

MODELS OF ORDER AND IRON-FLUORINE AVOIDANCE IN BIOTITE

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ABSTRACT

Simple models are presented concerning the relationship between order of cations on octahedrally coordinated sites and Fe-F avoidance in biotite. The models assume that F is coordinated only to groups of three Mg cations and that Mg and Fe are the only occupants of the octahedrally coordinated sites. It is predicted that biotite may have cation disorder on these sites only if the F content is below a maximum level (X_F^{\max}) given by $X_F^{\max} = X_{Mg}^3$. Biotite with F greater than X_F^{\max} must have "clusters" (Mg_3 groups in excess of the number expected for a random distribution of cations) if it is to comply with Fe-F avoidance. This model of cluster formation is consistent with the results of spectroscopic studies from the literature, although there are complications arising from the substitution of cations other than Fe and Mg in the octahedra. Long-range order of Fe on $M(2)$ is predicted to be compatible with Fe-F avoidance in a composition range that is closely similar to that for disorder, but long-range order of Fe on $M(1)$ is predicted to be compatible with Fe-F avoidance only in a more restricted range of composition. It is postulated that cluster formation is dependent on cooling history. This is discussed in the context of data for biotite from the Klokken intrusion in South Greenland. The kinetics of cluster formation may be a factor controlling the extent of F,OH exchange with a fluid.

Keywords: biotite, cation order, cluster formation, Fe-F avoidance, Klokken intrusion, South Greenland.

SOMMAIRE

Ce travail propose des modèles simples de la relation entre le degré d'ordre des cations occupant les sites à coordination octaédrique de la biotite et le principe de l'évitement de la liaison Fe-F. Ces modèles supposent que le F est seulement en coordination avec trois cations Mg, et que le Mg et le Fe sont seuls à occuper les sites à coordination octaédrique. La biotite posséderait un désordre cationique impliquant ces sites seulement si la teneur en F est inférieure à un niveau maximum (X_F^{\max}) déterminé par la relation $X_F^{\max} = X_{Mg}^3$. Toute biotite qui possède une teneur en F supérieure à X_F^{\max} doit posséder des regroupements de Mg_3 en excès du nombre attendu dans un modèle de distribution aléatoire des cations, si les liaisons Fe-F sont à éviter. Cette prédiction concorde avec les résultats d'études spectroscopiques prélevés de la littérature, quoiqu'il y a des complications causées par la présence de cations autres que Fe et Mg dans ces sites. La mise en ordre de Fe sur $M(2)$ à longue échelle serait compatible avec l'évitement des liaisons Fe-F dans un intervalle de composition très semblable au cas du désordre, mais la mise en ordre de Fe sur $M(1)$ à longue échelle serait compatible avec ce principe seulement sur un intervalle restreint de composition. La formation de ces regroupements dépendrait de l'évolution du système au cours de son refroidissement. Les données sur la biotite du massif de Klokken (Groënland du Sud) servent d'illustration. La cinétique de formation de ces regroupements de cations pourrait influencer le degré d'échange F,OH avec une phase aqueuse.

(Traduit par la Rédaction)

Mots-clés: biotite, degré d'ordre cationique, formation de regroupements cationiques, évitement des liaisons Fe-F, massif de Klokken, Groënland du Sud.

INTRODUCTION

The substitution of F in biotite is of considerable interest because of its possible stabilizing effect on phlogopite at high temperatures (see Guidotti 1984) and because of the importance of geothermometers involving Fe/Mg exchange between biotite and associated minerals. However, the substitution of F for OH is complicated by "iron-fluorine avoidance", a term that refers to the commonly observed antipathetic relationship between con-

centrations of iron and fluorine in many natural ferromagnesian minerals (Ramberg 1952, Ekström 1972, Speer 1984, Guidotti 1984). Fe-F avoidance was explained by Ramberg (1952) in terms of the greater strength of Mg-F bonds compared with Fe-F bonds. More recently, Rosenberg & Foit (1977) used crystal-field theory to account for the phenomenon.

It has been shown by Kalinichenko *et al.* (1975) and Sanz & Stone (1983a) that the distribution of cations on octahedral sites in biotite may not be

random. The latter authors further showed that Fe-F avoidance is an important control on cation distributions. The present work focuses on the relationships between the composition of the octahedral sheet, the site population of cations in this sheet, and F, OH site occupancies. These relationships are explored theoretically using simplifying assumptions. Predictions of the relationship between cation order and F substitution are compared with Nuclear Magnetic Resonance (NMR) and infrared (IR) data from Sanz & Stone (1983a) and Kalinichenko *et al.* (1975). It is shown that in biotite, the *distribution* of octahedrally coordinated cations cannot be considered independently of the substitution of F for OH and that the types of cation distribution that are compatible with Fe-F avoidance depend on composition of the biotite.

It is postulated that the kinetics of cluster formation (see definitions below) can be a control on F,OH exchange between biotite and a fluid. This postulate is discussed in the context of compositional data for biotite from the Klokken syenite intrusion of South Greenland (Parsons *et al.* 1991), a brief description of which is given below.

The Klokken intrusion

The Klokken intrusion (South Greenland) is an ovoid stock (3 × 4 km) consisting of a gabbro rim enclosing a layered syenite series. Details of the field relations, layering and mineral chemistry are given by Parsons (1979, 1981) and Mason *et al.* (1985).

Biotite from Klokken was studied by Parsons *et al.* (1991). Analyses were made by energy-dispersion electron-microprobe methods except for F, which was determined by ion microprobe using natural biotite for standardization. The detection limit for F was estimated as 1 ppm by weight. Full details of the analytical methods are given by Parsons *et al.* (1991). Biotite in the layered series covers a range of X_{Fe} from 0.47 to 0.92 and has a minimum $X_{Fe} + X_{Mg}$ of 0.88. (X_{Fe} is defined as $Fe/(Fe + Mg + Mn + [^{6}Al] + [^{6}Ti])$, where Fe is the number of Fe^{2+} cations in the formula unit. Similar definitions apply for X_{Mg} , etc.) Titanium is the most important "other" octahedrally coordinated cation with, typically, X_{Ti} in the range 0.1 to 0.13.

The assemblages in which biotite are found are dominated by feldspar (micro- to cryptoperthite in syenites, plagioclase in gabbro), clinopyroxene, Fe-Ti oxide and olivine. Apatite and minor quantities of quartz are almost ubiquitous, and amphibole is common, especially in the laminated syenites. Calculated oxygen fugacities are close to or below those of the QFM buffer, which, by

analogy with biotite described by de Albuquerque (1973), implies that little of the analyzed Fe is in the form of Fe^{3+} (Parsons 1981, Parsons *et al.* 1991).

Biotite at Klokken occurs in two different textures. In most rocks, it forms crystals (always less than or equal to 0.4 mm, and mostly 0.1 to 0.2 mm, in maximum dimension) that fringe oxide or olivine grains. In four of the rocks studied, the biotite occurs interstitially to feldspar or pyroxene and olivine and has dimensions between 0.5 and 2 mm. From considerations of texture and the distribution of Fe and Mg between biotite and other ferromagnesian minerals, Parsons *et al.* (1991) showed that in the majority of these rocks the biotite is a subsolidus phase, at least in part.

OCCUPANCIES OF OCTAHEDRAL SITES AND F-FOR-OH SUBSTITUTION

Discussion of the relationship between occupancies of octahedral site and the substitution of F for OH is based on the geometry of the octahedral sheet of biotite (Fig. 1). The cations (principally Mg and Fe) occupy two types of *M* site, *M*(1) and *M*(2), which are present in the ratio 1:2 [*M*(1):*M*(2)]. Cations at these sites are coordinated by six anions, two of which are OH or F. Each OH,F anion is bonded to three metal cations. The octahedrally coordinated sites differ in that *M*(1) lies on a mirror plane and the two adjacent OH,F anions are in the *trans* configuration, whereas for *M*(2), the neighboring OH,F anions are in the *cis* configuration.

Nomenclature

In this work, the term "disorder" refers to distributions that are random; it is applied to element distributions on the octahedral sites, the F,OH anion sites or both. The term "cluster" (Strens 1966) refers to groupings of like atoms (*e.g.*, Mg-Mg, F-F or Fe-Fe); biotite is described as having clusters *if these groupings occur more frequently than is predicted on the basis of random occupancy of the octahedral sites or F,OH anion sites*. The term "short-range order" is used to describe the preferential formation of associations such as Mg-F or Fe-OH, irrespective of the presence or absence of clusters.

Types of cation configuration around F,OH anion sites

For a biotite with octahedrally coordinated sites filled by Mg and Fe, there are four ways in which the octahedra adjacent to a given F,OH anion site can be occupied: Mg_3 , Mg_2Fe , $MgFe_2$, and Fe_3 .

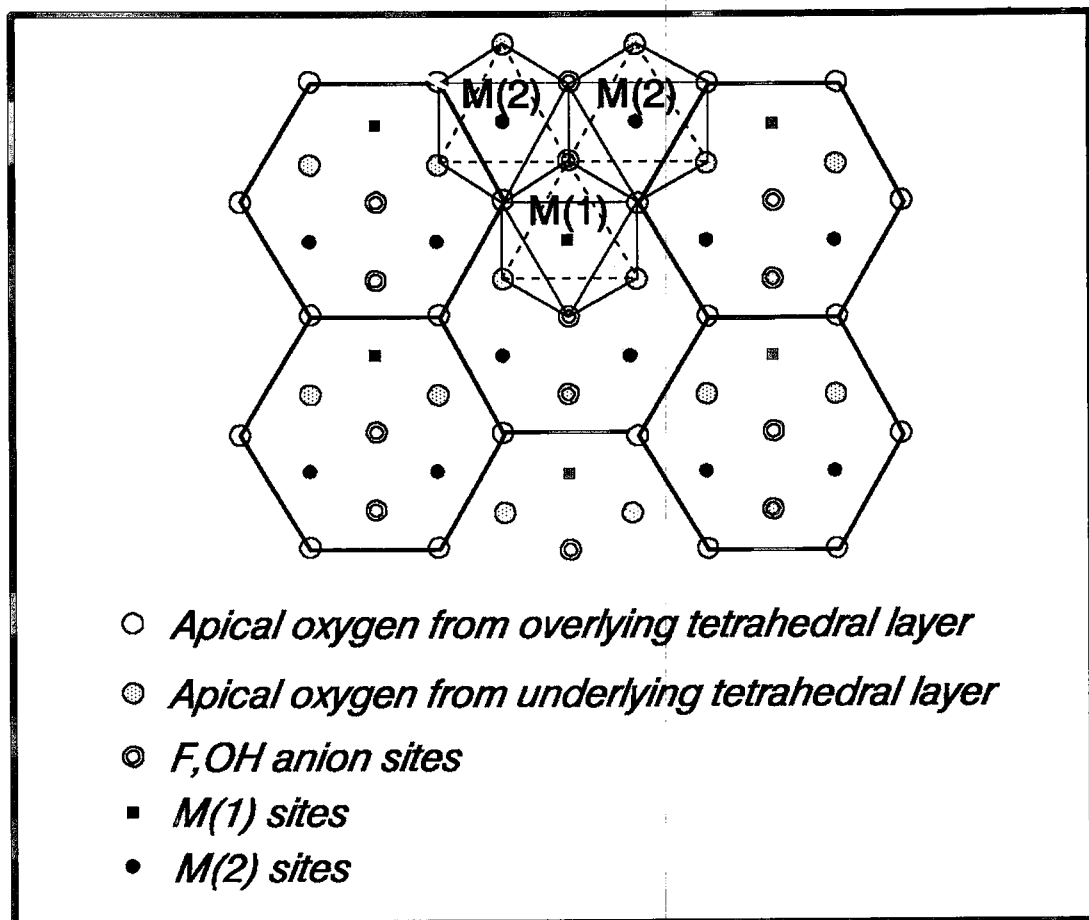


FIG. 1. Idealized geometry of the sheet of octahedra in mica (modified from Bailey 1984).

The NMR, IR and EXAFS data of Sanz & Stone (1979, 1983a,b) and Manceau *et al.* (1990) suggest that Fe-F bonds do not occur, at least in the biotite they studied, implying that Fe-F avoidance is "perfect". This observation is used here as the basis for exploring the relationship between the F and Mg contents and the occupancies of octahedral sites, although it is shown below that the relationship cannot be strictly correct.

If bonds between Fe and F do not occur, then only one configuration of occupancies of octahedra, Mg_3 , can accommodate F because any other requires the formation of an Fe-F bond. The maximum mole fraction of F (X_F^{\max}) that can be accommodated in the F,OH site (without violating Fe-F avoidance) is then given by:

$$X_F^{\max} = (X_{Mg}^{M(1)})(X_{Mg}^{M(2)})^2, \quad (1)$$

in which $X_{Mg}^{M(1)}$ and $X_{Mg}^{M(2)}$ are, respectively, the fractions of M(1) and M(2) sites containing Mg.

For complete *disorder* of Fe and Mg on octahedral sites, $X_{Mg}^{M(1)} = X_{Mg}^{M(2)} = X_{Mg}$, where X_{Mg} is the mole fraction Mg in the biotite. Equation (1) thus becomes

$$X_F^{\max} = X_{Mg}^3. \quad (2)$$

This function, which is plotted as a *solid line* in Figure 2, represents the maximum mole fraction of F that can be accommodated whilst retaining disorder of Fe and Mg over the octahedral sites and without violating Fe-F avoidance. Whereas, in this model, the octahedrally coordinated cations are disordered over the available sites, there is short-range order between F and Mg and between OH and Fe.

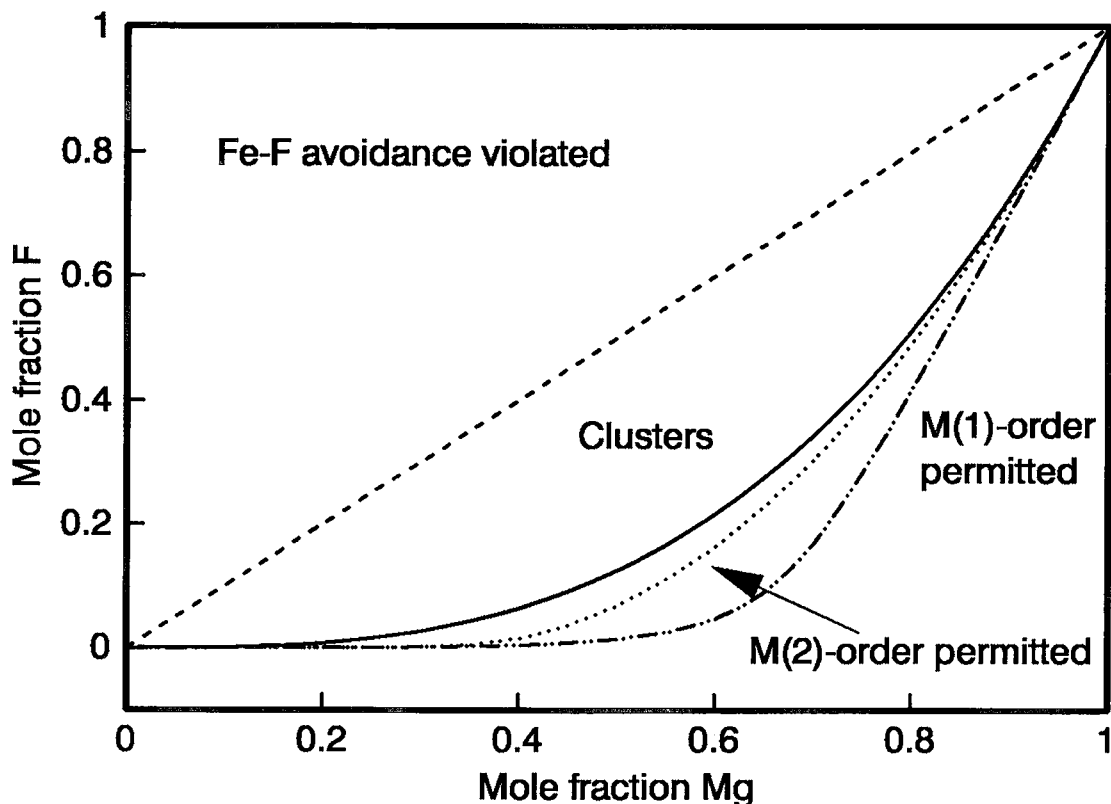


FIG. 2. Fields of cluster formation, $M(1)$ - and $M(2)$ -order, disorder and violation of Fe-F avoidance predicted using equations 1 to 4. The unlabeled field lying below the solid line is one in which disorder (of octahedrally coordinated cations) is permitted; the fields labeled " $M(1)$ -order permitted" and " $M(2)$ -order permitted" superimpose over it (see text).

Two schemes of long-range order are considered: the case where Fe shows a preference for the $M(1)$ site is called " $M(1)$ -order", the case where Fe prefers $M(2)$ sites is called " $M(2)$ -order". The distribution of Fe and Mg between the $M(1)$ and $M(2)$ sites can be expressed in terms of a distribution coefficient,

$$K_D(3) = \frac{X_{Mg}^{M2} \cdot X_{Fe}^{M1}}{X_{Mg}^{M1} \cdot X_{Fe}^{M2}} \quad (3)$$

from which X_{Mg}^{M1} and X_{Mg}^{M2} can be calculated for any assumed value of $K_D(3)$ and bulk Mg content and substituted in equation (1). The case where Fe is concentrated in $M(1)$ is shown [for $K_D(3) = 100$] as a dot-dashed line on Figure 2. The case where Fe is enriched on $M(2)$ is illustrated [for $K_D(3) = 0.01$] as a dotted line on Figure 2. In the limiting case where $K_D(3) = 1$, there is disorder of Fe and

Mg on octahedral sites, and equation 2 applies. Although in these two models the octahedrally coordinated cations exhibit *long-range* order, Fe-F avoidance requires *short-range* order between Mg and F and between Fe and OH.

Finally, there is the case of formation of Mg-Mg clusters and Fe-Fe clusters. If the clusters are large, the maximum mole fraction of F that can substitute without violating Fe-F avoidance is given by

$$X_F^{max} = X_{Mg} \quad (4)$$

This is shown as a *dashed* line in Figure 2.

The types and combinations of short- and long-range order described above allow a subdivision of F-Fe space according to the cationic and F,OH anion distributions that are compatible with Fe-F avoidance. In Figure 2, the solid curve is the compositional limit of biotite with cation disorder, but which fulfills the requirements of

Fe-F avoidance. Biotite plotting above this line *must* develop both cation and F-F, OH-OH clusters to minimize violations of Fe-F avoidance (field labeled "clusters"). Biotite plotting between the solid line and the abscissa need not develop clusters in order to maintain Fe - F avoidance. This field is called the "disorder-permitted" field (for clarity it is not labeled on Fig. 2). The fields labeled "M(1)-order permitted" and "M(2)-order permitted" extend from, respectively, the dot-dashed curve and the dotted curve to the abscissa. Biotite compositions plotting in these fields may develop long-range order up to the degree specified by $K_D(3) = 100[M(1)\text{-order}]$ or $K_D(3) = 0.01[M(2)\text{-order}]$ without violating Fe-F avoidance. With lower degrees of long-range order [$K_D(3)$ nearer 1], both fields expand, and the limiting curves approach the solid line [$K_D(3) = 1$]. The limiting curve for M(2)-order plotted in Figure 2 is practically indistinguishable from that for the hypothetical case where $K_D(3) = 0$ [Fe only substituted on M(2) sites]. Figure 2 shows that M(2)-order differs relatively little from complete disorder in its effect on F occupancy. In contrast, M(1)-order places more severe constraints on F occupancy; where $K_D(3) = \infty$ [Fe substituted only on M(1) sites], the limiting curve becomes a straight line originating at $X_{Mg} = X_F = 1$ and terminating at $X_{Mg} = 0.66$ and $X_F = 0$.

Finally, the dashed line in Figure 2 represents the compositional limit of Fe-F avoidance. Biotite compositions plotting above this line *must* violate Fe-F avoidance, irrespective of the cation distribution (field labeled "Fe-F avoidance violated").

Figure 2 shows that in phlogopite-rich biotite, a high F content is compatible with any of the possible distributions among cations described above. With higher Fe contents (in F-bearing biotite), the development of long-range cationic order becomes less likely, and the formation of clusters more likely. The tendency to cluster formation will be greatest at high Fe or F concentrations.

COMPARISON WITH SPECTROSCOPIC DATA

Although order involving octahedrally coordinated sites is common in the trioctahedral micas as a whole (Bailey 1984), evidence for such order in *biotite* is contradictory. Site-occupancy data from structure refinements indicate an absence of long-range order (Bailey 1984), and IR spectra are generally consistent with the absence of clusters, at least in OH-bearing biotite (Vedder 1964, Wilkins 1967, Farmer 1974). In contrast, Mössbauer data (Bancroft & Brown 1975, Babushkina & Nikitina 1985, Annersten 1974, 1975, Dyar & Burns 1986, Dyar 1987, 1990, Guidotti & Dyar 1991) show that

Fe can order on M(1) or M(2) or may be disordered over these sites. NMR, IR and EXAFS data on F-bearing biotite and phlogopite (Kalinichenko *et al.* 1975, Sanz & Stone 1977, 1979, 1983a, 1983b, Rausell-Colom *et al.* 1978, Sanz *et al.* 1978, Manceau *et al.* 1990) demonstrate the existence of clusters in which the octahedral sites are exclusively occupied by Mg and the F, OH sites are fully occupied by F. Complementing these Mg-F clusters are those in which Fe is enriched (but within which some Mg-Fe neighbors also occur) and in which the F, OH anion site is exclusively occupied by OH (Sanz & Stone 1983b). This evidence for the formation of clusters in biotite allows predictions regarding the compositional dependence of cluster formation to be tested.

Sanz & Stone (1983a) presented their NMR data in terms of the ratios of intensities of four NMR lines (A, B, C and D) corresponding to the configurations $Mg_3\text{-OH}$ (A), $Mg_2Fe\text{-OH}$ (B), $MgFe_2\text{-OH}$ (C) and $Fe_3\text{-OH}$ (D). I used these intensity data to calculate the fraction of sites around the OH that are occupied by Mg:

$$X_{Mg}^{OH} = [Mg/(Mg + Fe)]_{OH}. \quad (5)$$

Knowing the bulk Mg/(Mg + Fe) ratio (X_{Mg}) from results of chemical analyses (Sanz & Stone 1983a), the fraction of sites around the F that are occupied by Mg (X_{Mg}^F) was calculated from:

$$X_{Mg} = X_{Mg}^F \cdot X_F + X_{Mg}^{OH} \cdot X_{OH}. \quad (6)$$

Finally, the distribution of Mg and Fe around the F and OH anions was quantified using the distribution coefficient:

$$K_D(7) = \frac{X_{Mg}^F \cdot X_{Fe}^{OH}}{X_{Fe}^F \cdot X_{Mg}^{OH}}, \quad (7)$$

where $X_{Fe}^{OH} = 1 - X_{Mg}^{OH}$ and $X_{Fe}^F = 1 - X_{Mg}^F$.

A $K_D(7)$ value of 1 indicates a random distribution of Mg and Fe about the OH, F anion site, whereas a $K_D(7)$ of greater than 1 indicates that Fe - F avoidance occurs, and a $K_D(7)$ equal to ∞ indicates perfect Fe-F avoidance. Two samples (B13 and P2) are from Manceau *et al.* (1990) and are deduced to have clusters, based on their Table 4 (p. 369). Kalinichenko *et al.* (1975) did not provide numerical data from their NMR spectra, but simply stated whether the Mg - Fe distribution about the OH ion was "statistical" (*i.e.*, disordered) or "non-statistical" (*i.e.*, clustered).

In considering data from natural biotite, account must be taken of cations other than Fe^{2+} and Mg occupying octahedrally coordinated sites. These are principally Al, Fe^{3+} , Mn, Ti and Li. Experimental

evidence (Munoz & Ludington 1974) shows that Al avoids F, and Munoz (1984) concluded that Li readily bonds to F. There are no data pertaining to the behavior of Fe^{3+} , Mn and Ti^{4+} with respect to F in minerals.

Arguments based on crystal-field theory (Rosenberg & Foit 1977) cannot be used to predict the behavior of Mn^{2+} , Fe^{3+} and Ti^{4+} with respect to F because Ti^{4+} has no *d*-orbital electrons, and high-spin Mn^{2+} and Fe^{3+} (the common electronic configuration for these cations in silicates) receive no net crystal-field stabilization energy (Burns 1970). Instead, the behavior of these ions is treated qualitatively using equilibrium constants (at 25°C) for reactions of the type

$$\text{Mg}(\text{OH})^+ + \text{MeF}^+ \rightleftharpoons \text{MgF}^+ + \text{Me}(\text{OH})^+$$

in aqueous solution, derived from the data in Smith & Martell (1976). This approach can be criticized on the grounds that the structures and thermodynamic properties of these aqueous complexes are quite different from those of octahedrally coordinated sites in biotite. The results do, however, agree qualitatively with experimental observations on biotite and siderophyllite (Munoz & Ludington 1974) in that $\log K = 2.96$ if $\text{Me} = \text{Fe}^{2+}$, and $\log K = 1.83$ if $\text{Me} = \text{Al}^{3+}$, indicating that the above reaction would run from left to right and that both Fe^{2+} and Al^{3+} avoid bonding to F in aqueous complexes. The results for Mn^{2+} ($\log K = 1.77$) and Fe^{3+} ($\log K = 5.29$) suggest that, like Fe^{2+} , these ions will avoid bonding to F.

Similar arguments cannot be used to infer the behavior of Ti^{4+} because of the paucity of data on hydroxy-compounds of Ti. Compounds and aqueous complexes of Ti with F are easily synthesized and of wide stability, whereas those involving Ti and OH are more difficult to produce (McAuliffe & Barratt 1987, Kleinberg *et al.* 1960). On this basis, Ti is presumed to prefer bonding to F rather than OH. This is contrary to the assumption made by Gunow *et al.* (1980).

The substitution of Al^{3+} and Ti^{4+} for divalent Mg and Fe will undoubtedly complicate patterns of long- or short-range order involving the latter two elements because of the necessity for charge-balancing substitutions or vacancies. Unfortunately, there is no reliable method by which the population of vacancies in octahedral sites can be calculated from chemical analysis alone because altermultivalent substitutions can be compensated by more than one mechanism (*e.g.*, replacement of OH or F by O^{2-} , local coupling of trivalent species with Li^+). Indeed, assignment of some cations between the octahedral and tetrahedral sites from chemical analysis alone is problematic; Guidotti & Dyar (1991) have shown that Fe^{3+} can substitute in tetrahedral sites in biotite even where there is sufficient Si + Al to fill them. If reliable

concentrations of vacancies could be calculated, there remains the problem of interaction between the vacancies and the F,OH anions, because it is not known whether either of these species shows a preference for neighboring vacant octahedrally coordinated sites. Patterns of order among Mg, Fe, F and OH also would be complicated by any short- or long-range order or clusters of Al and Ti and associated vacancies (Krzanowski & Newman 1972, Ash *et al.* 1987).

For the Sanz & Stone (1983a) data, cations other than Fe^{2+} and Mg amount to 3 to 19% of the octahedral sites (with Al the dominant "other" cation), so that the vacancy problem is not considered to be too severe. For the Kalinichenko *et al.* (1975) data, "other" cations (mainly Al) occupy 11 to 40% of the octahedrally coordinated sites, and the possible complications arising from vacancy substitution should be borne in mind. Neither of these data sets contain evidence concerning the distribution of Fe^{3+} between tetrahedral and octahedral sites; sufficient Si and Al were assigned to fill the tetrahedral sites, with the excess Al being assigned to octahedral sites. (If the doubts expressed by De Pieri (1980) concerning the assumption of complete filling of the tetrahedral sites are valid, then this scheme is subject to an additional uncertainty of unknown magnitude).

The F,OH anion site of biotite can be partially occupied by Cl. Just as Fe and F avoid each other, Mg and Cl show mutual avoidance (*e.g.*, Schullien 1980, Munoz & Swenson 1981, Volfinger *et al.* 1985). However, in most examples of igneous and metamorphic biotite, Cl is minor compared to F and OH (Speer 1984, Guidotti 1984) and, in the absence of analyses for Cl, it is assumed that this generalization holds for the data of Sanz & Stone (1983a) and Kalinichenko *et al.* (1975).

Apparent deficiencies in the occupancy of the F,OH site generally are attributed to the oxidation of Fe to Fe^{3+} , with concomitant loss of H^+ (Eugster & Wones 1962), as well as to analytical error. Because the analyses are incomplete (lacking Cl and, for four samples, H_2O), it is difficult to assess whether apparent deficiencies in the F,OH site are real. Consequently, the mole fraction F has been defined as $X_F = F/4$, where F is the number of fluorine atoms in a formula unit with 4 F,OH anion sites.

Figure 3 shows X_{Mg}^{F} plotted against $X_{\text{Mg}}^{\text{OH}}$ for the data of Sanz & Stone (1983a). The fraction of sites around F that are occupied by Mg scatters about a value of approximately 0.9, so that $K_D(7)$ increases as Mg content decreases. Figure 4 shows data from Sanz & Stone (1983a), Manceau *et al.* (1990) and Kalinichenko *et al.* (1975) plotted in relation to the "cluster" and "disorder permitted"

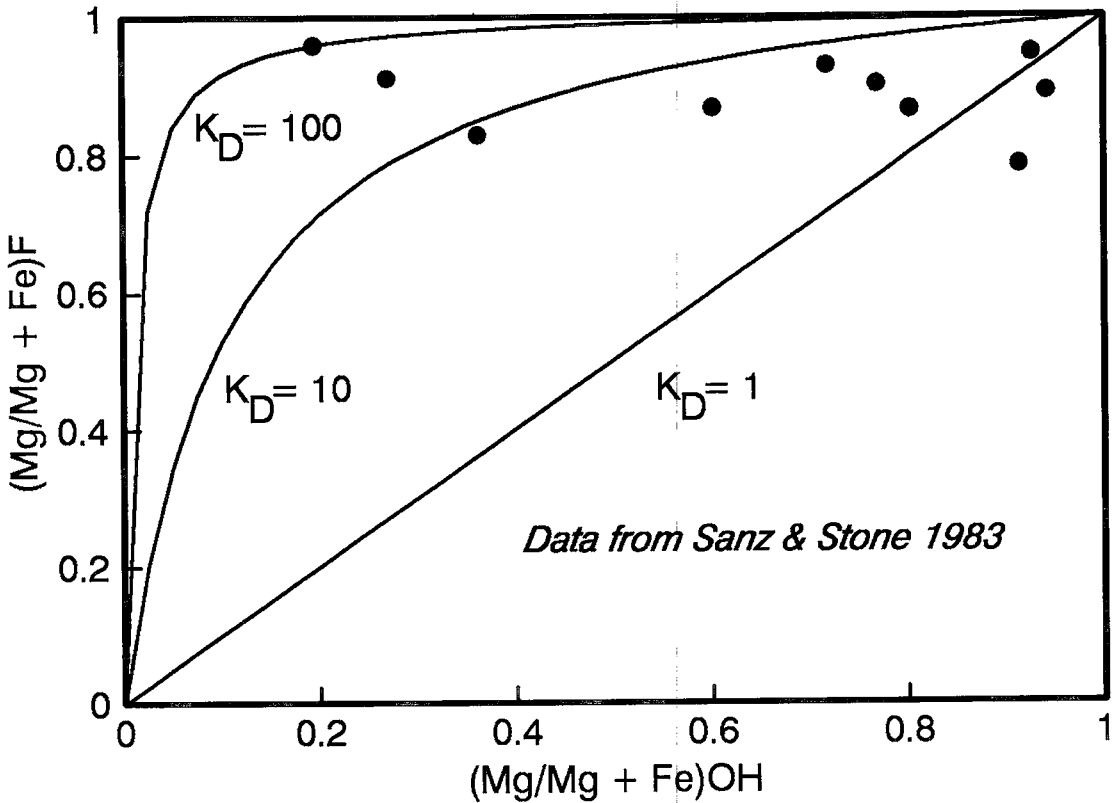


FIG. 3. Distribution of Mg and Fe about OH and F calculated from the data of Sanz & Stone (1983a).

fields of Figure 2. Each datum from Sanz & Stone (1983a) has the corresponding value of $K_D(7)$ written beside it. The two data points from Manceau *et al.* (1990) are labeled by sample number (B13 and P2). It was not possible to calculate values of $K_D(7)$ for these samples because NMR intensity data were not provided by Manceau *et al.* (1990), but based on their Table 4 (their p. 369), both samples have clusters. Sample B13 has a large number of vacant octahedra (Manceau *et al.* 1990, Fig. 7) compared with their other biotite and phlogopite samples. The sample labeled "3" is from Kalinichenko *et al.* (1975) and is discussed below.

Bearing in mind the *caveats* regarding altrivalent and other substitutions, the following points emerge from Figure 3 and 4:

(a) Fe - F avoidance is demonstrated by most of the data of Sanz and Stone (1983a) [*i.e.*, $K_D(7)$ greater than 1], but it is imperfect [$K_D(7)$ less than ∞].

(b) Virtually all the Sanz & Stone (1983a) data plotting in the "cluster" field (Fig. 4) have $K_D(7)$ significantly greater than 1 (minimum 2.8, maximum 99.1), whereas the data plotting in the "disorder" field have $K_D(7)$ nearer to 1 (maximum 5.2).

(c) The "statistical" samples of biotite of Kalinichenko *et al.* (1975) plot in the "disorder permitted" field (with one exception, labeled "3" on Fig. 4).

Data that would permit testing of the predicted relationships between long-range order and Fe-F avoidance are sparse. Of the Mössbauer studies quoted above, only those of Bancroft & Brown (1975) and Dyar & Burns (1986) contain data for biotite samples of known F content. These studies were made on samples from Dodge *et al.* (1969) and give generally similar values of the distribution of Fe between $M(1)$ and $M(2)$ for the samples common to both. Values of $K_D(3)$ calculated from these two data sets fall in the range 0.3 to 1. Only

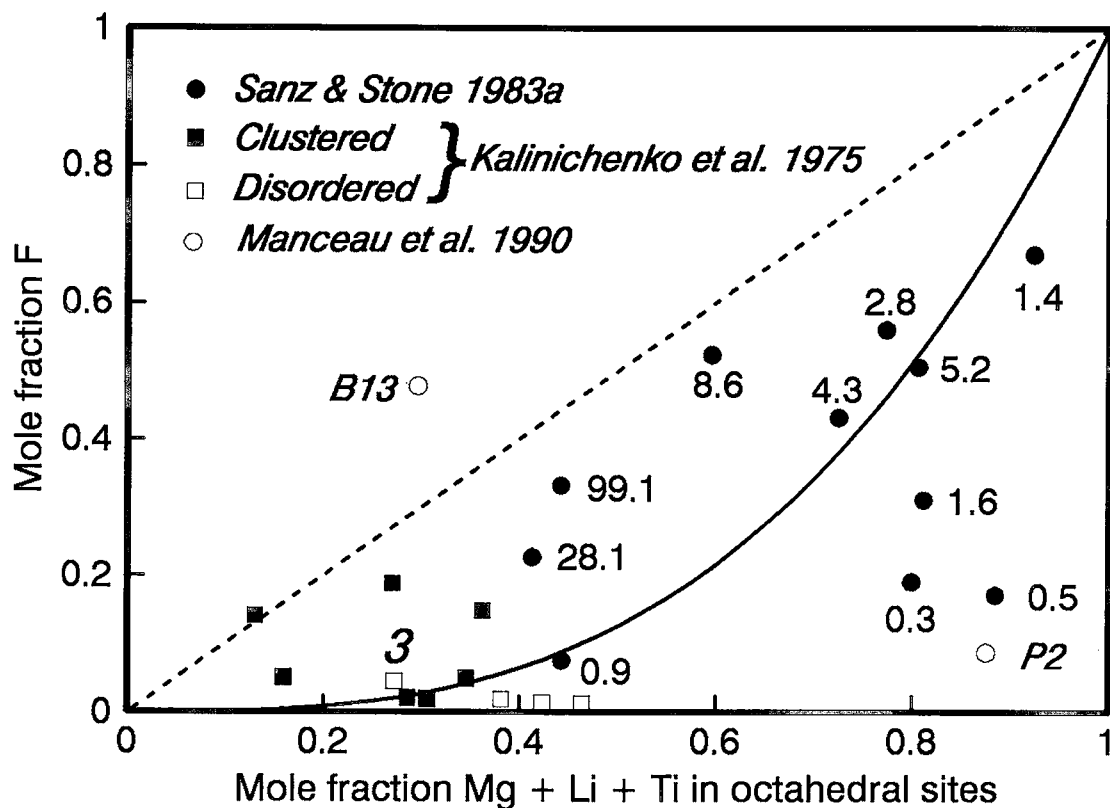


FIG. 4. Model lines and data from spectroscopic studies. The solid curve is that of $X_F^{\max} = X_{Mg}^3$, the dashed line that of $X_F^{\max} = X_{Mg}$. Each datum from Sanz & Stone (1983a) has the corresponding value of $K_D(7)$ next to it. Sample B13 from Manceau *et al.* (1990) and sample 3 from Kalinichenko *et al.* (1975) are discussed in the text.

one sample contains more F than the limit predicted for its composition and ratio of Fe occupancy in $M(1)$ and $M(2)$. It is not known whether this violation of the model arises from errors in the model or from errors in the Mössbauer or chemical data.

DISCUSSION

Imperfection of Fe - F avoidance is to be expected on thermodynamic grounds. Indeed, it is possible to synthesize pure fluor-annite (Munoz & Ludington 1974) and high-F siderophyllite is known in nature (Nash *et al.* 1985). Nevertheless, such gross violations of Fe-F avoidance are comparatively rare (at least in igneous rocks: Speer 1984, Fig. 23), and only one datum from the twenty-three in Figure 4 plots in the "Fe-F avoidance violated" field (B13 on Fig. 4). This biotite has the highest octahedral $Al^{3+} + Ti^{4+} + Fe^{3+}$ and vacancy population of the suite of biotite and phlogopite

studied by Manceau *et al.* (1990, their Table 4 and Fig. 7), so that the *caveats* expressed above regarding altrivalent substitutions and vacancies may apply.

In spite of the imperfection of Fe-F avoidance evidenced by the $K_D(7)$ values, the simple models derived above appear to account for the relationship between cluster formation and biotite chemistry quite well, although the data are few in number and represent a restricted set of parageneses (the latter point is discussed below). Within the "disorder permitted" field (Fig. 4), none of the biotite samples have $K_D(7) = 1$, corresponding to an absence of clustering, but range in $K_D(7)$ from 0.3 to 5.2. For those (two) biotite samples with $K_D(7)$ less than 1, an excess (over the statistically expected frequency) of Mg-OH bonds is implied. In principle, this could be explained in terms of Mg-Cl avoidance, but in the absence of analyses for Cl, this possibility cannot be tested. The biotite samples with $K_D(7)$

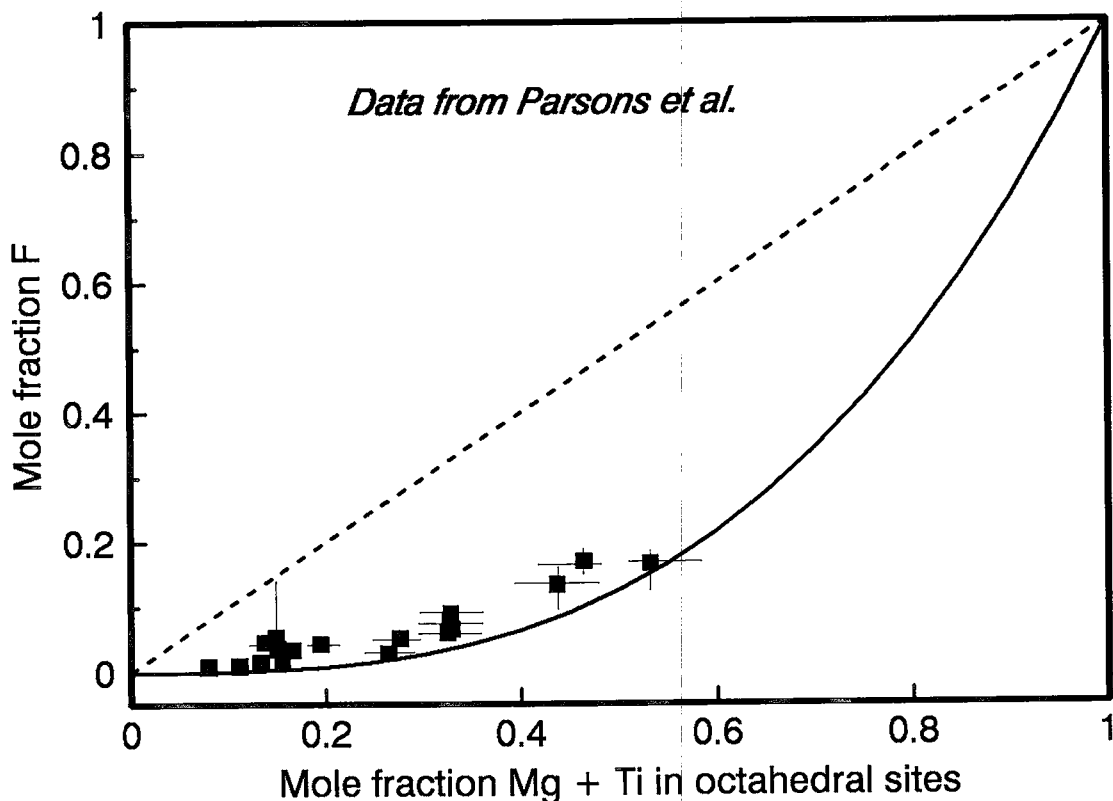


FIG. 5. Data from the Klokken intrusion, South Greenland, compared with the model lines from Fig. 2. Each datum represents biotite composition in one syenite sample. The bars (shown where they exceed the symbol size) represent the range of analytical data for each sample. Source of data: Parsons *et al.* (1991).

greater than 1, but which plot in the “disorder permitted” field, do not violate the model; there is no reason why biotite plotting in this field *must* have disorder on octahedral sites. Given a suitable cooling history, it is to be expected that clusters would develop in such biotite. It is significant that biotite plotting in the “cluster” field generally has the highest values of $K_D(7)$. This arises because in order to minimize the number of Fe - F bonds, a greater proportion of the available Mg must be associated with F when the Fe or F content is high.

Kalinichenko *et al.* (1975) suggested that variations in the extent of cluster formation among their samples (from granites, granite pegmatites and high-grade gneisses) arise from differences in environment of formation, especially the inferred temperature of biotite growth. Figure 4, however, shows that the primary controls on cluster formation are the Mg and F contents, with clusters being absent in biotite with a low concentration of F. Only the point labeled “3” on Figure 4 violates the

model for disorder of Fe and Mg on octahedral sites. It is not clear whether this violation arises from uncertainty in chemical composition (the Cl content was not given), from analytical error (methods and errors were not reported by Kalinichenko *et al.* 1975), from inadequacies in the model (*e.g.*, treatment of cations other than Fe and Mg), or because there is an effect caused by temperature of formation, as Kalinichenko *et al.* proposed.

The comparisons presented above suggest that F content is the primary control on cluster formation. In principle, the formation of clusters may be subject to a kinetic control exerted by the rate of intracrystalline diffusion of Mg, Fe, F and OH, or species containing these elements. Specifically, it is to be expected that biotite that has undergone a long cooling history at moderate temperatures will have developed Fe-Fe clusters rich in OH and Mg-Mg clusters rich in F, even for compositions plotting in the “disorder permitted” field of Figure

2. Conversely, it is to be expected that a biotite of similar composition grown at relatively low temperature or having a short cooling history will retain (metastably) partial or complete disorder in the octahedral sites. Indeed, it is conceivable that exchange of F and OH with a fluid could be limited by the rate of cluster formation if this was sufficiently slow. For example, from Figure 2, a biotite with $X_{Mg} = X_{Fe} = 0.5$ could accommodate F up to $X_F = 0.125$ if the Mg and Fe were in a state of disorder, but up to $X_F = 0.5$ if extensive clusters were able to form in the time interval over which biotite growth and F,OH exchange took place. The biotite samples studied by Kalinichenko *et al.* (1975) and by Sanz & Stone (1983a) do not provide a test of this hypothesis because those of the former all came from environments with (presumably) long cooling histories, and because the geological contexts of the latter were not described. [The samples studied by Sanz & Stone (1983a) were cut from flakes larger than 10 mm × 10 mm, implying that they were derived from coarsely crystalline rocks, presumably with long cooling histories].

Circumstantial evidence for a kinetic effect on the equilibration of F and OH between biotite and a fluid comes from the Klokken gabbro-syenite intrusion, where the textural relationships of biotite (see Introduction) imply that it grew in those conditions where kinetic effects might be important. It is necessary to bear in mind that the compositions of the Klokken biotite depart from the idealization used to derive the models of cation order. Biotite from the Klokken syenite has cations other than Fe^{2+} and Mg occupying up to 12% of the octahedrally coordinated sites, with Ti dominant among them. [There is insufficient Si + Al to fill the tetrahedral sites and, lacking information on Fe^{3+} contents, it was assumed that Ti fills the remaining tetrahedral sites, with the excess assigned to octahedral sites. Direct evidence for tetrahedrally coordinated Ti in biotite is lacking, but such evidence has recently been presented for Ti in amphiboles (Oberti *et al.* 1991)].

Figure 5 illustrates the data for biotite from the Klokken syenites, along with curves of X_F^{max} taken from Figure 2. The data lie close to or very slightly above the limiting curve for disorder. It seems quite unlikely that, fortuitously, the fluid composition (in terms of HF/H₂O) and Fe/Mg ratio of the biotite [controlled by associated ferromagnesian minerals: Parsons *et al.* (1991)], would combine so as to produce the observed relation between X_{Mg} and X_F . This relationship may indicate instead that only limited development of clusters of octahedra occurred and that this restricted F-OH exchange. Whereas these data do not provide an adequate test of the postulated kinetic dependence of F,OH

exchange on cluster formation, they do suggest that systematic work on cluster formation as a function of paragenesis is warranted.

CONCLUSIONS

(1) The relationship between cluster formation and Fe-F avoidance in biotite can be modeled using simple expressions based on the approximation that Fe-F bonds do not occur.

(2) These models predict the existence of a region of X_{Mg} - X_F space in which clusters *must* occur, and one in which they *may* occur, in response to Fe-F avoidance.

(3) Comparison of the model predictions with published spectroscopic studies of cluster formation in biotite confirm their general validity.

(4) It is predicted that long-range order of Fe and Mg on the octahedrally coordinated sites in biotite is less likely as substitution of F for OH increases.

(5) In some cases, the development of clusters and substitution of F for OH in biotite may be kinetically limited, depending on the conditions of growth and on subsequent thermal history.

(6) Systematic spectroscopic studies of site occupancies in biotite, as a function of paragenesis and halogen content, as well as cation chemistry, would be valuable.

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