The decomposition of struvite

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Summary. The subaerial decomposition of struvite has been investigated at room temperature ($21 \pm 2°$ C), from which it has been concluded that the decomposition product is newberyite. X-ray power patterns of newberyite, both from a diffractometer and Debye–Scherrer cameras, are given. Comparison of these patterns with other newberyite patterns suggest that the camera pattern is more reproducible; this may be due to grain orientation in the diffractometer mounts.

An investigation of the sub-aerial room temperature decomposition of struvite has recently been completed and in view of the statement of Cohen and Ribbe (1966) that 'subaerial decomposition of struvite to newberyite and/or bobierrite is unlikely' the results would appear to be worth reporting.

MacIvor (1887) reported that 'when exposed for a long time to the air crystals of struvite lose some of their water of crystallisation and become coated with a white powder'. He did not identify the decomposition product, although it appears that he believed the composition to be the same as a nodular phosphate (which he believed to be altered struvite) found in the older and drier deposits of guano. This he later reported as having the composition $Mg_3(PO_4)_2 + xH_2O$ (MacIvor, 1902). He found newberyite and struvite in guano, the former in dry guano ($< 20\%$ water) and the latter in wet ($> 30\%$ water). It appears that he did not feel that the newberyite was formed by decomposition of struvite, but in any case, in view of the water content the decomposition could be either subaqueous or subaerial.

Whitaker (1965) found that a single crystal of struvite left in the atmosphere became coated with newberyite; a conclusion confirmed by Lonsdale and Sutor (1966).

Since then Cohen and Ribbe (1966) have found newberyite as a decomposition product of struvite and have inferred from the dissociation pressure data of Kiehl and Hardt (1933) that the subaerial decomposition of struvite to newberyite is unlikely.

Unfortunately the sources of the struvite in these investigations are varied: that of MacIvor (1887) was bat guano, Whitaker's (1965) source was human excreta, Lonsdale and Sutor (1966) found theirs in human urinary calculi, while Cohen and Ribbe (1966) found their newberyite in bird guano (the evidence that this was from struvite is circumstantial). No chemical analyses were given for any of the samples and in view of this, the present investigation was conducted on synthetic struvite.

Three samples were used:

Commercial magnesium ammonium phosphate hexahydrate (B.D.H. Laboratory Reagent).

Laboratory prepared struvite, made by mixing solutions, one containing 6 g of ANALAR magnesium chloride hexahydrate and $37\frac{1}{2}$ ml concentrated hydrochloric acid (3N) in 1·5 l water, the other containing $37\frac{1}{2}$ g ANALAR diammonium hydrogen phosphate in 100 ml water.

Struvite single crystals prepared by making a solution in 150 ml water of 1·2 g magnesium sulphate heptahydrate, 77 ml concentrated hydrochloric acid and 2·5 g diammonium hydrogen phosphate. This was placed in a beaker in the top of a dessicator, while in the bottom was placed a solution of 25 ml of 0·880 sp. gr. ammonia and 550 ml water; the whole was allowed to stand for two weeks, at the end of which time a number of large crystals (up to 1 mm equant) had grown.

The identity of the first two samples were confirmed by comparison of the X-ray powder photograph with that of Jeffrey (1966). The commercial sample gave a few unidentified extraneous lines while the laboratory-prepared specimen did not. The identity of the single crystals was confirmed by measurement of the cell dimensions.

Small quantities, 2 or 3 g, of the powders were placed in shallow dishes in a thermostatically controlled, well-ventilated room together with about twenty mounted single crystals. During the period of the investigation the temperature of the room varied in the range 19° to 23° C.

Powder specimens were examined at twice weekly intervals in a Debye–Scherrer camera until the presence of another phase was detected and then at approximately weekly intervals until struvite was no longer detected.

One or other of the crystals was examined daily until powder lines were visible and then at longer arbitrary intervals to reduce the effect, if any, of X-rays on the decomposition.

Both powder samples showed additional faint but distinct lines after 36 days, although the change was insufficient to identify newberyite.

No struvite was detected after 214 days in the laboratory prepared specimen or after 283 days in the commercial specimen. The difference in these times may be due to a difference in particle size; Cohen and Ribbe (1966) reported that small particles change before large ones in the decomposition of newberyite; or it may be due to difference in quantity of material in the dishes. Neither was measured.

The decomposition of the single crystals was far more noticeable, all crystals showed distinct and identifiable powder patterns after six days, and the largest crystal (1·0×0·7×0·6 mm) changed completely in 176 days. Although the powder kept the shape of the original crystal no evidence of preferred orientation was found on the patterns. The fact that the crystals decomposed quicker than the powders is probably due to better ventilation about each crystal.

According to Kiehl and Hardt (1933), struvite decomposes to the magnesium ammonium phosphate monohydrate if the reaction proceeds at less than 50° C and the gas is removed as it is formed; also ammonia is not given off below 50° C. To check that the decomposition product was newberyite and not this monohydrate, some phosphor-rösslerite crystals were grown by the method given by Mellor (1929) and allowed to decompose in the atmosphere. This decomposition product is reported to be newberyite (Hägele and Machatschki, 1939). Comparison of X-ray powder films showed that the decomposition products of both struvite and phosphor-rösslerite were identical.

Hence there can be no doubt that struvite will decompose subaerially to newberyite at 20° C. The fact that this occurs at such low temperatures raises the point that newberyite found in kidney and bladder stones (Parsons, 1956; Murphy and Pyrah, 1962; Lonsdale and Sutor, 1966) may not have been deposited as newberyite but be due to decomposition of struvite after the stone has been removed.

The X-ray diffraction patterns of newberyite (table I) were obtained in two different ways; using a diffractometer and Co-*Kα* radiation and using a Debye–Scherrer camera and Cu-*Kα* radiation. Both sets of intensities are averages of several results. The lattice spacings obtained are in good agreement with those of Cohen and Ribbe (1966) but the agreement of the diffractometer intensities is poor, the order of the strongest lines is very different for the two sets of data. This may be due to the difficulty of obtaining randomly oriented specimens in the diffractometer mounts due to the cleavage of newberyite (Cohen and Ribbe, 1966); it is interesting to note that the poorest agreement is for the 020 reflection at 5·34 Å and the prominent cleavage is {010}.

On the other hand the agreement of the relative order of the strongest lines is quite good between the original powder data (X-ray powder data file and card 1-0597) and the present pattern if one allows for close doublets being unresolved in the original pattern, which was taken with Mo-$K\alpha$ radiation. The agreement is even better if the present results are compared with those of Parsons (1956) or Lonsdale and Sutor (1966).

TABLE I. X-ray powder pattern of synthetic newberyite. Debye–Scherrer camera, Cu-$K\alpha$ radiation

d_{obs}	I/I_0	d_{obs}	I/I_0	d_{obs}	I/I_0	d_{obs}	I/I_0
5·95	91	2·798*	53	2·137	9	1·6403	8
5·34	64	2·721	40	2·095	13	1·6152	2
5·12	7	2·665	1†	2·072	12	1·6005	13
4·71	97	2·576	64	2·041*	20	1·5872	15
4·60	26	2·523	17	1·976	11	1·5651	13
4·49	37	2·486*	10	1·930	31	1·5338	1†
4·14	37	2·428	23	1·882*	18	1·5030	6
3·67	20	2·400*	24	1·797	19	1·4911	7
3·57	8	2·367	28	1·758*	17	1·4647	6
3·460	100	2·305	3	1·720	10	1·4458	7
3·185	20	2·272	2	1·6990	3	1·4152	13
3·088	79	2·201	25	1·6789	20	1·4021	6
3·033	90	2·172	13	1·6538	10	1·3864	5
2·971	1†						

* Found to be doublets on diffractometer traces.

† Visible by eye, but too weak to measure on a photometer, intensity given is half the weakest measured.

In this sense the reproducibility is better between the camera patterns than between the diffractometer patterns. As agreement between the present diffractometer and camera patterns is also rather poor, it is felt that the camera patterns are probably the more reliable.

Finally, Sutor and Scheidt (1968) have calculated the intensities of the newberyite powder pattern, down to a spacing of 2·55 Å from knowledge of the single crystal data obtained during the crystal structure determination (Sutor, 1967). Their calculated intensities are in excellent agreement with the film pattern observed in the present investigation allowing for overlapping lines in the present case. This would suggest that orientation effects are very small or absent in the powder data of table I.

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