ISSN 1028-334X, Doklady Earth Sciences, 2007, Vol. 413A, No. 3, pp. 339–342. © Pleiades Publishing, Ltd., 2007.
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GEOLOGY

Pseudomorphism of Weddellite in Uroliths

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Presented by Academician N.P. Yushkin April 26, 2006

Received May 10, 2006

DOI: 10.1134/S1028334X07030038

The crystals of calcium oxalate attract attention because of their wide abundance in different human organs and tissues (urinoexcretory pathways, teeth, bones, mammary glands, and others). Calcium oxalate in uroliths occurs in two (dihydrate and monohydrate) crystalline forms. It is important to study the crystal genesis and transformation of oxalates, because no reliable methods of their nonsurgical removal from the human organism have been found as yet.

The crystals of calcium oxalate monohydrates $CaC_2O_4 \cdot H_2O$ (whewellite) are colorless, orthorhombic, and monoclinic. The space group is $P21/n$, $Z = 8$, with unit cell parameters $a_0 = 6.290$ Å, $b_0 = 14.583$ Å, $c_0 = 10.116$ Å, and $\beta = 109.46°$ [13]. In nature, whewellite mainly occurs in sedimentary rocks that contain syngenetic or migration organic matter.

Calcium oxalate dihydrates $CaC_2O_4 \cdot 2H_2O$ (weddellite) form dipyramidal tetragonal crystals. The space group is $I4/m$ ($Z = 8$). The unit cell parameters are $a_0 =$ 12.40 Å, $c_0 = 7.37$ Å [1]. Calcium oxalate dihydrate was found for the first time in the bottom sediments of the Weddell Sea. It is noteworthy that weddellite shows signs of transformation into whewellite after storage for one month [10]. In monograph [2], Zuzuk reported the presence of faces of dipyramids {101}, {112}, {111}, and prisms {100}, {110} on equant weddellite crystals. Goniometric studies carried out by Kadurin and Chepizhko [3] revealed that the crystals of calcium oxalate dihydrates also have tetragonal dipyramids {113}, which impart a flattened appearance along the fourth-order axis. According to [6, 7, 11], weddellite occurs as spherulites, while whewellite forms dipyramidal crystals. This conclusion is inconsistent with our observations. Nevertheless, we do not consider it erroneous, because the conditions of transformations of oxalates and formation of their pseudomorphs have not been established as yet. It should be noted that some features of oxalate transformation were discussed in [4, 5, 11, 12].

It was found that calcium oxalate uroliths account for 60–70% of all cases of urolithiasis [4]. Based on analysis of the morphology and anatomy of the biomineral formations, oxalate uroliths are divided into three major types: spherulitic uroliths (nodular zoned aggregates), crystalline uroliths (druse intergrowths of randomly oriented crystals), and mixed uroliths (consisting of both spherulites and crystals). X-ray diffraction analysis showed that spherulitic oxalate-bearing uroliths consist of whewellite. XRD patterns of the crystalline aggregates display reflections typical of both whewellite and weddellite. The weddellite-only reflections are rare. In thin sections, biominerals are well distinguished by optical properties and morphology.

Our study was aimed at establishing the features of transformation (pseudomorphism) of weddellite in uroliths, as well as at studying the morphology of whewellite crystals from pseudomorphs after weddellite. The study objects were oxalate uroliths.

The samples were studied with optical (MBC-10, MIN-8) and scanning electron (JSM 6400 JEOL) microscopes. XRD powder diffraction patterns were obtained on a DRON-2 diffractometer.

Weddellite in druse-like crystalline uroliths looks like flattened dipyramidal crystals from 0.05 to 1.5 mm in size (Fig. 1). Under binocular microscope, they are colorless, more rarely whitish, of variable transparency. In the SEM images, calcium oxalate dihydrates look as well-shaped crystals with no signs of disintegration or dissolution. Two crystal habits are predominant: pyramid {101} in combination with prism {100} and rarer {111} and {110}.

The study of oxalate stones in thin sections under a polarization microscope showed that calcium oxalate dihydrates typically occur as individual well-shaped (orthorhombic in plan view) crystals and their aggregates. In crossed nicols, they demonstrate characteristic bright interference colors (yellow, blue, and red). In transmitted light, the weddellite crystals show a zoned (Fig. 2a) and less common homogenous pattern. X-ray

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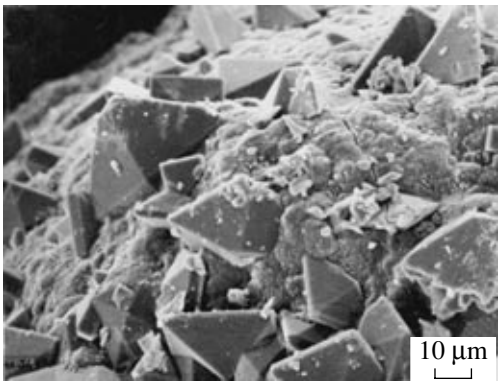

Fig. 1. Crystalline type of urolith: dipyramidal crystals of weddellite (sample 10).

study of zoned and homogenous dipyramidal crystals revealed only weddellite reflections. According to our data, the weddellite-bearing uroliths account for ~1.5% of all oxalate uroliths. XRD patterns of these samples obtained after five and nine years revealed no weddellite transformation into whewellite at dry storage.

The opacity of some dipyramidal crystals of calcium oxalate dihydrates may indicate chemical and structural transformations (pseudomorphism) of the biomineral. In thin sections, pseudomorphed crystals have a block structure (Fig. 2b). XRD patterns indicate that some transformed crystals are calcium oxalate monohydrates. The weddellite matrix contains a variable number of whewellite inclusions (Table 1), with universal predominance of weddellite. During preparation of thin sections, brittle weddellite crystals are often crushed to release whewellite.

Whewellite grains extracted as individual crystals or intergrowths from pseudomorphs after weddellite are pale yellow or gray, with an average size of about 100 μm (Fig. 3). The crystals are well shaped. Study of single crystals confirmed that individual whewellite crystals are monocrystals. However, all unit cell parameters from one of the studied crystals seemed to be 0.5–1% lower than the table values according to ASTM data [9], while the unit cell volume was 2% less.

Morphological analysis of calcium oxalate monohydrates extracted from pseudomorphs after one urolith showed that usual equilibrium simple whewellite forms {100}, {021}, {010}, and $\{12\bar{1}\}$ are supplemented with faces $\{21\bar{4}\}$, {130}, $\{10\bar{1}\}$, and $\{16\bar{3}\}$, and macrosteps with flat surfaces $\{11\bar{1}\}$, which were not observed in the synthesized inorganic systems [8]. Some crystals contain splitted sectors with the formation of faces $\{13\bar{4}\}$ in cracks. Edges between adjacent faces (021) and $(0\bar{2}1)$, as well as between faces $(\bar{1}21)$ and $(\bar{1}\bar{2}1)$, on monocrystal grains are typically smoothed, with macrosteps and rough relief observed

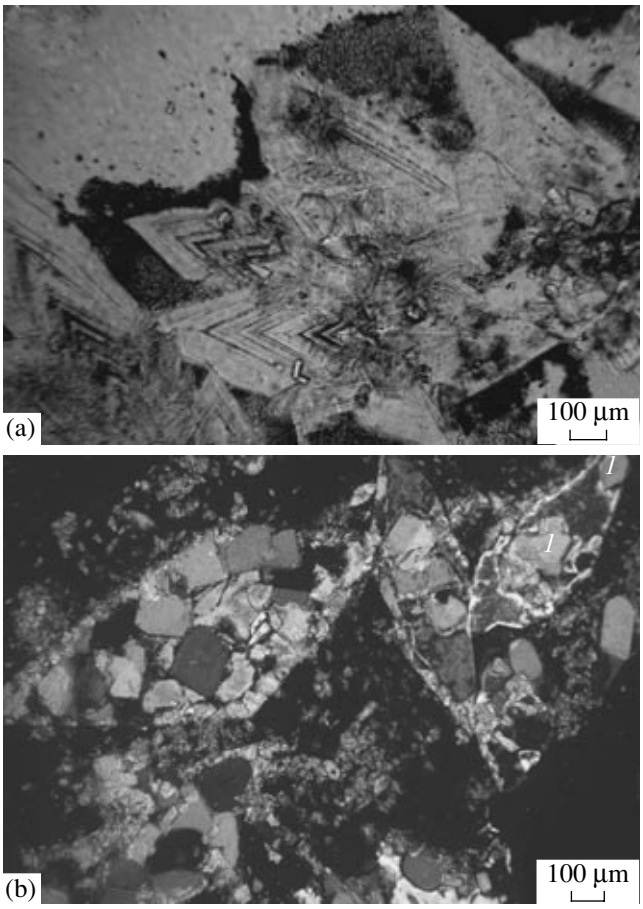

Fig. 2. Crystals of (a) zoned and (b) block weddellite (sample 5) in thin section of urolith, crossed nicols. *1*, whewellite grains.

under high magnification. We believe that the unusual shapes of crystals attest to an active disequilibrium transformation of weddellite into whewellite, which contained the studied grains at the moment of the urolith extraction from the human organism. Never did we find uroliths composed of equilibrium euhedral whewellite crystals.

Whewellite-bearing uroliths of monomineral composition have a spherulitic-zoned structure. Similarly to rhythmic zoning of calcium oxalate crystals described in [7], concentric zoning of three orders is also observed in spherulites. Spherulite aggregates are morphologically different. They can consist of acicular, platy, and prismatic individuals. The studied spherulite aggregates rarely contain weddellite, attesting to the triviality of calcium oxalate dihydrates confined to the spherulite cores. Some monohydrate grains, which compose pseudomorphs after weddellite, often serve as nuclei that initiate spherulite growth. In addition to weddellite and pseudomorphs after weddellite, clots of organic matter can occur in the growth center of spherulites.

Thus, the results of our investigations suggest the following conclusions: (i) dipyramidal weddellite crys-

XRD data on partially pseudomorphed crystalline aggregates of weddellite

d	Sample 4		Sample 5		Sample 10		Sample 10*		Sample 44		Sample 50	
	h k l (*I*)		*h k l* (*I*)		*h k l* (*I*)		*h k l* (*I*)		*h k l* (*I*)		*h k l* (*I*)	
	1	2	1	2	1	2	1	2	1	2	1	2
8.75	–	–	–	–	1 1 0 (17)	–	–	–	1 1 0 (16)	–	1 1 0 (10)	–
6.18	2 0 0 (100)	–	2 0 0 (63)	–	2 0 0 (100)	–	2 0 0 (100)	–	2 0 0 (100)	–	2 0 0 (100)	–
5.94	–	1 0 –1 (37)	–	1 0 –1 (32)	–	1 0 –1 (66)	–	1 0 –1 (22)	–	1 0 –1 (49)	–	1 0 –1 (24)
5.80	–	–	–	–	–	1 1 0 (9)	–	The same	–	1 1 0 (10)	–	–
4.41	2 1 1 (61)	–	2 1 1 (40)	–	2 1 1 (56)	–	2 1 1 (45)	″	2 1 1 (54)	–	2 1 1 (31)	–
3.89	–	–	3 1 0 (8)	–	3 1 0 (16)	–	3 1 0 (10)	″	3 1 0 (8)	–	3 1 0 (7)	–
3.64	0 0 2 (11)	–	0 0 2 (23)	0 2 0 (13)	The same	0 2 0 (44)	0 0 2 (27)	″	The same	0 2 0 (23)	0 0 2 (7)	0 2 0 (12)
3.08	–	–	4 0 0 (11)	–	4 0 0 (13)	–	4 0 0 (15)	″	4 0 0 (12)	–	4 0 0 (8)	–
2.96	–	2 0 –2 (2)	–	2 0 –2 (20)	–	2 0 –2 (38)	–	2 0 –2 (11)	–	2 0 –2 (35)	–	2 0 –2 (14)
2.91	–	3 1 0 (8)	–	–	–	3 1 0 (6)	–	–	–	3 1 0 (4)	–	–
2.809	2 2 2 (29)	–	2 2 2 (16)	–	2 2 2 (25)	–	2 2 2 (13)	–	2 2 2 (29)	The same	2 2 2 (12)	–
2.77	4 1 1 (74)	–	4 1 1 (100)	–	4 1 1 (98)	–	4 1 1 (60)	–	4 1 1 (97)	″	4 1 1 (46)	–
2.48	–	–	–	–	–	1 1 2 (8)	–	–	The same	1 1 2 (8)	–	–
2.419	5 1 0 (10)	–	5 1 0 (10)	–	–	–	–	–	–	–	–	–
2.394	–	–	1 0 3 (16)	–	–	–	–	–	–	–	1 0 3 (20)	–
2.337	5 0 1 (11)	–	5 0 1 (10)	–	–	–	5 0 1 (24)	–	–	–	5 0 1 (4)	–
2.24	2 1 3 (7)	–	2 1 3 (32)	–	2 1 3 (30)	–	2 1 3 (24)	–	2 1 3 (53)	–	2 1 3 (20)	–
2.114	5 3 0 (5)	–	5 3 0 (8)	–	5 3 0 (18)	–	5 3 0 (8)	–	5 3 0 (11)	–	5 3 0 (7)	–
2.076	–	–	–	–	The same	3 2 1 (5)	–	–	–	3 2 1 (4)	–	–
1.95	6 1 1 (15)	–	6 1 1 (11)	–	6 1 1 (10)	–	6 1 1 (15)	–	6 1 1 (17)	The same	6 1 1 (8)	–
1.90	4 1 3 (20)	–	4 1 3 (15)	–	4 1 3 (17)	–	4 1 3 (18)	–	4 1 3 (38)	″	4 1 3 (21)	–
1.83	–	–	5 3 2 (8)	–	5 3 2 (13)	–	5 3 2 (6)	–	5 3 2 (12)	″	5 3 2 (5)	–
1.74	–	–	–	3 2 –3 (5)	5 0 3 (15)	–	–	–	5 0 3 (11)	″	–	–

Note: (1) Weddellite, (2) whewellite. (*) Two druse stones were analyzed in sample 10.

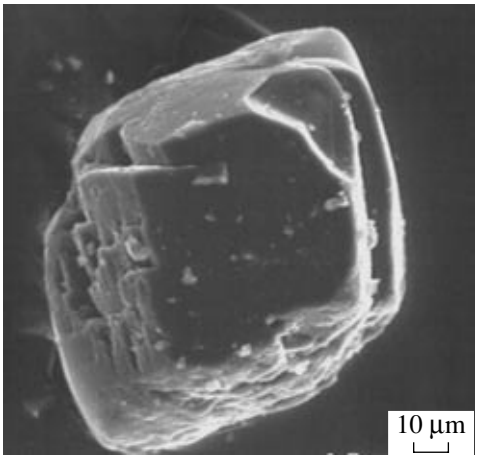

Fig. 3. Whewellite crystal from pseudomorphs after weddellite.

tals, which underwent partial pseudomorphism and retained the outer shell, mainly represent normal weddellite in terms of XRD characteristics; (ii) oxalate dihydrate crystals from uroliths are not transformed under dry conditions; (iii) whewellite grains taken from pseudomorphs after weddellite monocrystal demonstrate unusual disequilibrium simple forms, testifying to active transformation of dihydrate calcium oxalate into the monohydrate variety; and (iv) complete pseudomorphs of whewellite after weddellite occur in spherulite cores and often serve as their nucleation centers.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 06-05-64755a), the Foundation of the President of the Russian Federation for the Support of Leading Scientific Schools (project no. NSh-5191.2006.5), and the Presidium of the Russian Academy of Sciences (Basic Research Programs "Origin and Evolution of the Biosphere" and "Development of Methods for Obtaining Chemical Matters and Synthesis of New Materials").

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