Uric acid dihydrate: occurrences in Austria and Norway

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Introduction

Organic minerals are not widespread in Nature and, unlike the most common representatives such as mellite, whewellite and weddellite, the rarer species are often found as inconspicuous crusts and tiny crystals only. For example, uricite (natural uric acid, $C_5H_4N_4O_3$), which was originally described from a bird guano deposit in a cave in Western Australia (Bridge 1974), generally occurs as microscopic whitish platelets. The present contribution describes two occurrences of uric acid dihydrate, an unnamed, naturally occurring compound closely related to uricite, and discusses the origin of the samples. Uric acid dihydrate, chemically $C_5H_4N_4O_3 \cdot 2H_2O$, was previously only described from Italy where it occurred either as single crystals or as aggregates of vitreous transparent microcrystals on the surface of a serpentinite (Artioli et al. 1993). The authors state "These crystals probably result from the weathering of bird droppings and so not meet the strict criteria of the IMA for a new mineral species."

The Austrian specimen

In 2007, the first author obtained a small specimen for analysis which the collector, Josef Metzger, had found on temporary dumps deposited during construction of a new power station near Sportgastein in Gastein valley, Hohe Tauern Mountains, Salzburg, Austria. These dumps are known for micromount-sized specimens of typical Alpine minerals (hosted by gneiss, schists and quartz veins), but also include some rare sulphides (http://www.mindat.org/loc-159262.html). The specimen consists of pale gneiss and shows a spot-like area, on a freshly broken, quartz-rich surface, which is covered with tiny, pale pinkish to flesh-coloured, sometimes also white platelets with a rounded acute-elliptical outline (lancet-like). Some crystals also show sword-like morphologies. The platelets tend to aggregate into subparallel growths. The phase is fragile and either strongly or loosely connected to the matrix. Amidst the crystals lie a few tiny fragments of a brownish chitinous exoskeleton. The sample and especially the morphology of the crystals strongly reminded the first author of several uricite samples identified in the last three years from several localities in Austria, Germany and Italy. In all cases these uricites were more or less clearly the result of (re-?)crystallisation of bird droppings on various rocks and minerals. An X-ray powder diffraction analysis of the Sportgastein sample, however, surprisingly demonstrated that the phase was not uricite, but uric acid dihydrate. The pattern showed good agreement with both the published data (ICDD-PDF 19-1996) and a calculated pattern based on the structure model of Parkin & Hope (1998). The analysis (employing Gandolfi-like X-ray patterns recorded from uncrushed crystal aggregates with a single-crystal diffractometer and Mo *Kα* radiation) was repeated using further crystals from a different area on the specimen, but the result was unchanged. Attempts to measure a single-crystal Raman spectrum were unsuccessful since the laser illumination only led to an intense luminescence background and no visible bands in the spectrum.

The Norwegian specimen

In 1989, the second author received a sample for identification, collected by Lars O. Kvamsdal from the surface of one of the dumps at the Glomsrudkollen zinc mines, Åmot, Modum, Buskerud, Norway. On inspection under a microscope, it showed an area of 3 x 12 mm with tiny, white, elongate platelets grown on a rusty sphalerite matrix (Fig. 2). The crystals were opaque and showed a weak pearly lustre. A small area of hydrozincite also is present on the specimen. It was therefore assumed that the white crystals were another

Fig. 1. Colour photograph of thin crust of tiny elongate uric acid dihydrate (UAD) platelets (pale pinkish to whitish) on quartz-rich gneiss matrix. Maximum size of the crystals is ~0.2 mm. Note the red-brown tiny fragments of a chitinous exoskeleton below the centre. Photo Fritz Schreiber.

Fig. 2. SEM micrograph showing sheaf-like to subparallel intergrowths of elongate plates of uric acid dihydrate from the Glomsrudkollen zinc mines, Åmot, Modum, Buskerud, Norway. SEM photo by Harald Folvik (Natural History Museum, University of Oslo); enhanced in Corel Photopaint by G. Raade.

secondary Zn mineral. A Debye-Scherrer X-ray powder diffraction pattern evidenced a weakly, but reasonably diffracting phase, but the lines of the pattern could not be attributed to any known natural or synthetic compound. The scarce amount of material precluded further studies at that time. In 2010, an EDS spectrum was recorded at the Natural History Museum, University of Oslo, which surprisingly showed only C, N and O as elemental components of the crystals. After exchanging information on natural occurrences of uricite with the first author, a re-evaluation of the powder pattern led to the unambiguous identification of the phase as uric acid dihydrate. The shape of the crystals is very similar to that of the Italian sample (Artioli et al. 1993) and the Austrian sample described above.

Discussion

Before the genesis of the two samples is discussed, the prior knowledge on uric acid dihydrate (hereafter abbreviated as UAD) will be briefly summarised.

UAD has been widely studied since it is, together with uricite/uric acid (Ringertz 1965 and 1966, Shirley & Sutor 1968, Lonsdale & Mason 1966, Artioli et al. 1997) and calcium oxalates (whewellite, weddellite), a common component of human urinary stones (Ringertz 1965, Lonsdale & Mason 1966, Shirley 1966, Hesse et al. 1975, Yong Go et al. 1980, Dosch 1981, Babic-Ivancic et al. 1987, Parkin & Hope 1998). Much less frequently observed in such urinary stones is uric acid monohydrate (Schubert et al. 2005, Zellelow et al. 2010), a compound which has not yet been identified in a geological environment. Uric acid monohydrate appears to be stabilised by a small organic component containing long aliphatic chains (Schubert et al. 2005).

UAD has also been identified as the major component of the white excrement from a budgerigar (Lonsdale & Sutor 1971) and other birds, as well as reptiles (Artioli et al. 1997). It seems that no systematic study on these occurrences has been done yet.

The UAD samples from Austria and Norway are clearly the result of bird droppings. A direct proof are the remnants of a chitinous exoskeleton embedded in the crystal crust from Austria. Occurrences of both UAD and uricite in Nature are typically characterised by a more or less spot-like, crystal-covered area on matrix, often with a rounded outline that reflects the former outline of a wet drop(ping).

The status of UAD as a possible mineral species was addressed by Artioli et al. (1993) who concluded "These crystals [do] not meet the strict criteria of the IMA for a new mineral species." However, if rain or surface humidity (i.e., meteoric water) as part of the hydrogeologic environment is taken into account, the recrystallisation of bird droppings due to interaction with such water could be considered as a natural geological process. Birds are living organisms as are also, for example, lichens and other plants which are known to "produce" metal oxalates on interaction with rocks. Bat droppings often result in guano deposits which may contain various IMA-approved phosphate minerals.

The question arises why some bird droppings cause the crystallisation of uricite and others - apparently more rarely - form UAD. It is well-known that synthetic UAD crystals are not particularly stable; most begin to lose their optical transparency due to dehydration after a few hours or days in air at room temperature (Ringertz 1965, Hesse et al. 1975, Boistelle & Rinaudo. 1981, Zellelow et al. 2010). Metastable UAD precipitated in synthetic urine can be destabilized by a variety of macromolecules (Yong Go et al. 1980). On the other hand, natural UAD crystals are stable at ambient conditions for months and years, even after prolonged X-ray exposures (Artioli et al. 1997, this work).

If bird droppings recrystallise on interaction with rainwater, the concentration of uric acid in the resulting solution and the temperature and speed of crystallisation will influence which compounds form. In colder climates, such as in Alpine Austria and Norway, the higher hydrate, i.e. UAD, might preferentially crystallise instead of uricite. Furthermore, there seems to exist an influence of organic impurities in the droppings, which can be linked to the crystallisation behaviour as well as overall crystallinity and stability.

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