right side represents the associations of the magnetite facies.

As is well known, the TiO_2 content of magnetite in granites is low (usually 1–3% TiO_2), and corresponds to temperatures of 400°–600°C, according to the magnetite–ilmenite geothermometer (Ghiorso & Sack 1991). Such temperatures correspond to a postmagmatic stage and show that reaction (1) predominantly takes place in the solid state.

The ratio R [$Fe^{3+}/(Fe^{2+} + Fe^{3+})$] in coexisting biotite and hornblende from granitic and metamorphic rocks depends on the physical and chemical conditions of equilibration at the magmatic and postmagmatic stages, as well as on the crystallochemical features of the minerals. Determining the relative influence of these factors is important to reconstruct the conditions of formation of the rocks chosen for a study of the compositions of the coexisting biotite and hornblende.

SAMPLES AND METHODS

In addition to our own compositional data for 30 pairs of coexisting hornblende and biotite in granitic and metamorphic rocks from the Uralian Paleozoic orogen (Votyakov *et al.* 1998), previously published results for approximately 100 pairs of these minerals from all over the world have been used in this work. Included are minerals from granitic rocks from the following massifs:

(1) High-level (epizonal) massifs: Magnitogorsk, Karabulak, Khabarninsk (the Urals), Guadelupe, California (Best & Mercy 1967), Aregos, northern Portugal (de Albuquerque 1973, 1974), Ben Nevis, Scotland, U.K. (Haslam 1968), and the early series of New England batholiths, Australia (Wilkinson *et al.* 1964).

(2) Middle-level (mesozonal) massifs: Stepninsk, Novoburanovsk, Krasninsk, Vladimirsk, Gorodischensk (the Urals), Sierra Nevada (Dodge *et al.* 1968, 1969), Southern California (Larsen & Draisin 1950), granite bodies near the San Andreas fault (Dodge & Ross 1971), Adamants, British Columbia (Fox 1969), and Kitakami, Japan (Kanisawa 1972).

(3) Deep-level (catazonal) massifs and surrounding gneisses and amphibolites: Mursinsk, Verkhisetsk (the Urals), Ukrainian and Aldan shields (Kalinichenko *et al.* 1988, Siroshtan *et al.* 1965, Kitsul *et al.* 1983), the charnockitic rocks of Kondapalli, India (Leelanandam 1970), and amphibolites and granulites from Western Australia (Stephenson 1977).

In order to get some idea of how much Fe^{2+} and Fe^{3+} is present in coexisting biotite and hornblende, we had to consider results of wet-chemical analyses provided in the "pre-microprobe" literature. Because of this, we relied predominantly on older results. The composition of the Ural minerals was determined by Mössbauer spectroscopy and wet-chemical analyses, in cases in combination with X-ray-fluorescence analysis. The amounts and ratio of Fe^{3+} and Fe^{2+} determined by wet-chemical analyses and by Mössbauer spectroscopy (Votyakov *et al.* 1998) are in good agreement.

FEATURES OF Fe^{3+} INCORPORATION IN BIOTITE AND HORNBLENDE FROM GRANITIC ROCKS: CONSTRAINTS ON EXISTING THEORETICAL AND EXPERIMENTAL DATA

The biotite under consideration, in terms of the coordinates determining its nomenclature (Rieder *et al.* 1998), has a ratio 100Fe/(Fe + Mg) in the range 20–60, and the proportion of ^{IV}Al is in the range 1.0–1.35 atoms per formula unit (*apfu*). The Fe^{3+} ion in this mineral is known to be largely in octahedral coordination, with rare exceptions where Si and Al abundances in the rock are insufficient to fill the tetrahedral sites in biotite and thus require $^{IV}Fe^{3+}$ (Lalonde *et al.* 1996, Dawson & Smith 1977, Delaney *et al.* 1980). Fe^{3+} forms by the dehydrogenation reaction (Wones & Gilbert 1982, Guidotti 1984, Tikhomirova *et al.* 1989):

$$Fe^{2+} + OH^- = Fe^{3+} + O^{2-} + \tfrac{1}{2} H_2 \qquad (2)$$

According to results of a Mössbauer study of biotite from the Ural granitic rocks (Votyakov *et al.* 1994), the Fe^{3+} content increases predominantly owing to the oxidation of Fe^{2+} ions in *cis* positions in the mineral structure. In this case, the excess charge of Fe^{3+} is compensated by an H^+ vacancy near the Fe^{3+} in accordance with reaction (2). Alternatively, Fe^{3+} ions may follow ^{VI}Al ions according to the following "ferritschermakitic" substitution (Dymek 1983):

$$^{VI}Fe^{2+} + {}^{IV}Si = {}^{VI}Fe^{3+} + {}^{IV}Al \qquad (3)$$

A positive correlation between the Fe^{3+} and ^{IV}Al or $^{IV}Al/^{VI}Al$ should be observed in the latter case. There is no such correlation in the biotite samples under consideration, however, which confirms the view of Guidotti (1984) regarding the absence of a substitution in biotite according to mechanism (3), since there is sufficient ^{VI}Al to compensate for "excess" ^{IV}Al.

In hornblende, Fe^{3+} occurs in octahedral coordination also. The dehydrogenation reaction (2) results in an oxyamphibole component; it is a well-known and experimentally confirmed mechanism of oxidation in amphibole (Clowe *et al.* 1988, Phillips *et al.* 1988). As shown for the hornblende samples from the Ural granitic rocks (Votyakov *et al.* 1998), Fe^{3+} content rises predominantly owing to the oxidation of Fe^{2+} ions in *M*1 positions according to reaction (2); in this case, the excess charge is compensated by vacancy at the H site, *i.e.*, O-for-OH substitution.

Given the diversity of mineral compositions, a number of charge-compensation mechanisms have been proposed in the past (Hawthorne 1981). In addition to the mechanism mentioned, from the theoretical point of view, substitution involving Al also may occur (Clowe *et al.* 1988), in one of two variants: (i) a tschermakitic type, in which Fe^{3+} ions, as well as ^{VI}Al, replace divalent cations, compensated by the Al-for-Si substitution in the tetrahedral position, and (ii) a glaucophane type, where the replacement of the divalent cation by Fe^{3+} or Al is compensated by the Na–for–Ca substitution.

R.K. Popp and his coworkers (Clowe *et al.* 1988, Phillips *et al.* 1988, 1989, Popp *et al.* 1994) have documented the mechanism of Al incorporation along with the formation of an oxyamphibole component for calcic and subcalcic amphiboles in experiments on amphibole oxidation under different buffers. They concluded that the extent to which each of the two mechanisms determines the Fe^{3+} content of any natural amphibole is unknown, but both processes are involved in natural samples.

In our collection of hornblende compositions, the occurrence of the above-mentioned Al incorporation (Clowe *et al.* 1988) is confirmed by the correlation of Fe^{3+} and ^{IV}Al, as well as by the correlation of Fe^{3+} and the sum of alkalis in all types of rocks except charnockites and granulites (Fig. 1).

Thus, the available data make it possible to suggest that dehydrogenation is the main mechanism of oxidation of iron in biotite, whereas in amphibole, it is supplemented by the heterovalent substitution $^{VI}Fe^{2+} \rightarrow {}^{VI}Fe^{3+}$), in which case the excess charge due to the Fe^{3+} ions is compensated by the incorporation of alkalis and ^{IV}Al.

THE DISTRIBUTION OF Fe^{3+} AND Fe^{2+} IN COEXISTING BIOTITE AND HORNBLENDE

The most important geochemical feature of Fe ions in coexisting hornblende and biotite is the higher degree of oxidation of Fe in hornblende than in biotite, regardless of the conditions of formation of the granitic rocks and gneisses (Borodina & Votyakov 1996). The

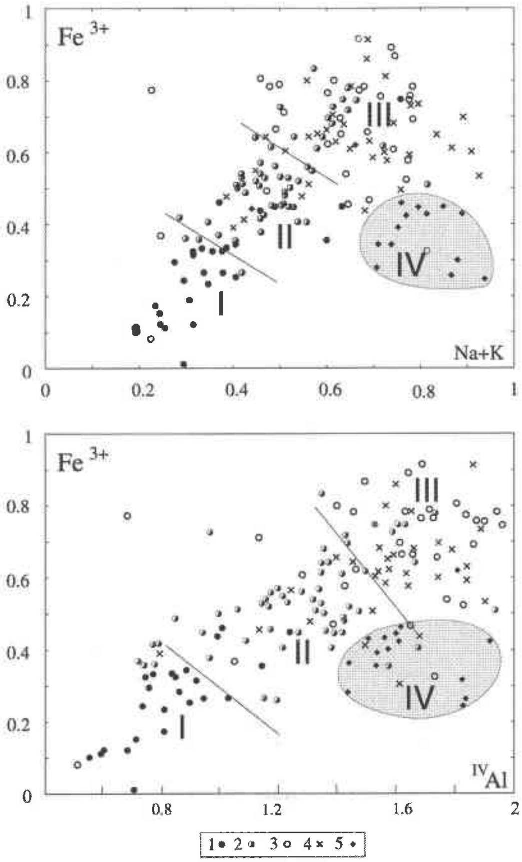

FIG. 1. Fe^{3+} – (Na + K) and Fe^{3+} – ^{IV}Al diagrams for hornblende from granitic (1–3) and metamorphic rocks (4, 5). 1. Rocks of high-level (epizonal) granitic plutons (field I), belonging to the magnetite facies. 2. Rocks of middle-level (mesozonal) granitic plutons, transitional between magnetite and magnetite-free facies (field II). 3. Rocks of deep-level (catazonal) granitic plutons, belonging to magnetite-free facies (field III). 4. Migmatites and metamorphic rocks of amphibolite grade (field III). 5. Metamorphic rocks of granulite grade (field IV).

relation of R_{Bt} to R_{Hbl} is shown in Figure 2; almost all the points lie in the field indicative of the higher degree of oxidation of hornblende. The diagram can be divided into three fields. Field 1 consists mainly of minerals from epizonal and mesozonal granitic plutons, field 2 includes predominantly minerals from metamorphic rocks of the amphibolite facies and associated catazonal granitic plutons, and field 3 contains mostly metamorphic rocks of the granulite facies. In fields 1 and 2, a correlation is observed between the degree of Fe oxidation R in coexisting hornblende and biotite. The difference between R_{Hbl} and R_{Bt} is insignificant in field 1, much higher in field 2, and reaches a maximum in field 3, where biotite has a minimal degree of oxidation.

Hornblende samples from different geological units differ in their Na, K and Al contents, which is of significance for the state of Fe in hornblende. Hornblende in epizonal granitic plutons contains the lowest amount of alkalis, ^{IV}Al, ^{VI}Al and Fe^{3+}, and has the lowest degree of Fe oxidation (Figs. 1, 2). Hornblende in catazonal granitic plutons, derived from H_2O-rich magmas, is characterized by the highest values of these parameters, whereas hornblende from mesozonal granitic plutons occupies an intermediate position.

Hornblende from metamorphic rocks of the amphibolite facies has a variable composition; however, it lies mainly in the same field as hornblende in catazonal granitic plutons. Hornblende in granulites and charnockites stands out in having the lowest R values, whereas its trend on the $^{IV}Al – (Na + K)$ diagram is similar to that of the other hornblende samples (Fig. 1).

Epizonal granitic rocks mainly belong to the magnetite facies. Magnetite appears as a result of oxidation of primary hornblende and biotite at 400-600°C in the solid state. The mafic silicates from such granitic rocks have lower values of $Fe/(Fe + Mg)$ and $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ in comparison with catazonal and mesozonal granitic plutons formed under conditions of the magnetite-free facies (Figs. 2, 3). Magnetite does not form during cooling and oxidation of hornblende and biotite from these rocks; the R of the silicates increases, whereas the $Fe/(Fe + Mg)$ value remains at the same level, imposed during magmatic crystallization.

T–P–$f(O_2)$ Conditions of Biotite and Hornblende Oxidation

We have summarized the available experimental data on biotite and hornblende stability, and shown the relationships between coexisting minerals in $f(O_2)$ – T coordinates (Fig. 4); not all data are known with the same degree of certainty. The stability fields of the minerals in as a function of $Fe/(Fe + Mg)$ are shown on the basis of experimental data. The values of hornblende oxidation are calculated using the data of Popp *et al.* (1994), whereas the same values for biotite are based on the trends of "buffered" compositions of biotite trends in the $Fe^{3+} – Fe^{2+} – Mg$ system (Wones & Eugster 1965), which the authors themselves called an "educated guess". These assumptions are not consistent with some experimental work (Tikhomirova *et al.* 1989), possibly because the latter did not take the presence or absence of magnetite into account, but they are confirmed by

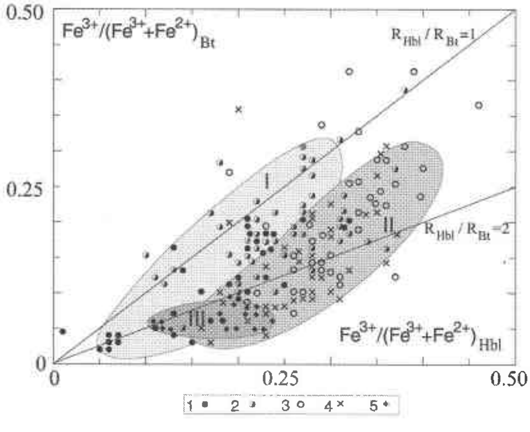

FIG. 2. Values of $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ in coexisting hornblende and biotite in granitic and metamorphic rocks. Groups 1–5 are the same as in Figure 1. The shaded fields correspond to the minerals of epizonal and mesozonal granitic plutons (I), catazonal granitic rocks and related metamorphic rocks of amphibolite grade (II), and metamorphic rocks of granulite grade (III).

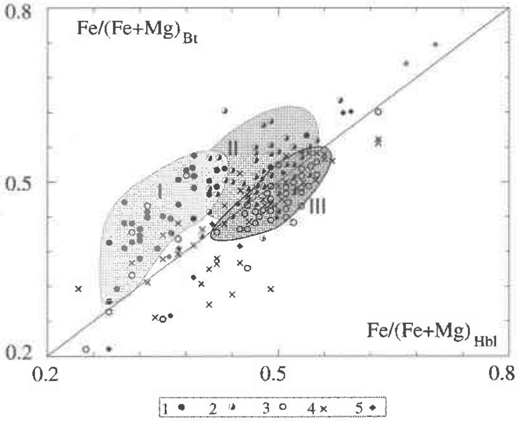

FIG. 3. Values of $Fe/(Fe + Mg)$ in coexisting hornblende and biotite in granitic and metamorphic rocks. Groups 1–5 are the same as in Figure 1. Shaded fields represent the minerals from epizonal (I), mesozonal (II) and catazonal (III) granitic plutons.

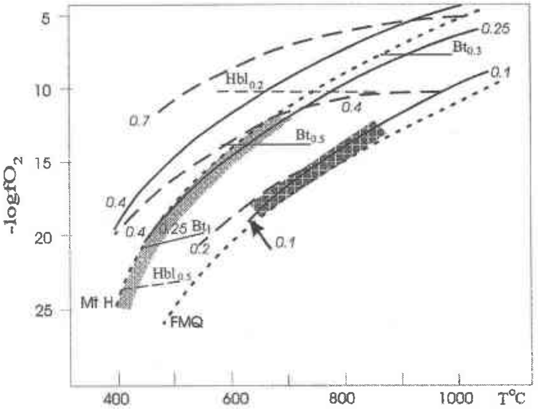

FIG. 4. Plot of $f(O_2)$ *versus* T showing coexisting hornblende and biotite from granitic and metamorphic rocks. Thin lines represent Fe/(Fe + Mg) values (solid lines for Bt, dashed lines for Hbl); thick lines of the same types correspond to $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ values of Bt and Hbl (Wones & Eugster 1965, Popp *et al.* 1977, 1994). The figures near the symbols of minerals represent the Fe/(Fe + Mg) values, whereas $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ values are shown in italics near the corresponding lines. Fe/(Fe + Mg) lines fix the upper limit of hornblende and biotite stability for a given Fe/(Fe + Mg) value. Note the lower level of hornblende stability in comparison with biotite. Hornblende with Fe/(Fe + Mg) = 0.5 starts to oxidize at $-\log f(O_2)$ between 24 and 23, whereas biotite with the same Fe/(Fe + Mg) value is stable up to $-\log f(O_2) = 15$. The $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ lines for biotite were estimated according to Wones & Eugster (1965), and the same lines for hornblende were estimated according to Popp *et al.* (1994). Short-dashed lines labeled as MtH and FMQ represent the magnetite – hematite and fayalite – magnetite - quartz equilibria. The shaded area is the field of the magnetite facies, and the patterned area is the field of primary crystallization of titanian magnetite.

the data on natural biotite (Speer 1984) and the results of the present study. In particular, as Figure 4 shows, there is a large range of $f(O_2)$ – T values over which the degree of oxidation of the iron in hornblende must be greater than that in biotite. An inverse ratio is possible only in the low-temperature region. In spite of the relative temperature and $f(O_2)$ values inferred from the diagram, these help to qualitatively evaluate mineral-equilibrium conditions.

The diagram also shows that the initial Fe^{3+}/Fe value of the hornblende and biotite must be very low. The compositions of magnetite and the mafic silicates such as biotite and hornblende in granitic rocks are considered to have equilibrated in the solid state after solidification of magmatic rocks. The composition of the newly formed silicates depends on the fugacity of oxygen. The epizonal plutons belong to the magnetite facies; the oxidation of both mafic silicates in these plutons at a low pressure is usually accompanied by precipitation of magnetite, and so R_{Hbl} and R_{Bi} as well as the Fe/(Fe + Mg) value in these cases is relatively low. The adjustment can be illustrated for the *Y* site of hornblende by the reaction:

$$(Fe^{3+}_{0.5}Fe^{2+}_{2.5}Mg_2) + 0.2O_2 =$$
$$(Fe^{3+}_{0.3}Fe^{2+}_{2.4}Mg_2\square_{0.3}) + 0.1(Fe^{3+}_2Fe^{2+}O_4) \qquad (4),$$

where $\square$ represents a vacancy.

As Fe^{3+}, Fe^{2+} and Mg cations occupy an octahedral position in which their sum equals 5, their deficit in the right part of the equation is adjusted according to one of the above-mentioned mechanisms of heterovalent substitution. As is apparent from reaction (4), newly formed hornblende coexisting with low-Ti, low-temperature magnetite is characterized by a lower degree of oxidation in comparison with primary hornblende (since the Fe^{3+}/Fe value of magnetite, 0.7, is always higher than that of amphibole) and by a lower Fe/(Fe + Mg).

The mesozonal and catazonal granitic rocks belong to the magnetite-free facies. The increase in H_2O pressure expands the fields of stability of hornblende and biotite in these rocks; in the case of their oxidation, the rise of $P(H_2O)$ prevents the formation of magnetite (Fershtater *et al.* 1978).

The Fe/(Fe + Mg) and *R* values of hornblende and biotite from these rocks are higher than in the epizonal plutons. These values increase gradually, passing from low-$P(H_2O)$ conditions in the epizonal plutons to higher-$P(H_2O)$ conditions in the mesozonal and catazonal plutons (Figs. 2, 3, 5). In the case of granulite-facies metamorphic rocks, where a small amount of H_2O is present, the data points of hornblende lie off the main trend (field IV in Fig. 5). Their position confirms the important role of $P(H_2O)$ conditions in the oxidation of hornblende.

The well-known fact that the Al content in hornblende correlates with pressure at the time of its formation is the basis of some effective geobarometers (Hammarstrom & Zen 1986, Fershtater 1990). Fe^{3+} contents and *R* values in turn are directly proportional to Al contents, although these parameters vary significantly within every pressure zone (Fig. 5). The rise of pressure thus is recorded not only in the Al content but also in the Fe^{3+} content and redox state of the hornblende; all these parameters may serve as indicators of the pressure of crystallization and can be used for a semi-quantitative determination of pressure [mostly $P(H_2O)$] during the oxidation of hornblende.

ACKNOWLEDGEMENTS

We are indebted to Drs. André E. Lalonde, University of Ottawa, and Catherine McCammon, University of Bayreuth, for their helpful reviews of the manuscript, and to Robert F. Martin for his valuable comments and suggestions. This work was supported by the Russian Fundamental Science Foundation (grant 98–05–64826).

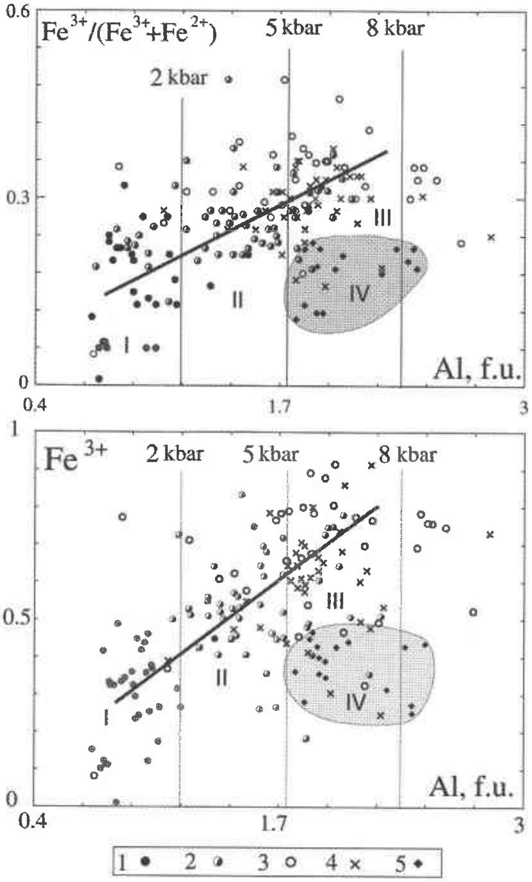

FIG. 5. Plot of $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ and Fe^{3+} *versus* Al for hornblende from granitic and metamorphic rocks. Groups 1–5 are the same as in Figure 1. Isobars are those of Hammarstrom & Zen (1986).

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Received February 2, 1998, revised manuscript accepted November 29, 1999.