Factors Affecting Formation and Stability of Calcium Oxalates, Main Crystalline Phases of Human Urinary Tract Stones

A.R. Izatulina, Yu.O. Punin, A.G. Shtukenberg, O.V. Frank-Kamenetskaya, V.V. Gurzhiy

Saint-Petersburg State University, Dept. Crystallography, Saint-Petersburg, Russia
E-mail: alina.izatulina@mail.ru

Oxalate mineralization in living organisms is paid a high attention due to its wide distribution. Calcium oxalates occur in the human body (urinary tract stones, calcifications in lungs, the crystals in the bone marrow, etc.), animals (cats urinary tract stones), as well as in plants. Most of calcium oxalates are found in the pathogenic formations in human urinary system. The part of oxalate kidney stones ranges from 50 % to 75 % depending on the geographical region.

Monogene oxalate stones usually consist of calcium oxalate monohydrate (whewellite, $CaC_2O_4 \cdot H_2O$), or (more rarely) calcium oxalate dihydrate (weddellite, $CaC_2O_4 \cdot 2H_2O$). Quite often there are also bimineral stones, formed by the both oxalates. Under normal conditions physiological liquid (urine) is several times supersaturated with respect to calcium oxalate, i.e. formation of oxalate kidney stones should occur in any healthy human organism, however, it is not happening in reality. The literature survey has shown a strong contradictory of the available data – for the same growth conditions not only significantly different solidification rates, but also formation of different crystalline phases (whewellite and weddellite) are reported. Moreover, weddellite to whewellite phase transformation can occur with quite different rates under the same crystallization conditions. Thus, there are some additional factors affecting formation and stability of the calcium oxalate phases. The main role belongs to various impurities, which can strongly shift the phase equilibria, change crystal structure of the calcium oxalate, or influence the crystallization kinetics.

The main aim of this work is to determine factors, which control formation and stability of weddellite. Model experiments on the weddellite synthesis and identification of factors affecting its formation along with analysis of weddellite crystal chemical features have formed the main approach used here.

Weddellite stability was shown to increase at higher supersaturation, admixture of impurities such as CO_3^{2-}, Mg^{2+} ions, proteins (gelatin, ovalbumin), bacteria and virus.

The rate of weddellite to whewellite phase transformation can depend on the amount of water in the weddellite crystal structure (its correct formula should be written as $CaC_2O_4 \cdot (2+x)H_2O$). Single crystal structure refinement carried out for 10 weddellite samples has shown a strong correlation between amount of “zeolitic” water (x = 0.13 – 0.37 apfu) and the values of lattice constants (a = 12.336 – 12.371 Å, c = 7.345 – 7.360 Å), so that a = 0.149x +12.317 (R^2 = 0.912). These variations reflect changes of interatomic distances. For example, the distance between two W1 water molecules, neighbor to “zeolitic” water from one layer parallel to (001) varies in the range 3.211 – 3.287 Å.

The relationship found allows us to estimate the value of x from the measured lattice constant a in weddellite crystals from renal stones. In most cases x is close to the upper limit. Thus the composition of physiological liquid can control stability of weddellite via amount of water in its crystal structure.

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