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THE NATURE OF Mg²⁺—Fe²⁺ DISTRIBUTION IN SOME FERROMAGNESIAN SILICATE MINERALS

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ABSTRACT

Recent structure determinations of cummingtonite and pigeonite indicate that Fe²⁺ usually prefers the Ca-position rather than Mg-position in ferromagnesian silicates. Schemes of Mg²⁺—Fe²⁺ ordering in cummingtonite, anthophyllite, hypersthene and pigeonite are described and a scheme of Mg²⁺—Fe²⁺ ordering for olivine is predicted. A crystal chemical explanation is given for the fact that among coexisting silicate minerals in equilibrium, Fe—Mg silicates are richer in Fe²⁺ than the corresponding Ca—Mg silicate.

INTRODUCTION

Since Mg—Fe members of mineral systems form continuous solid solution series, it is generally believed that Mg²⁺ and Fe²⁺ can replace each other with equal ease and they play an equivalent role in silicate minerals. Similar ionic size and charge are supposed to explain this phenomenon. That this is not strictly the case has been shown by Ramberg and DeVore (1951) and Ramberg (1952). They showed that in coexisting silicates in equilibrium, Fe²⁺ goes preferentially to the less polymerised silicate than Mg²⁺. Subsequently, DeVore (1957) presented a case for Mg—Fe ordering in an orthopyroxene of (Mg₀.₅—Fe₀.₅)SiO₃ composition. In the two types of six-coordinated positions, the Ca-position (by comparison with diopside) has two of its anions shared between two Si cations, which would not be very polarisable. For this reason, he predicted that an orthopyroxene of composition En₅₀ would be an ordered compound with all the Mg in the Ca-position and all the Fe²⁺ cations in the regular six-coordinated position.

However, a completely different scheme of Mg—Fe ordering in ferromagnesian pyroxenes and amphiboles evolved from the detailed structure determination of pigeonite (Morimoto et al., 1960) and two members of the cummingtonite-grunerite series (Ghose and Hellner, 1959; Ghose, 1961).

Mg²⁺—Fe²⁺ ORDERING

Mg²⁺—Fe²⁺ ordering in the cummingtonite series

Determination and three dimensional refinement of the structure of a grunerite with about 30 mole per cent of the Mg component derived from the metamorphosed iron formations of Quebec (Mueller, 1960) in-

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dicated that $M_4$ position (Whittaker notation, Fig. 1) is principally occupied by $\text{Fe}^{2+}$, while the rest of the $\text{Mg}$ and $\text{Fe}^{2+}$ are randomly distributed over $M_1$, $M_2$, and $M_3$ positions. To determine the $\text{Mg} - \text{Fe}$ distribution over the four different metal positions more exactly, the structure of a cummingtonite with about 60 mole per cent of the $\text{Mg}$ component was determined very accurately. For details of the structure determination and refinement of these two structures, see Ghose and Hellner (1959) and Ghose (1961). In the cummingtonite $\text{Mg} - \text{Fe}$ distribution over the four positions is as follows:

$$
M_1 = M_2 = 67 \text{ per cent } \text{Mg}^{2+}, \ 33 \text{ per cent } \text{Fe}^{2+} \\
M_2 = 85 \text{ per cent } \text{Mg}^{2+}, \ 15 \text{ per cent } \text{Fe}^{2+} \\
M_3 = 75 \text{ per cent } \text{Fe}^{2+}, \ 25 \text{ per cent } \text{Mg}^{2+}
$$

$M_4$ position is principally occupied by $\text{Fe}^{2+}$, $M_2$ by $\text{Mg}^{2+}$, whereas $M_1$ and $M_3$ are occupied by the rest of the $\text{Mg}^{2+}$ and $\text{Fe}^{2+}$ in a random manner.

The $M_4$ position corresponds to the calcium position in the tremolite structure. One would expect this position to accommodate the larger of the two cations, namely, $\text{Fe}^{2+}$. However, the interatomic bond distances indicate that this explanation is not acceptable. The $M_4-O_4$ bond distance is $2.04$ Å, $M_4-O_2$ 2.18 Å and $M_4-O_6$ 2.70 Å. The very short $M_4-O_4$ bond indicates that there is covalent bonding between these two oxygens and $M_4$, which is mostly occupied by $\text{Fe}^{2+}$. Since the oxygen $O_6$ is shared by two silicons, its charge is virtually neutralised and its at-
traction to the $M_4$-ion is weak as indicated by the long $M_4-O_6$ distance. The oxygen $O_4$ is bonded to one silicon and two metals $M_2$ and $M_4$, whereas oxygens $O_1$ and $O_2$ are bonded to one silicon and three metals each. Therefore, the $M_4-O_4$ linkage is stronger than a single $M-O$ bond.

Since Fe$^{2+}$ is more electronegative than Mg$^{2+}$, $O_2$ and $O_4$ oxygens are strongly bonded to the $M_4$ atom. The neighboring $M_2$ position, therefore, is occupied by a less electronegative atom, if it is available, Mg$^{2+}$ in the present case, so that the structure may not be highly strained.

The environments of $M_1$ and $M_3$ positions are very comparable and this fact is reflected in the metal content of these two positions which is the same.

The Mg$^{2+}$—Fe$^{2+}$ ions lie in planes parallel to $b$ $c$ in cummingtonite. The nature of the Mg$^{2+}$—Fe$^{2+}$ ordering is shown in Fig. 3(a), which is a section of the cummingtonite structure at $x=0$. If we designate A equal to Fe$^{2+}$, B equal to Mg$^{2+}$, and C equal to a mixture of Mg$^{2+}$ and Fe$^{2+}$, we can describe the sequence as strings of CCC $\cdots$ flanked by two single chains of ABAB $\cdots$ parallel to $c$.

$Mg^{2+}$—Fe$^{2+}$ ordering in anthophyllite

The structure of anthophyllite (Warren and Modell, 1930B) is very similar to that of cummingtonite, Mg$_1$, Mg$_3$, Mg$_4$ and Mg$_4$ in anthophyllite correspond to $M_1$, $M_2$, $M_4$, and $M_3$ in cummingtonite. By analogy, the scheme of Mg$^{2+}$—Fe$^{2+}$ ordering in anthophyllite will be the same as that in cummingtonite and will look very similar to Fig. 3A, which will be a section of the anthophyllite structure parallel to $bc$ at $x=0.13$.

$Mg^{2+}$—Fe$^{2+}$ ordering in orthopyroxene

The environments of the metal atoms in the structure of hypersthene are very comparable to those of cummingtonite. In hypersthene, however, there are two crystallographically different metal positions as compared to four in cummingtonite. The $M_1$ position (Fig. 2) corresponds to the Mg position in diopside or $M_2$ position in cummingtonite, whereas $M_{11}$ position is comparable to the calcium position in diopside or $M_4$ position in cummingtonite. The oxygens $O_2$ and $O_6$ in hypersthene are very similar to the oxygen $O_4$ in cummingtonite, in that they are bonded to one silicon and two metals. Therefore, by analogy, it is expected that $M_{11}$ position will be richer in Fe$^{2+}$ than Mg$^{2+}$, in a partially ordered intermediate hypersthene.

The least-squares refinement of the (001) projection of an intermediate hypersthene ($En_{58.5}Fs_{46.7}$) from a granulite facies rock from Green-
land indicates the following $\text{Mg}^{2+}$—$\text{Fe}^{2+}$ distribution over the two metal sites (Ghose, 1960):

- $M_I = \text{Fe}^{2+}$ 25%, $\text{Mg}^{2+}$ 75% 
- $M_{II} = \text{Fe}^{2+}$ 80%, $\text{Mg}^{2+}$ 20%

However, this distribution is tentative and the exact $\text{Mg}^{2+}$—$\text{Fe}^{2+}$ distribution over the two sites, as well as the bond lengths etc. must await the completion of the three dimensional refinement of the structure, which is in progress.

The nature of $\text{Mg}^{2+}$—$\text{Fe}^{2+}$ ordering is shown in Fig 3(b) which is a section of the hypersthene structure parallel to $bc$ at $x = 0.125$. The sequence can be described as two parallel chains of ABAB $\cdots$ parallel to $c$.

The determination of the structure of a ferromagnesian pigeonite by Morimoto et al. (1960) corroborates this scheme of Mg—Fe ordering in ferromagnesian pyroxenes. In the pigeonite (Wo$_{12}$En$_{26}$Fs$_{62}$) studied, the $M_I$ position is occupied by 52 per cent $\text{Mg}^{2+}$, 48 per cent $\text{Fe}^{2+}$ and $M_{II}$ position by 24 per cent $\text{Ca}^{2+}$, 76 per cent $\text{Fe}^{2+}$. ($M_I$ and $M_{II}$ in this paper
correspond to Mg₁ and Mg₂ notation of Warren and Modell (1930A); this is reverse of that used by Morimoto et al. (1960). Cation ordering scheme in pigeonite is shown in Fig. 3(c), which is a section of the pigeonite structure parallel to bc at \( x \approx 0.25 \).

\[ \text{Mg}^{2+} - \text{Fe}^{2+} \text{ ordering in olivine} \]

The natural olivine series has been studied by Eliseev (1958) by the powder method. The variation of the unit cell with composition in olivine does not follow Vegard’s law, the deviation being most pronounced in the \((\text{Mg}_{0.5} - \text{Fe}_{0.5})\text{SiO}_4\) range. It is proposed that \( \text{Mg}^{2+} - \text{Fe}^{2+} \) ordering takes place in the intermediate olivines at lower temperature.

The nature of the \( \text{Mg}^{2+} - \text{Fe}^{2+} \) ordering can be predicted from the analogy of monticellite \( \text{CaMgSiO}_4 \). Monticellite is isostructural with olivine, both belonging to the space group \( \text{Pmcn} \). There are two crystallographically independent \( \text{Mg}^{2+}, \text{Fe}^{2+} \) positions in olivine—\( \text{M_I} \) corresponding to the Mg-position and \( \text{M_{II}} \) corresponding to the Ca-position in monticellite. From the consideration of the difference in the ionic sizes of \( \text{Fe}^{2+} \) and \( \text{Mg}^{2+} \), it can be predicted that \( \text{Fe}^{2+} \) will be preferred in the \( \text{M_{II}} \) position in olivine, whereas \( \text{Mg}^{2+} \) will be preferred in the \( \text{M_I} \) position.
Mg$^{2+}$—Fe$^{3+}$ DISTRIBUTION AMONG COEXISTING PYROXENES AND AMPHIBOLES

Four of the coordination oxygens (O2 and O4) around M4 position are much closer in cummingtonite than they are in actinolite. This causes a further distortion of the silicate double chains away from the plane of the metal atoms in cummingtonite. This structural difference explains why there is no solid solution relationship between these two amphibole series.

The environment of the metal positions of the two amphiboles except M4 are very similar. Between coexisting cummingtonite and actinolite in equilibrium, Fe$^{3+}$ will be preferred in the M4 position of cummingtonite. The other three metal positions will accommodate comparable amounts of Mg$^{2+}$, Fe$^{3+}$ in both the structures. Mg$^{2+}$/(Mg$^{2+}$ + Fe$^{2+}$) ratios of coexisting cummingtonite and actinolite from a metamorphosed iron formation near Quebec (Mueller, 1960, Table 4, Fig. 4) indicate that cummingtonite is relatively richer in Fe$^{3+}$ than actinolite.

Upon extension of the above arguments one would expect that between coexisting orthopyroxene and calcium pyroxene, Fe$^{3+}$ will be preferred in the MII position of the orthopyroxene. Compositions of coexisting orthopyroxene and Ca-pyroxene, compiled by DeVore (1957, Table 1) indicate that eighteen, out of twenty-two examples, have Fe$^{3+}$ relatively enriched in the orthopyroxene.

On the other hand, between coexisting Ca-pyroxene and actinolite Mg$^{2+}$—Fe$^{3+}$ fractionation is found to be equal (Mueller, 1960, Table 4, Fig. 2). Since MII position in Ca-pyroxene and M4 position in actinolite are filled by calcium, there are no metal positions in either structure that will prefer Fe$^{3+}$ over Mg$^{2+}$. However, the replacement of some Si$^{4+}$ by Al$^{3+}$ in hornblende may make it accept somewhat more Fe$^{3+}$ than the coexisting Ca-pyroxene (DeVore, 1957, Table 4).

Conclusions

At subsolidus temperatures Fe$^{3+}$ and Mg$^{2+}$ do not play the same crystal chemical roles in ferromagnesian silicate minerals. This is shown by Fe$^{3+}$—Mg$^{2+}$ ordering as well as different Mg/Mg+Fe$^{2+}$ ratios in coexisting minerals in equilibrium. Fe$^{3+}$ usually prefers the Ca-position rather than Mg-position in a ferromagnesian mineral and Fe—Mg silicates are usually richer in Fe$^{3+}$ than the coexisting Ca—Mg silicates.

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