

Whewellite crystallization from uric acid solutions

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ABSTRACT. — The influence of the anhydrous uric acid ($C_5H_4N_4O_3$) on the whewellite ($CaC_2O_4 \cdot H_2O$) 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.

RIASSUNTO. — È stata evidenziata l'influenza dell'acido urico anidro ($C_5H_4N_4O_3$) sulla cristallizzazione della whewellite ($CaC_2O_4 \cdot H_2O$) a 40° C, pH = 3,0 e 5,0. Tenori crescenti di acido urico nelle soluzioni fanno diminuire la nucleazione della whewellite, ma ne determinano un aumento di dimensione dei cristalli. Nelle condizioni sperimentali studiate non si è osservata nucleazione eterogenea, né epitassia di whewellite su cristalli di acido urico.

Parole chiave: whewellite, acido urico anidro, crescita cristallina, nucleazione.

Introduction

According to many authors the uric acid could have some influence on the whewellite ($CaC_2O_4 \cdot H_2O$) crystallization. LONSDALE (1968 a,b) supposed that the two modifications of the uric acid, anhydrous $C_5H_4N_4O_3$ and dihydrated $C_5H_4N_4O_3 \cdot 2H_2O$, 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 evidence 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: $[Ca]_i = [Ox]_i = 0.2 \cdot 10^{-3}$ M, initial pH = 5.0; $[Ca]_i = [Ox]_i = 0.4 \cdot 10^{-3}$ M, initial pH = 3.0. In both cases the uric acid concentration did not exceed $10.7 \cdot 10^{-4}$ 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

pH=3.0 [HU]	12 h	24 h	48 h	72 h	96 h	120 h	pH=5.0 [HU]	12 h	24 h	48 h	72 h	96 h	120 h
0.0	24	24	25	24	26	26	0.0	25	26	24	25	27	26
$2.97 \cdot 10^{-4}$ M	0.18	1.01	1.19	1.21	1.22	1.21	$2.97 \cdot 10^{-4}$ M	1.02	1.87	1.80	1.91	1.95	1.95
$5.95 \cdot 10^{-4}$ M	0.09	0.75	0.84	1.06	1.06	1.10	$5.95 \cdot 10^{-4}$ M	0.59	0.84	1.02	1.02	1.02	1.06
$8.92 \cdot 10^{-4}$ M	0.08	0.25	0.49	0.50	0.53	0.53	$8.92 \cdot 10^{-4}$ M	0.50	0.90	1.00	1.06	1.03	1.05
$10.70 \cdot 10^{-4}$ M	0.05	0.21	0.32	0.38	0.38	0.39	$10.70 \cdot 10^{-4}$ M	0.19	0.42	0.43	0.47	0.47	0.51

The crystal number is referred to 1 mm² on the photographs. - a) $[Ca]_i = [Ox]_i = 0.4 \cdot 10^{-3}$ solutions initial pH = 3.0. b) $[Ca]_i = [Ox]_i = 0.2 \cdot 10^{-3}$ 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 $CaCl_2 \cdot 2H_2O$ and 25 ml of $H_2C_2O_4 \cdot 2H_2O$ solutions properly concentrated in order to obtain final calcium and oxalate concentration of $0.2 \cdot 10^{-3}$ M and $0.4 \cdot 10^{-3}$ 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 evidenced 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 $0.4 \cdot 10^{-3}$ 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

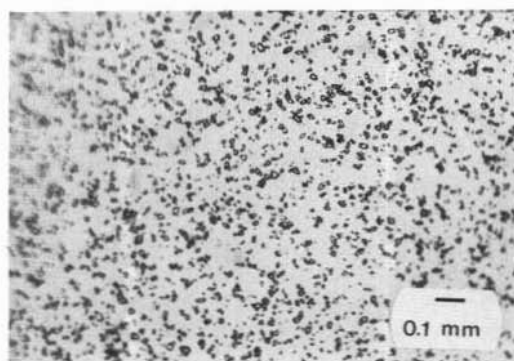
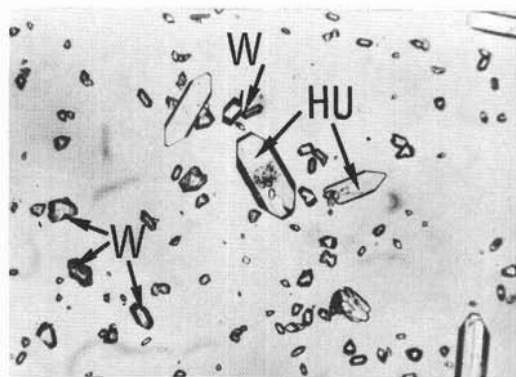
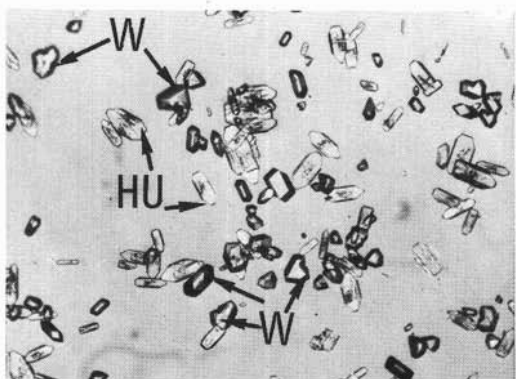


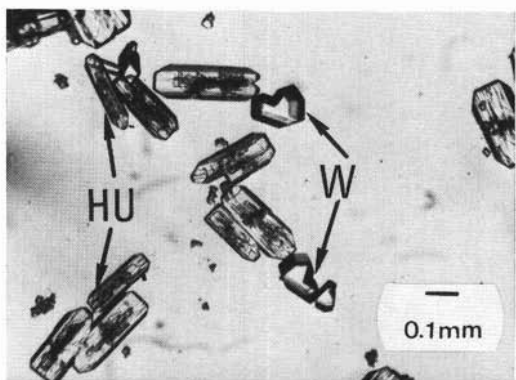
Fig. 1. — Whewellite crystals precipitated from pure aqueous solution: $[Ca]_i = [Ox]_i = 0.4 \cdot 10^{-3}$ M, initial pH = 3.0.



a)



b)



c)

Fig. 2 (a, b, c). — Whewellite crystals grown, during a same interval of time, from solutions with the same Ca-oxalate concentrations as in fig. 1, and increasing uric acid concentration. From the top: $2.97 \cdot 10^{-4}$ M, $5.95 \cdot 10^{-4}$ M, $8.92 \cdot 10^{-4}$ M. W = whewellite crystals; HU = monoclinic anhydrous uric acid crystals.

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).

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