THE NATURE OF Mg^{2+}—Fe^{2+} DISTRIBUTION IN SOME FERROMAGNESIAN SILICATE MINERALS

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ABSTRACT

Recent structure determinations of cummingtonite and pigeonite indicate that Fe^{2+} usually prefers the Ca-position rather than Mg-position in ferromagnesian silicates. Schemes of Mg^{2+}—Fe^{2+} ordering in cummingtonite, anthophyllite, hypersthene and pigeonite are described and a scheme of Mg^{2+}—Fe^{2+} 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 Fe^{2+} than the corresponding Ca—Mg silicate.

INTRODUCTION

Since Mg—Fe members of mineral systems form continuous solid solution series, it is generally believed that Mg^{2+} and Fe^{2+} 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, Fe^{2+} goes preferentially to the less polymerised silicate than Mg^{2+}. Subsequently, DeVore (1957) presented a case for Mg-Fe ordering in an orthopyroxene of $(Mg_{0.5}$—$Fe_{0.5})SiO_3$ 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 En_{50} would be an ordered compound with all the Mg in the Ca-position and all the Fe^{2+} 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).

Mg^{2+}—Fe^{2+} ORDERING

Mg^{2+}—Fe^{2+} 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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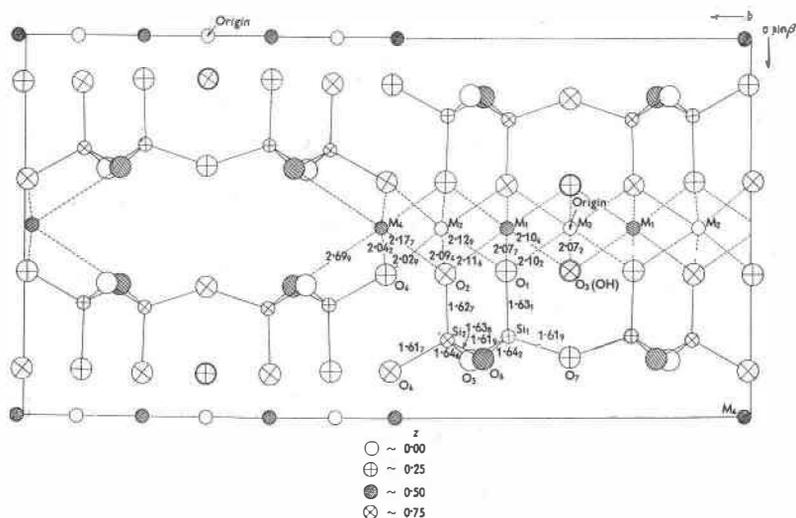
FIG. 1. Projection of the crystal structure of cummingtonite on (001).

dicated that M_4 position (Whittaker notation, Fig. 1) is principally occupied by Fe^{2+}, while the rest of the Mg and Fe^{2+} are randomly distributed over M_1, M_2, and M_3 positions. To determine the Mg—Fe distribution over the four different metal positions more exactly, the structure of a cummingtonite with about 60 mole per cent of the 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 Mg—Fe distribution over the four positions is as follows:

$$M_1 = M_3 = 67 \text{ per cent } Mg^{2+}, \ 33 \text{ per cent } Fe^{2+}$$
$$M_2 = \qquad 85 \text{ per cent } Mg^{2+}, \ 15 \text{ per cent } Fe^{2+}$$
$$M_4 = \qquad 75 \text{ per cent } Fe^{2+}, \ 25 \text{ per cent } Mg^{2+}$$

M_4 position is principally occupied by Fe^{2+}, M_2 by Mg^{2+}, whereas M_1 and M_3 are occupied by the rest of the Mg^{2+} and 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, 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 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 $x = o$. 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_2, Mg_3 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_I position (Fig. 2) corresponds to the Mg position in diopside or M_2 position in cummingtonite, whereas M_{II} position is comparable to the calcium position in diopside or M_4 position in cummingtonite. The oxygens O_2 and O_5 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_{II} 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 ($En_{53.3}Fs_{46.7}$) from a granulite facies rock from Green-
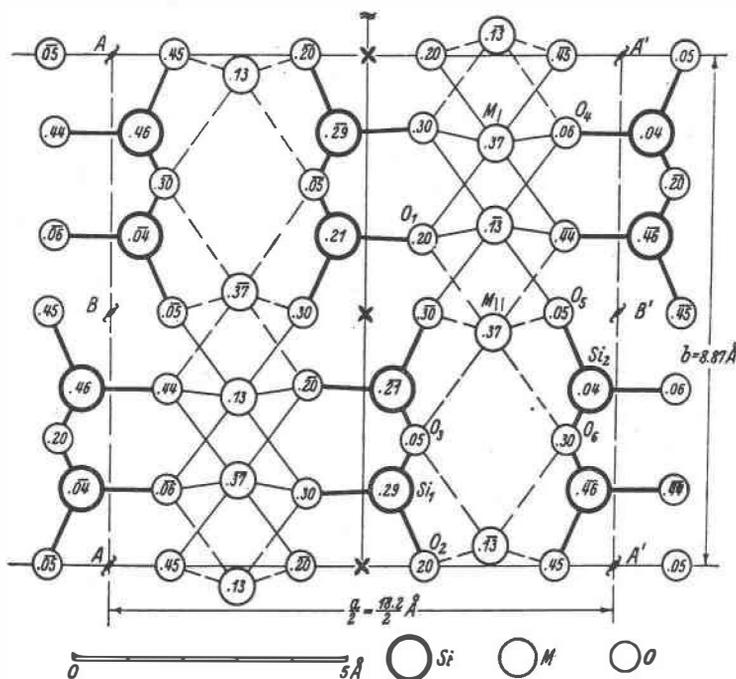
FIG. 2. Projection of the crystal structure of hypersthene on (001).
[After Warren and Modell, 1930B]

land indicates the following Mg^{2+}—Fe^{2+} distribution over the two metal sites (Ghose, 1960):

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

However, this distribution is tentative and the exact Mg^{2+}—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 Mg^{2+}—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 Mg^{2+}, 48 per cent Fe^{2+} and M_{II} position by 24 per cent Ca^{2+}, 76 per cent Fe^{2+}. (M_I and M_{II} in this paper
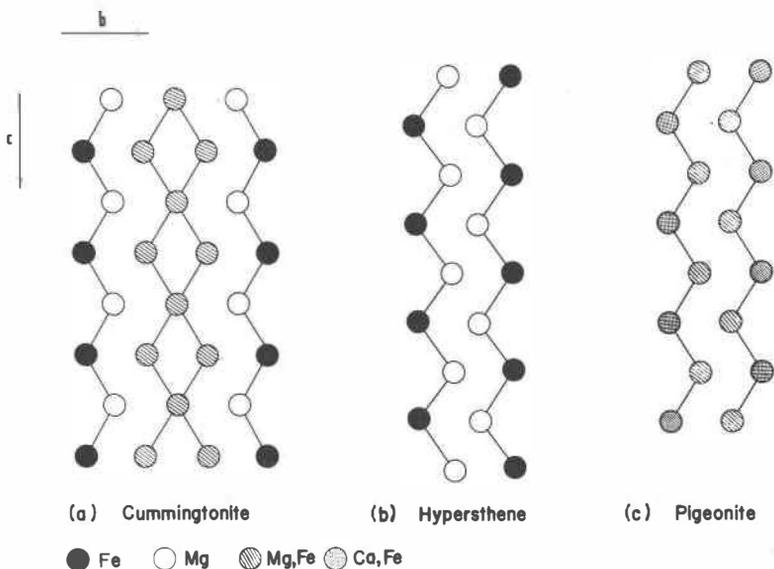
FIG. 3. Schemes of Mg^{2+}—Fe^{2+} ordering in (a) cummingtonite—three dimensional section of the structure parallel to bc at $x=0$. (b) hypersthene—three dimensional section through the structure parallel to bc at $x=0.125$. (c) pigeonite—three dimensional section through the structure parallel to bc at $x\sim0.25$.

correspond to Mg_1 and Mg_2 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 $x\sim0.25$.

Mg^{2+}—Fe^{2+} 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 $(Mg_{0.5}$—$Fe_{0.5})SiO_4$ range. It is proposed that Mg^{2+}—Fe^{2+} ordering takes place in the intermediate olivines at lower temperature.

The nature of the Mg^{2+}—Fe^{2+} ordering can be predicted from the analogy of monticellite $CaMgSiO_4$. Monticellite is isostructural with olivine, both belonging to the space group Pmcn. There are two crystallographically independent Mg^{2+}, Fe^{2+} positions in olivine—M_I corresponding to the Mg-position and M_{II} corresponding to the Ca-position in monticellite. From the consideration of the difference in the ionic sizes of Fe^{2+} and Mg^{2+}, it can be predicted that Fe^{2+} will be preferred in the M_{II} position in olivine, whereas Mg^{2+} will be preferred in the M_I position.

Mg²⁺—Fe²⁺ Fractionation Among Coexisting Pyroxenes and Amphiboles

Four of the coordination oxygens (O_2 and $\bullet_4$) around M_4 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 M_4 are very similar. Between coexisting cummingtonite and actinolite in equilibrium, Fe^{2+} will be preferred in the M_4 position of cummingtonite. The other three metal positions will accommodate comparable amounts of Mg^{2+}, Fe^{2+} 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^{2+} than actinolite.

Upon extension of the above arguments one would expect that between coexisting orthopyroxene and calcium pyroxene, Fe^{2+} will be preferred in the M_{II} 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^{2+} relatively enriched in the orthopyroxene.

On the other hand, between coexisting Ca-pyroxene and actinolite Mg^{2+}—Fe^{2+} fractionation is found to be equal (Mueller, 1960, Table 4, Fig. 2). Since M_{II} position in Ca-pyroxene and M_4 position in actinolite are filled by calcium, there are no metal positions in either structure that will prefer Fe^{2+} over Mg^{2+}. However, the replacement of some Si^{4+} by Al^{3+} in hornblende may make it accept somewhat more Fe^{2+} than the coexisting Ca-pyroxene (DeVore, 1957, Table 4).

Conclusions

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

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