Poster Presentations

[MS18-P12] Crystallization Conditions of Biogenic Calcium Oxalates with Different Water Content

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Biogenic calcium oxalates are quite widespread in nature. Thus, weddellite, $CaC_2O_4 \cdot (2+x) H_2O$ ($x \leq 0.5$), occurs in peat and calcareous lake sediments, in biofilms on the surface of limestone, in plants. Whewellite, $CaC_2O_4 \cdot H_2O$, is often found in cracks and cavities in coalbed, sedimentary rocks containing organic substance (in bituminous shale, etc.) and in biological concretions. And both whewellite and weddellite are the main minerals of the human urinary system stones. The purpose of given work is to analyze the influence of crystallization conditions on the formation of different biogenic calcium oxalates: in renal stones and in biofilms on the surface of carbonate rocks, as well as to clarify the effect of additives on the weddellite formation with different amounts of zeolitic water.

According to our collection (more than 1000 renal stones), 46% of samples contain weddellite, and 5% are monoweddellite. The results of thermodynamic calculations shows that whewellite is the stable phase of calcium oxalate under physiological conditions, despite the fact that the frequency of weddellite occurrence in calcium oxalate uroliths is very significant. In carrying out the biomimetic synthesis it was found that in human's physiological liquid conditions (urine) simulating on the inorganic components only whewellite can be obtained. Joint crystallization of whewellite and weddellite occurs in the presence of organic substance (ovalbumin, gelatin, protein-containing media) or microorganisms (bacteria and viruses), as well as with the addition of magnesium ions and sodium to the solution.

Metasomatic crystallization of calcium oxalate hydrates was investigated under the influence of *Aspergillus niger* strain, active producer of organic acids. The crystallization of calcium oxalate hydrates starts with formation of almost ideal dipyramidal and dipyramidal-prismatic crystals of weddellite at pH values < 5. Morphology and size of the tetragonal weddellite crystals are closely related to the weddellite crystals observed in the oxalic patina on the surface of marble and limestone monuments in Tauric Chersonesos (Ukraine, Crimea). At lower pH values whewellite forms as well. It was found that weddellite crystals obtained in different conditions differs in values of a unit cell parameter as well as in 'zeolitic' water amount. Thus the values of a unit cell parameter for the weddellite crystals from renal stones range from 12.336 to 12.378 Å. The values of *a* unit cell parameter for the weddellite crystals obtained in the presence of bacteria and viruses range from 12.341 to 12.354 Å. Based on the *a* unit cell parameter, the range of 'zeolitic' water amount variations in the structures of weddellite crystals from biofilms (from 12.347 to 12.368 Å) is substantially less than in the crystals synthesized under the action of microscopic fungi in vitro (от 12,329 до 12.368 Å).The maximum value of *x* (0.37 a.p.f.u.) was determined for weddellite crystals from renal stones. According to the *a* unit cell parameter, the limiting value of *x* for the weddellite from biofilms formed on the surface of carbonate rocks are very close to this value.

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