HEATING-INDUCED CONVERSION OF Sr-CONTAMINATED BRUSHITE — EXAFS DATA ANALYSIS

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The extended X-ray absorption fine structure method was applied to determine changes of the coordination parameters of Sr atoms during the thermal conversion of Sr-contaminated brushite into calcium pyrophosphate. The results revealed that the changes of the crystallographic structure induced by heating are correlated with the rearrangement of the Sr environment. It was also confirmed that Sr may be used as a marker of Ca in cases of thermal conversions of orthophosphate groups into pyrophosphate groups.

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It has been shown [1] that the substitution of Ca by Sr within calcium phosphates is a compound-dependent process. The results reported so far have dealt with the preparations of Sr-contaminated Ca–P compounds produced at a constant temperature. The status of Sr atoms incorporated into Ca–P crystal lattice during thermal treatment of the compound remains unclear.

The problem was investigated using the well-described [2, 3] transition of brushite (DCPD — CaHPO₄·2H₂O) to calcium pyrophosphate (CPR — Ca₂P₂O₇). Brushite, synthesized according to the procedure described previously [4], was heated in air for 8 h at 500°C. Such incineration parameters were selected on the basis of our studies of the bone mineralization process [5]. The simplest method to remove the organic matrix from bone samples, i.e. to produce a material useful for the investigations of the structure of the bone minerals, is ashing of the bone samples for ca. 8 h at 500°C. Therefore the results obtained are directly correlated with the studies of the bone mineralization process. To prepare Sr-contaminated DCPD the procedure for the synthesis of pure DCPD was modified by adding Sr ions (0.5 wt% of Ca) to a solution containing Ca ions. The heating procedure was performed for both pure and Sr-contaminated DCPD. The Sr-contaminated compounds were analysed by extended X-ray absorption fine structure spectroscopy.
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(EXAFS) at the Sr K absorption edge. Using the EXAFS spectra, the coordination parameters (N — coordination numbers, r — interatomic distances) of the Sr atoms were calculated. The thorough description of all experimental methods applied is given elsewhere [1].

Fig. 1. Results of EXAFS data analysis for Sr K edge of brushite at liquid nitrogen temperature. (a) $\chi(k)$ EXAFS oscillations, energy zero corresponds to 16106 eV; (b) magnitude of Fourier transform of $\chi(k)$ in the range $1 \leq k \leq 10$ Å$^{-1}$ using the Hanning window function; (c) the best fit of back Fourier transform taken in the region 1.3–3.0 Å of the $F(R)$ curve (b).

Fig. 2. Results of EXAFS data analysis for Sr K edge of γ-pyrophosphate at liquid nitrogen temperature. (a) $\chi(k)$ EXAFS oscillations, energy zero corresponds to 16106 eV; (b) magnitude of Fourier transform of $\chi(k)$ in the range $1 \leq k \leq 10$ Å$^{-1}$ using the Hanning window function; (c) the best fit of back Fourier transform taken in the region 1.5–3.3 Å of the $F(R)$ curve (b).

The results of the elemental composition studies confirm unequivocally that we were dealing with the compounds in question. No differences between pure and Sr-contaminated compounds are recorded. It should be noted that Sr/Ca atomic ratio did not change during heating. It equaled $(1.98 \pm 0.05) \times 10^{-3}$ for DCPD and $(1.96 \pm 0.04) \times 10^{-3}$ for CPR.
The thermogravimetric data agree with the previously reported results [2, 3] and reveal that two thermal transitions took place during heating of brushite to 500°C. At 180°C an anhydrous form (DCP, monetite — CaHPO₄) is produced which finally transforms at 500°C to γ-CPR. The production of other CPRs (β and α forms) needs heating at higher temperatures (850°C and 1200°C, respectively). The EXAFS data enable a comparison of the coordination parameters of Sr atoms incorporated into DCPD and γ-CPR. It should be emphasized that the structure of the γ-CPR crystals is assumed to be similar to β-CPR [3]. The only difference is the absence of the c-axis regularity characteristic of β-CPR.

The fine structures of the Sr K edge collected for both compounds (Figs. 1, 2) confirm that Sr atoms were incorporated into two different systems. The coordination parameters of Sr atoms are presented in Table. The investigated thermal conversion is related to considerable structural differences between both compounds. DCPD has the P atom tetrahedrally surrounded by four O atoms while γ-CPR contains the pyrophosphate group. The P₂O₇ group has two P atoms which share a bridging O but are also bonded to three other O atoms.

The expected substantial differences are not observed as far as the coordination parameters for the first O shell (Table) are considered. The N and r values for both structures differ slightly. Probably the only difference results from the removal of one O atom from the Sr environment while other Sr–O bonds remained unchanged. It is reflected by a decrease in N by about 1 (Table).

<table>
<thead>
<tr>
<th>Atom type</th>
<th>N</th>
<th>r [nm]</th>
<th>σ² [10⁻² nm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>brushite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>10.7 ± 2.4</td>
<td>0.252 ± 0.003</td>
<td>0.0050</td>
</tr>
<tr>
<td>P</td>
<td>1.0 ± 0.2</td>
<td>0.312 ± 0.004</td>
<td>0.0040</td>
</tr>
<tr>
<td></td>
<td>γ-pyrophosphate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>9.6 ± 1.1</td>
<td>0.256 ± 0.012</td>
<td>0.0085</td>
</tr>
<tr>
<td>P</td>
<td>2.8 ± 0.4</td>
<td>0.332 ± 0.001</td>
<td>0.0080</td>
</tr>
</tbody>
</table>

The major differences between both structures originate from the rearrangement of P atoms at distances greater than 0.3 nm. It might be expected that the appearance of the pyrophosphate group results in an increase in N for the second P shell. Moreover, the Sr–P bond distances are markedly larger for γ-CPR than for DCPD, probably because PO₄ and P₂O₇ are crystallographically independent groups and Sr–P distance are governed by the group dimensions.

Summarizing, it may be stated that in case of DCPD–γ-CPR transition the change of the Sr coordination is directly correlated with the rearrangement of the crystal structure. Probably the same pertains to all thermal conversions of the Ca–P compounds associated with the transition of orthophosphate groups into a
pyrophosphate group. This conclusion offers a new possibility to use Sr atoms as markers of Ca atoms in the experiments dealing with thermal treatment of Ca–P compounds.

References