Cation partitioning in hydrothermally prepared olivine-related (Fe,Mn)-sarcopsides

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Abstract

Solid solutions of \((\text{Fe}_{1-x}\text{Mn}_x)\text{(PO}_4\text{)}_2\) \(0 < x \leq 0.20\), with the olivine-related sarcopside structure \((P2_1/a)\), have been prepared hydrothermally and analyzed by means of X-ray powder diffraction and \(^{57}\text{Fe Mössbauer spectroscopy. The cation sites, M1 and M2, are octahedrally coordinated and are closely related to the corresponding sites in olivine. At 10 K, the solid solutions show magnetic interaction for iron at M2 but no magnetic order at M1. The cations show strong inverse order with Fe\(^{2+}\) preferring the M2 site and Mn\(^{2+}\) the M1 site, with \(K_p(\text{Fe},\text{Mn}) \approx 0.2\). A comparison of other phases with sarcopside or olivine structure is made, and a method is described to predict cation partitioning in these structure types."

Introduction

We have recently investigated cation distribution in solid solutions with the olivine structure (e.g., Annersten et al., 1982, 1984; Nord et al., 1982). To supplement these studies, we have now initiated studies on solid solutions with the sarcopside structure, which is closely related to that of olivine (Moore, 1972). Both structures contain two distinct octahedrally coordinated metal cation sites, M1 and M2. Sarcopside-type solid solutions are more easily prepared and equilibrated than the corresponding olivine phases: \((\text{Fe}_{1-x}\text{Mn}_x)\text{(PO}_4\text{)}_2\) phases prepared hydrothermally (cf. Kabalov et al., 1973; Ericsson and Nord, 1984) and \((\text{Ni}_{1-x}\text{Mn}_x)\text{(PO}_4\text{)}_2\) phases at 1 bar (Nord, 1984). We present here Mössbauer studies of hydrothermally prepared \((\text{Fe},\text{Mn})\)-sarcopsides down to 10 K, primarily to determine cation distributions. We also describe a method to predict cation partitioning in solid solutions with the sarcopside or the olivine structure.

Experimental

Solid solutions with the empirical formula \((\text{Fe}_{1-x}\text{Mn}_x)\text{(PO}_4\text{)}_2\) \(x = 0.05, 0.10, 0.15, \ldots, 0.90\), were prepared and equilibrated in evacuated and sealed silica tubes at 1070 K as described by Nord and Ericsson (1982). These products are isomorphous with the mineral graf-tonite, \((\text{Fe}_{1-x}\text{Mn}_{0.25}\text{Ca}_{0.25}\text{Mg}_{0.5})\text{(PO}_4\text{)}_2\), and with \(\text{Fe}_2\text{(PO}_4\text{)}_2\) (graf-tonite phase) which have been described as having 7,5,5- or 6,5,5-coordinated metal sites, respectively (Calvo, 1968; Kostiner and Rea, 1974). \(\text{Fe}_2\text{(PO}_4\text{)}_2\)-sarcopside was prepared by heating pure \(\text{Fe}_{2}\)graf-tonite in a hydrothermal Nimonic-105 autoclave at 800 bar, 570 K for seven days. The synthetic \((\text{Fe},\text{Mn})\)-graftonites were heated hydrothermally at various temperatures and pressures, giving sarcopside phases with \(X_{Fe} \leq 0.20\) (cf. Table 1). The phase identification was confirmed by means of X-ray powder diffraction data, obtained with a Guinier-Hägg type focusing camera (CrK\(\alpha\) radiation, \(\lambda = 2.28975 \text{ Å, KCl internal standard).}

The \(^{57}\text{Fe Mössbauer spectroscopy data were obtained as described by Ericsson and Nord (1984). The centroid shifts (CS) are given in mm/s relative to metallic iron (a-Fe) at room temperature."

Results

X-ray diffraction data

The (Fe,Mn)-sarcopside samples studied crystallize in the monoclinic space group \(P2_1/a\), originally determined for a natural sarcopside mineral by Moore (1972). The unit cell parameters are given in Table 1. Other sarcopside phases are also included for comparison. Accurate X-ray powder diffraction data for pure \(\text{Fe}_2\text{(PO}_4\text{)}_2\)-sarcopside, evaluated with a computer-controlled film scanner (Johansson et al., 1980), are given in Table 2.

The unit cell volumes \((Z = 2)\) are around 300 \(\text{Å}^3\). For pure Fe-sarcopside it is 301.2(2) \(\text{Å}^3\), i.e., \(V/Z = 150.6(1) \text{ Å}\), which is a curious coincidence with Fe-graf-tonite, where \(V/Z = 150.4(1) \text{ Å}\) (Kostiner and Rea, 1974). The increase in unit cell volume with Mn substitution is greater for (Fe,Mn)-sarcopsides than for (Fe,Mn)-graftonites. Al-
though high temperature and pressure are needed to transform graffinite into sarcopside, it is doubtful whether sarcopside can be regarded as a high pressure phase.

The cell volume increases slightly with respect to Fe₂(PO₄)₂-sarcopside with the substitution of the Mn²⁺ ion for Fe²⁺. The octahedral cation radii are 0.83 and 0.78 Å for divalent high-spin manganese and iron, respectively (Shannon, 1976). The smaller cations (Table 1) imply a corresponding decrease of the unit cell volume, which is very likely due to the second order Doppler shift (Ingalls, 1964). The smaller cations (Table 1) imply a corresponding decrease of the unit cell volume, which is very likely due to the second order Doppler shift (Ingalls, 1964). The smaller cations (Table 1) imply a corresponding decrease of the unit cell volume, which is very likely due to the second order Doppler shift (Ingalls, 1964).

Mössbauer data: paramagnetic region

At room temperature (~295 K) as well as at liquid nitrogen temperature (77 K) the spectra of (FeₓMn₁₋ₓ)(PO₄)₂ (0 ≤ x ≤ 0.20) are rather similar and consist of two peaks (Fig. 1). At 295 K the high velocity peak is not quite as intense as the low velocity peak but is broader by ~0.02 mm/s. Since peak areas are similar, the asymmetries are not due to textural effects introduced during the absorber preparation (Ericsson and Wåppling, 1976). At 77 K the two peaks are approximately symmetric. The peaks are not broadened by the Mn substitution in the structure, and the hyperfine parameters CS and ΔE₀ are not significantly influenced by variations in Mn/Fe nearest neighbors around the Fe atoms. The Mössbauer parameters at 77 and 295 K are given in Table 3.

CS increases by ~0.13 mm/s for the Fe₂(PO₄)₂-sarcopside when the temperature is lowered from 295 to 77 K; apparently the temperature-induced distortions at M₁ and M₂ sites are more pronounced in Mn-substituted sarcopsides and almost cancel the expected increase in ΔE₀ at lower temperatures. According to the theory of Ingalls (1964), an increased distortion is expected to cause a decrease in ΔE₀ for Fe²⁺. From the variations of CS with temperature the metal-oxygen oc-
taledra apparently contract more when the temperature is lowered for Mn-substituted sarcopside.

Mössbauer data: magnetically ordered region

The two peaks in the 295 and 77 K spectra (Fig. 1) originate from two overlapping doublets, as in (Ni,Fe)-sarcopside studied earlier (Ericsson and Nord, 1984). Mössbauer data were collected at ~ 10 K in order to get resolved patterns containing the crucial information of the cation distribution. There is a magnetic transition at 44 K in Fe₃(PO₄)₂-sarcopside. However, only iron at M2 takes part in the magnetic coupling, and the same is true for the (Fe,Mn)-sarcopside (cf. Fig. 2). The magnetic and electric interactions at M2 are of comparable strengths, even at low temperatures. Accordingly, we have used the full Hamiltonian with theoretical intensities without thickness corrections in the fitting procedure (Jernberg and Sundqvist, 1983). The Mössbauer parameters are listed in Table 4.

One paramagnetic doublet for M1 and one magnetically split set of lines for M2 were used as the fitting model. The actual situation is more complicated in the Mn-substituted sarcopside, since both sites show very broad lines and the widths increase with increasing Mn content (Table 4; Fig. 2). The reason for this behavior is not obvious, but could be due to local effects like variations in dipolar fields and/or spin cantings as a result of varying numbers of configurations of Fe and Mn neighbors around the Mössbauer atoms. The data in Table 4 are therefore not as accurate as the data in Table 3. In any case, the preference of Mn to substitute for Fe and M1 is quite clear although not as strong as for Ni in the (Ni,Fe)-sarcopside studied earlier (Ericsson and Nord, 1984).

Discussion

Structural features

There is a close structural relationship between olivine and sarcopside (Fig. 3). Olivine (denoted as Ms(SiO₄)₂) is orthorhombic (Pbm) with two four-fold, six-coordinated sites M1 and M2 (point symmetries: 1 and m). In sarcopside (denoted M3(PO₄)₂) the symmetry has been lowered to monoclinic (P2₁/a; β ≈ 91°), and the four M1 sites in olivine are split into two two-fold sites, a filled “M1” site and a vacant “E” site; the M2 sites in olivine are preserved as “M2” in sarcopside. M1 and M2 sites in sarcopside are octahedrally coordinated with point symmetries 1 and 1.

All atoms occupy similar positions in the two structures (Fig. 3), and the respective unit cell dimensions are very similar. There are some slight structural differences, e.g., the P-O distances are about 0.1 Å shorter than corresponding Si-O distances. In olivine, the nearly regular MO₆ octahedra are connected in serrated chains, but in sarcopside these chains are broken due to the vacant “E” positions, and instead contain trimers of edge-sharing, slightly distorted MO₆ octahedra (Moore, 1972; cf. Figs. 3, 4).

In both structure types the “(M2)O₆” octahedra are slightly larger and display a somewhat larger scatter in metal-oxygen distances and O-M-O angles than “(M1)O₆.” For example, the average metal-oxygen distances (M1-O) and (M2-O) are 2.095(2) and 2.133(2) Å in Mg₃SiO₆ (Smyth and Hazen, 1973), 2.119(1) and 2.146(1) Å in Mg₅Fe₂₋₅SiO₆ (Wenk and Raymond, 1973), 2.081(2) and 2.084(2) Å in Ni₆(PO₄)₂ (Calvo and Faggiani, 1975), 2.11(1) and 2.15(2) Å in Fe₃Ni(PO₄)₃ (Ericsson and Nord, 1984), and 2.16(1) and 2.18(1) Å in (Fe₀.₇₈Mn₀.₂₂)(Mg₀.₀₁)₃(PO₄)₂ (Moore, 1972). Unfortunately, no structural investigation

Table 3. Mössbauer parameters at 77 K and 295 K for (Feₓ₋ₓMnₓ)₃(PO₄)₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>T(K)</th>
<th>Low vel. peak</th>
<th>High vel. peak</th>
<th>Averaged*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pos. W.</td>
<td>Int. Pos. W.</td>
<td>Int. CS</td>
</tr>
<tr>
<td>Fe₃(PO₄)₂</td>
<td>77</td>
<td>-0.17</td>
<td>0.31 0.31</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>-0.26</td>
<td>0.28 0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>(Fe₀.₇₈Mn₀.₂₂)₃(PO₄)₂</td>
<td>77</td>
<td>-0.16</td>
<td>0.29 0.51</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>-0.25</td>
<td>0.24 0.49</td>
<td>0.51</td>
</tr>
<tr>
<td>(Fe₀.₇₈Mn₀.₂₂)₃(PO₄)₂</td>
<td>77</td>
<td>-0.16</td>
<td>0.28 0.51</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>-0.21</td>
<td>0.27 0.33</td>
<td>0.47</td>
</tr>
</tbody>
</table>

* Average values for iron at M1 and M2 sites
b) These values are somewhat increased due to a small (~1%) Fe³⁺-impurity in the spectrum.

The precision in the fitting procedure is ± 0.01 mm/s in positions, widths and CS, ± 0.08 mm/s in δE₀ and ± 0.01 in intensities.
Fig. 2. Mössbauer spectra of Fe₃(PO₄)₂-sarcopside, recorded at 12.4 K (above), (Fe₀.₉₆Mn₀.₀₄)(PO₄)₂ at 10 K (middle), and (Fe₀.₈₈Mn₀.₁₂)(PO₄)₂ at 10 K (below). The solid lines are the sum of the fitted functions and the dashed lines represent iron at M₁.

Table 4. Mössbauer parameters at low temperatures for (Fe₁₋ₓMnₓ)₃(PO₄)₂ (x = 0.1, 0.2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation</th>
<th>T (K)</th>
<th>CS</th>
<th>ΔE₀</th>
<th>W</th>
<th>Int.</th>
<th>X Fe</th>
<th>CS</th>
<th>ΔE₀</th>
<th>B</th>
<th>W</th>
<th>Int.</th>
<th>X Fe</th>
<th>K_D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃(PO₄)₂</td>
<td>800 bar/300°C</td>
<td>12.4</td>
<td>1.33</td>
<td>3.02</td>
<td>0.34</td>
<td>0.34</td>
<td>1</td>
<td>1.38</td>
<td>3.11</td>
<td>13.7</td>
<td>0.31</td>
<td>0.66</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>(Fe₀.₉₆Mn₀.₀₄)₃(PO₄)₂</td>
<td>200 bar/300°C</td>
<td>10</td>
<td>1.29</td>
<td>3.13</td>
<td>0.80</td>
<td>0.29</td>
<td>0.79</td>
<td>1.36</td>
<td>3.09</td>
<td>13.2</td>
<td>0.50</td>
<td>0.71</td>
<td>0.95</td>
<td>0.19</td>
</tr>
<tr>
<td>(Fe₀.₉₆Mn₀.₀₄)₃(PO₄)₂</td>
<td>800 bar/300°C</td>
<td>10</td>
<td>1.29</td>
<td>3.18</td>
<td>0.74</td>
<td>0.30</td>
<td>0.81</td>
<td>1.35</td>
<td>3.06</td>
<td>13.0</td>
<td>0.48</td>
<td>0.70</td>
<td>0.94</td>
<td>0.25</td>
</tr>
<tr>
<td>(Fe₀.₈₈Mn₀.₁₂)₃(PO₄)₂</td>
<td>200 bar/300°C</td>
<td>10</td>
<td>1.26</td>
<td>3.40</td>
<td>1.28</td>
<td>0.30</td>
<td>0.72</td>
<td>1.36</td>
<td>3.05</td>
<td>13.0</td>
<td>0.61</td>
<td>0.70</td>
<td>0.84</td>
<td>0.51</td>
</tr>
<tr>
<td>(Fe₀.₈₈Mn₀.₁₂)₃(PO₄)₂</td>
<td>800 bar/300°C</td>
<td>10</td>
<td>1.29</td>
<td>3.41</td>
<td>0.80</td>
<td>0.25</td>
<td>0.60</td>
<td>1.34</td>
<td>3.04</td>
<td>12.8</td>
<td>0.60</td>
<td>0.75</td>
<td>0.90</td>
<td>0.16</td>
</tr>
</tbody>
</table>

a) ΔE₀ is the quadrupole splitting (mm/s) and defined as ½ * eQₐₑ¹⁄₂₁/z for both positions.
b) W is the full width at half maximum (mm/s) of the fitted Lorentzian functions.
c) X Fe is the fraction of the M-sites occupied by iron.
d) B is the hyperfine field and given in Tesla.
e) The cation distribution factor K_D is defined in the text.

The precisions in the fitting procedure are: CS, W = ±0.01, ΔE₀, Int = ±0.02, B = ±0.1.
of Fe₄(PO₄)₃-sarcopside has been undertaken so far, but the above data suggest that in this structure "(M2)O₆" is very likely to be the larger octahedron.

Cation distributions and thermodynamical considerations

In a (Fe,M)n(PO₄)₃-sarcopside, the Fe²⁺/M²⁺ cation distribution can be defined by the equilibrium reaction

\[ \text{Fe}^{2+}(\text{M2}) + \text{M}^{2+}(\text{M1}) = \text{Fe}^{2+}(\text{M1}) + \text{M}^{2+}(\text{M2}) \]  

The equilibrium constant at the temperature \( T \) is given by the expression

\[ K_0 = \frac{[X\text{Fe}(\text{M1})]_f [X\text{M}(\text{M2})]_f}{[X\text{Fe}(\text{M2})]_f [X\text{M}(\text{M1})]_f} \]  

\[ K_0 = \frac{[X\text{Fe}(\text{M1})]_f [X\text{M}(\text{M2})]_f}{[X\text{Fe}(\text{M2})]_f [X\text{M}(\text{M1})]_f} \]  

Under this assumption, a random distribution of the metal cations is characterized by \( K_0 = 1 \), while \( K_0 > 1 \) shows that Fe²⁺ preferentially enters the M1 sites.

For the hydrothermally prepared (Fe,Mn)-sarcopside,

\[ K_0(\text{Fe,Mn}) \approx 0.2 \] (average value; cf. Table 4), indicating a strong inverse ordering of Fe²⁺ at the M2 and the larger Mn²⁺ ions at the (presumably) smaller M1 sites. A similar distribution pattern with stronger ordering was found in hydrothermally prepared (Fe,Ni)-sarcopside, with \( K_0(\text{Fe,Ni}) \approx 0.01 \) (Ericsson and Nord, 1984). From these \( K_0 \) values, the relevant cations may be arranged in a sequence with respect to their preference for M1 over M2:

\[ \text{Ni}^{2+} > \text{Mn}^{2+} > \text{Fe}^{2+} \]  

Binary (Ni,M)n(PO₄)₃-sarcopside have been prepared at 1 bar and 1070 K, with the following order of M1-site preference (Nord, 1984):

\[ \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mg}^{2+}, \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Fe}^{2+} \]  

Accordingly, sequence (4) agrees with (5) in spite of different equilibrium conditions and different "base" metals [Fe in (4), and Ni in (5)]. It is therefore worthwhile to estimate a cation distribution coefficient from thermodynamic considerations based on analogous, known \( K_0 \) values, and the assumption that a \( K_0 \) value is almost equal to the \( K_0 \) value in question. For example, \( K_0(\text{Fe,Mn}) \) in a sarcopside might be estimated from \( K_0(\text{Ni,Fe}) \) and \( K_0(\text{Ni,Mn}) \) (Ericsson and Nord, 1984; Nord, 1984) as

\[ K_0(\text{Fe,Mn}) = \frac{K_0(\text{Ni,Fe})}{K_0(\text{Ni,Mn})} \]

\[ K_0(\text{Fe,Mn}) = \frac{[X\text{Fe}(\text{M1})]_f [X\text{M}(\text{M2})]_f}{[X\text{Fe}(\text{M2})]_f [X\text{M}(\text{M1})]_f} \]

\[ K_0(\text{Fe,Mn}) = \frac{[X\text{Fe}(\text{M1})]_f [X\text{M}(\text{M2})]_f}{[X\text{Fe}(\text{M2})]_f [X\text{M}(\text{M1})]_f} \]

\[ K_0(\text{Fe,Mn}) = \frac{[X\text{Fe}(\text{M1})]_f [X\text{M}(\text{M2})]_f}{[X\text{Fe}(\text{M2})]_f [X\text{M}(\text{M1})]_f} \]

\[ K_0(\text{Fe,Mn}) = \frac{[X\text{Fe}(\text{M1})]_f [X\text{M}(\text{M2})]_f}{[X\text{Fe}(\text{M2})]_f [X\text{M}(\text{M1})]_f} \]

\[ K_0(\text{Fe,Mn}) = \frac{[X\text{Fe}(\text{M1})]_f [X\text{M}(\text{M2})]_f}{[X\text{Fe}(\text{M2})]_f [X\text{M}(\text{M1})]_f} \]

\[ K_0(\text{Fe,Mn}) = \frac{[X\text{Fe}(\text{M1})]_f [X\text{M}(\text{M2})]_f}{[X\text{Fe}(\text{M2})]_f [X\text{M}(\text{M1})]_f} \]

(data from Bish, 1981; Ghose and Weidner, 1974; Annersten et al., 1982). The experimental \( K_0 \) value for synthetic (Fe,Mn)-olivine annealed at 1000°C has recently been determined to ~4 (Annersten et al., 1984), so again good agreement is noted.
Mineralogical significance

The $K_{\text{D}}$(Fe,Mn) values, $\sim 4$ for olivine and $\sim 0.2$ for sarcopside, show that in olivine the larger cation ($\text{Mn}^{2+}$) is concentrated at the larger site (M2), while the inverse situation is found in sarcopside. Size effects are not significant and the cation partitioning is mainly controlled by crystal field stabilization energies (CFSE) for $\text{Fe}^{2+}$ ($d^6$, high spin). The divalent manganese ions are in a $d^5$ high spin configuration having no CFSE. Studies of sarcopside-type solid solutions are therefore a valuable complement to the numerous olivine cation distribution studies reported to date.

Sarcopside as a natural mineral, $(\text{Fe,Mn,Mg})_{3}(\text{PO}_4)_3$, is also of interest, because it has been found terrestrially as well as in meteorites. It is probably an exsolution product since it always seems to be associated with graf tonite, $(\text{Fe,Mn,Ca,Mg})_{3}(\text{PO}_4)_3$, or with triphylite, LiFePO$_4$ (Moore, 1972). The amount of manganese is usually less than 25% of the total metal content (cf. Peacor and Garske, 1964; Hurlbut, 1965; Bild, 1974; Fransolet, 1977), which agrees with the solubility limit of our hydrothermally prepared $(\text{Fe,Mn})$-sarcopside (~20%). When sarcopside and graf tonite occur together in nature, manganese is enriched in the latter phase (Olsen and Fredriksson, 1966), in accordance with the much greater solubility of Mn(PO$_4$)$_3$ in Fe$_3$(PO$_4$)$_3$-graf tonite, ~90% (Nord and Ericsson, 1982).

Considering the almost identical unit cell volumes of pure Fe-sarcopside and Fe-graf tonite, the existence of sarcopside is puzzling. Furthermore, there does not seem to be any need to stabilize either Fe-sarcopside or Fe-graf tonite with any other divalent cation. We have, therefore, started further studies of hydrothermal (Fe,M)-sarcopside in order to shed some light on this problem. Mössbauer studies of natural sarcopside samples might also be worthwhile.

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