Whewellite crystallization from uric acid solutions

CATERINA RINAUDO, MARJNELLA FRANCHINI-ANGELA
Dipartimento di Scienze della Terra dell’Università, Via San Massimo 22, 10123 Torino (Italy)

ABSTRACT. — The influence of the anhydrous uric acid (C₅H₄N₄O₃) on the whewellite (CaC₂O₄ · H₂O) crystallization has been evidenced at 40°C, pH = 3.0 and 5.0. Increasing amounts of uric acid in solutions reduce the number of whewellite crystals but increase their size. No heterogeneous nucleation or epitaxial growth of whewellite onto anhydrous uric acid was observed under the above experimental conditions.

Key words: whewellite, anhydrous uric acid, crystal growth, nucleation.

Introduction

According to many authors the uric acid could have some influence on the whewellite (CaC₂O₄ · H₂O) crystallization. LONSDALE (1968 a,b) supposed that the two modifications of the uric acid, anhydrous C₅H₄N₄O₃ and dihydrated C₅H₄N₄O₃ · 2H₂O, would be suitable substrates for epitaxial growth of the calcium oxalate. As a matter of fact the analysis of their structural features shows a good agreement between the lattice parameters for several contact planes (MANDEL and MANDEL, 1981). In order to evidentiate this epitaxy other authors carried out Ca-oxalate growth experiments both in aqueous (MEYER et al., 1976; DEGANELLO and COE, 1983) and in buffered solutions (COE et al., 1975; PAK and ARNOLD, 1975; PAK et al., 1976; SARIG et al., 1984) by adding small anhydrous uric acid seeds. From these experiments it turns out that whereas in aqueous solutions the uric acid seems to induce epitaxial growth of whewellite crystals (MEYER et al., 1976; DEGANELLO and COE, 1983) no heterogeneous nucleation of Ca-oxalate monohydrate is observed in the buffered ones (COE et al., 1975; PAK and ARNOLD, 1975; PAK et al., 1976).

We consider again this subject and we report here preliminary results on the crystallization of whewellite from aqueous solutions of oxalic acid and calcium chloride in which proper amounts of uric acid in order to obtain the crystallization of the anhydrous uric acid were added: in fact, under the T and P of the experiments, this is its thermodynamically stable phase.

Experimental

Preliminary experiments showed different behaviour in the whewellite crystallization when uric acid was added to the growth solutions. In particular, noticeable influence was observed at the following experimental conditions: [Ca]₀ = [Ox]₀ = 0.2 · 10⁻³ M, initial pH = 5.0; [Ca]₀ = [Ox]₀ = 0.4 · 10⁻³ M, initial pH = 3.0 In both cases the uric acid concentration did not exceed 10.7 · 10⁻⁴ M in order to avoid the precipitation of the dihydrated phase (MENTASTI et al., 1983).

Different amounts (50-180 mg/l) of uric acid (C.E. purity 99 %, trademark C. Erba)
TABLE 1

Number of whewellite crystals counted at regular intervals of time as function of increasing uric acid [HU] content

<table>
<thead>
<tr>
<th>pH=3.0</th>
<th>12 h</th>
<th>24 h</th>
<th>48 h</th>
<th>72 h</th>
<th>96 h</th>
<th>120 h</th>
<th>pH=5.0</th>
<th>12 h</th>
<th>24 h</th>
<th>48 h</th>
<th>72 h</th>
<th>96 h</th>
<th>120 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.18</td>
<td>0.21</td>
<td>0.22</td>
<td>0.21</td>
<td>0.18</td>
<td>0.18</td>
<td>0.0</td>
<td>0.19</td>
<td>0.42</td>
<td>0.43</td>
<td>0.47</td>
<td>0.51</td>
<td>0.51</td>
</tr>
<tr>
<td>2.97·10⁻³ M</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>2.97·10⁻³ M</td>
<td>1.02</td>
<td>1.07</td>
<td>1.00</td>
<td>1.06</td>
<td>1.08</td>
<td>1.09</td>
</tr>
<tr>
<td>5.95·10⁻³ M</td>
<td>0.09</td>
<td>0.75</td>
<td>0.84</td>
<td>1.06</td>
<td>1.06</td>
<td>1.06</td>
<td>5.95·10⁻³ M</td>
<td>0.59</td>
<td>0.84</td>
<td>1.02</td>
<td>1.02</td>
<td>1.02</td>
<td>1.06</td>
</tr>
<tr>
<td>8.92·10⁻³ M</td>
<td>0.08</td>
<td>0.25</td>
<td>0.49</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>8.92·10⁻³ M</td>
<td>0.60</td>
<td>0.90</td>
<td>1.00</td>
<td>1.06</td>
<td>1.03</td>
<td>1.05</td>
</tr>
<tr>
<td>10.70·10⁻³ M</td>
<td>0.05</td>
<td>0.24</td>
<td>0.32</td>
<td>0.38</td>
<td>0.38</td>
<td>0.39</td>
<td>10.70·10⁻³ M</td>
<td>0.19</td>
<td>0.42</td>
<td>0.43</td>
<td>0.47</td>
<td>0.47</td>
<td>0.51</td>
</tr>
</tbody>
</table>

The crystal number is referred to 1 mm³ on the photographs.  a) [Ca] = [Ox] = 0.4 · 10⁻³ solutions initial pH = 3.0.  b) [Ca] = [Ox] = 0.2 · 10⁻³ M solution, initial pH = 5.0.

were dissolved at about 60° C in 50 ml of bidistilled water, then cooled down to 40° C. This temperature reached, 25 ml of CaCl₂· 2H₂O and 25 ml of H₂C₂O₄· 2H₂O solutions properly concentrated in order to obtain final calcium and oxalate concentration of 0.2 · 10⁻³ M and 0.4 · 10⁻³ M were added. The solution pHs — 5.0 or 3.0 — were adjusted by addition of 0.2 M ammonia solutions. All the experiments were carried out at 40° C.

The solutions were observed, by optical microscope, at regular intervals of time and, every time, several photographs were taken. The crystals were recognized on the basis of their habit, which was well known in pure aqueous solutions (RINAUDO and BOISTELLE, 1980; BOISTELLE and RINAUDO, 1981; FRANCHINI-ANGELA and AQUILANO, 1984). For each experimental condition the number of oxalate crystals was counted on the photographs.

Results and discussion

The experiments evidentiated that the presence of uric acid in the Ca-oxalate solutions affects remarkably the nucleation of whewellite. In table 1 (a, b) the average number of whewellite crystals precipitated at regular intervals of time as a function of different uric acid concentrations is reported. It results that from pure solutions a lot of calcium oxalate crystals precipitates within 12 hours, then nucleation stops. On the contrary, from solutions poisoned with uric acid, at first a lower number of Ca-oxalate crystals precipitates, their number decreasing with the uric acid concentration. Furthermore the nucleation of whewellite continues with the time and stops only within 72 hours.

As it concerns the size of the precipitated whewellite crystals, it is strongly affected by the uric acid presence, as shown in figures 1 and 2 (a, b, c). The former shows whewellite crystals precipitated from 0.4 · 10⁻³ M Ca-oxalate solution, the latter shows crystals grown, after a same interval of time, from solutions equally concentrated with respect to the Ca-oxalate in which increasing amounts of uric acid were dissolved. From the figures it turns out that higher amounts...

Fig. 1. — Whewellite crystals precipitated from pure aqueous solution: [Ca] = [Ox] = 0.4 · 10⁻³ M, initial pH = 3.0.
of uric acid allow the growth of larger whewellite crystals. The phenomenon was observed also in solutions supersaturated with respect to the Ca-oxalate but undersaturated with respect to the uric acid ($< 4.57 \cdot 10^{-4}$ M at pH = 5.0). When the solutions were supersaturated with respect to both, the anhydrous uric acid precipitated first because of its shorter induction time.

It can be pointed out that, under our experimental conditions, any influence of the Ca-oxalate on the uric acid crystallization, neither heterogeneous nucleation or epitaxial overgrowth of whewellite on anhydrous uric acid crystals was observed.

As it concerns the crystal morphology and habit, no reciprocal influence was observed, the crystals of both, uric acid and whewellite, being the same as grown in pure aqueous solutions (Rinaudo and Boistelle, 1980; Boistelle and Rinaudo, 1981; Aquilano and Franchini-Angela, 1981; Franchini-Angela and Aquilano, 1984).

In conclusion four remarkable results can be evidenced from our experiments:

1) the presence of suitable amounts of uric acid reduces the nucleation of whewellite;
2) in the Ca-oxalate solutions poisoned with uric acid large whewellite crystals grow; although the reasons of the phenomenon has not still now been investigated, this suggests a method to obtain large whewellite crystals;
3) no heterogeneous nucleation or epitaxial overgrowth of whewellite on anhydrous uric acid crystals occur; 4) the crystal morphology and habit of whewellite is not affected by the presence of uric acid in the mother solutions.

**Acknowledgments.** — The authors wish to thank Prof. F. Abbona for the critical revision and the « Consiglio Nazionale delle Ricerche » (CNR, Italy) for the financial support (Grant N. 8300513.05).
REFERENCES


