MAGNESIUM PHOSPHATE MINERAL REPLACEMENT AT MONO LAKE, CALIFORNIA

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Abstract

A new and unique occurrence of newberyite, $MgHPO_4 \cdot 3H_2O$, and monetite, $CaHPO_4$, is reported from Paoha Island, Mono Lake, California. The newberyite is a decomposition product of struvite, $MgNH_4PO_4 \cdot 6H_2O$, which once formed as large crystals (often twinned) in or immediately below a guano deposit; the original struvite morphology has been preserved by a thin, dense veneer of monetite.

The Mono Lake newberyite is orthorhombic (*Pbca*) with cell constants $a = 10.203 \pm 0.005$; $b = 10.679 \pm 0.005$; $c = 10.018 \pm 0.006$ Å. An indexed *x*-ray powder pattern and new data on the dehydration of newberyite are presented. The replacement of struvite by newberyite is discussed in light of its known aqueous chemistry.

Introduction

Newberyite, $MgHPO_4 \cdot 3H_2O$, and monetite, $CaHPO_4$, were identified in unusual crystal relics (Fig. 1) collected on Paoha Island, Mono Lake, California, by Drs. C. M. Gilbert and S. E. Calvert of the University of California. The morphology of the relics indicates that they were once struvite, $MgNH_4PO_4 \cdot 6H_2O$. Struvite has been found mainly in deposits of guano or dung, in putrescent matter, in human urinary sediments and in one instance in the decaying tooth of a mammoth, but it is likely that the Mono Lake specimens grew originally in guano. The struvite crystals, coated with a thin, dense veneer of monetite, were subsequently replaced entirely by newberyite.

Dr. C. M. Gilbert of the University of California at Berkeley kindly consented to write a description of the geologic setting in which the crystal relics were found, and we quote from his personal communication:

"Paoha Island, near the center of Mono Lake, is about 2 miles long in north-south direction and about $1\frac{1}{2}$ miles wide. It is within 2 miles of shore on the south and $2\frac{1}{2}$ miles on the northwest. The deepest portions of the lake (120–170 feet) are close to the island along its south and east shores, and a pronounced sublacustrine trough, or small graben, runs parallel to the eastern shore of the island. Both the rocks of the island and the sublacustrine topography around it suggest that Paoha Island is an uplifted block, probably raised by underlying laccolithic intrusions which broke to the surface along the eastern and northern portions of the island and on Negit Island to the north (Scholl, *et al. in press*).

"Dark colored glassy andesite of recent date occurs on the eastern tip and throughout the northern quarter of Paoha Island, and sulphurous hot springs are locally active on the eastern shore. The remainder of the island consists of sedimentary strata tilted generally westward at a low angle. These strata are poorly consolidated and consist chiefly of silt-size volcanic ash, diatoms, and detrital silt and clay. In the higher parts of the island, 200 to
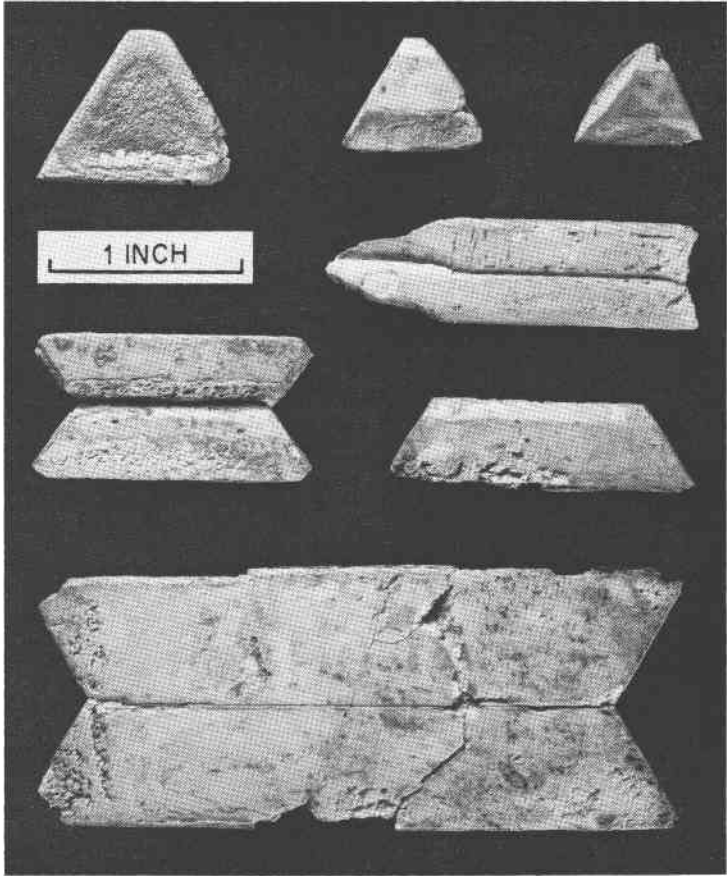
Fig. 1. Selected well-preserved relics of struvite, $MgNH_4PO_4 \cdot 6H_2O$, now replaced entirely by newberyite, $MgHPO_4 \cdot 3H_2O$, and coated with a thin, dense veneer of monetite, $CaHPO_4$. From Paoha Island, Mono Lake, California. Photography by T. Susuki, U.C.L.A.

300 feet above lake level, the sediments are particularly well exposed, and it was here that struvite relics (now newberyite), which are the subject of this paper, were observed and collected. The strata in this locality are largely gray to light brown silty diatomaceous ash interbedded with white diatomite. Some diatomite beds reach thicknesses of several inches and some layers of gray silty ash are as much as a foot or two thick, but much of the exposed section consists of interlaminated layers of ash and diatomite less than a centimeter thick. Several thin convolute layers of fine sand and silt occur in the section.

"These sediments are presumed to be deposits formed on the bottom of an expanded Mono Lake during the Pleistocene period. Cobbles and pebbles of Sierran bedrock occur scattered throughout the strata and are best explained as ice-rafted debris, suggesting a correlation of the ash and diatomite deposits with a stage of glacial advance. Furthermore, Pleistocene shorelines, which are so conspicuous in the landscape around the lake, are nowhere evident on Paoha Island, suggesting a recent elevation of the island.

"The struvite relics occur in various orientations with respect to bedding and seem to be concentrated in particular beds at any given collecting locality. They are found in layers of gray diatomaceous ash and in ash layers containing thin laminae of diatomite, but they have not been found in the thicker diatomite layers. How widely they are distributed is uncertain, but present information suggests that the crystals are stratigraphically controlled in the upper part of the section exposed on Paoha Island. Neither a source nor a means of concentration of the phosphate necessary for the crystals is suggested by field observations to date. An exhaustive examination of the entire island is necessary and will soon be made."

This paper is concerned with the method of replacement of struvite by newberyite. Experimental studies of the thermal decomposition and aqueous chemistry of these minerals when considered in light of this unique occurrence, give evidence that allows us to decide whether the decomposition was subaerial or subaqueous. Incidental to this purpose is a crystallographic study of newberyite.

Experimental Data

Chemical analyses. Wet chemical analyses of two specimens were obtained by C. M. Gilbert (private comm.). The two analyses yielded noticeably different results for Ca, Mg, P and H_2O because each specimen was a mixture of $CaHPO_4$ and $MgHPO_4 \cdot 3H_2O$ in undetermined ratios. The analyses show 0.03 wt.% SiO_2, 0.1% Al_2O_3, 0.04% Fe_2O_3 and traces of MnO, Na_2O and B_2O_3 in each specimen.

X-ray spectrographic analyses

(a) Monetite: Qualitative x-ray fluorescence analysis of the thin, dense veneer of the specimens showed Ca and P in approximately the correct proportions for monetite. During x-ray analysis, the color of monetite changed from off-white to purple, no doubt a result of radiation damage. The presence of other elements was not detected at the 0.05 wt.% level.

(b) Newberyite: Quantitative x-ray fluorescence analysis of newberyite attested to its Mg:P stoichiometry and essential chemical purity, although an electron microprobe analysis showed minor (0.05 wt.%) Ca, S and Cl. Si, Al and Fe were not detected at the 0.05 wt.% level, but a trace of K was recorded. Microscope examination reveals discreet, tiny impurities which probably account for a substantial part of the minor element concentration.

X-ray diffraction studies

(a) Monetite: The eggshell-like veneer of the more well preserved specimens was identified by x-ray diffraction to be monetite although its powder pattern indicates that it is very poorly crystallized. This is the only evidence, if it can be so considered, that monetite may have

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been formed by dehydration of brushite. A further comment on this possibility is presented below.

(b) Newberyite: Newberyite was identified by chemical methods and the x-ray pattern of its ignition product, $Mg_2P_2O_7$, since the relative intensities of the newberyite diffraction peaks do not agree with those cataloged in the ASTM Powder Data File. The unit cell constants measured by Pollman (1961) were used to calculate the d-spacings of reflections consistent with the space group *Pbca*, which Pollman determined for newberyite, and Miller indices were assigned to certain peaks in the newberyite powder pattern. Using CoK_α radiation and quartz as an internal standard, accurate lattice constants were then calculated for the Mono Lake newberyite. After three cycles of least-squares refinement using Burnham's (1962) program, the cell constants were found to be $a = 10.203 \pm 0.005$; $b = 10.679 \pm 0.005$; $c = 10.018 \pm 0.006$ Å. The d-spacings, both observed and calculated, for 60 indexed diffraction peaks are given in Table 1.

TABLE 1. INDEXED X-RAY POWDER PATTERN OF NEWBERYITE, $MgHPO_4 \cdot 3H_2O$,
FROM MONO LAKE, CALIFORNIA. $CoK\alpha$ RADIATION

hkl	d_{obs}	d_{calc}	I/I_0	hkl	d_{obs}	d_{calc}	I/I_0
111	5.94	5.94	30	142	2.300	2.296	5
020	5.34	5.34	100	332	2.207	2.207	5
200	5.10	5.10	5	233	2.197	2.198	5
021	4.71	4.71	60	323	2.175	2.176	5
210	4.60	4.60	20	242	2.139	2.139	5
102	4.49	4.50	10	043	2.091	2.085	5
112	4.14	4.14	10	224	2.071	2.072	5
220	3.69	3.69	10	143	2.043	2.043	5
022	3.65	3.65	5	431	2.031	2.030	5
202	3.57	3.57	5	511	1.966	1.965	5
221	3.460	3.461	40	152	1.929	1.929	20
122	3.441	3.439	10	324	1.886	1.887	5
131	3.186	3.186	20	521	1.8729	1.8725	5
311	3.083	3.083	40	144	1.7970	1.7980	5
113	3.039	3.042	30	225	1.7600	1.7606	5
222	2.969	2.970	1	334	1.7545	1.7547	5
302	2.812	2.814	10	513	1.7182	1.7185	5
132	2.791	2.791	20	600, 352	1.7005	1.7005, 1.7012	5
312	2.721	2.721	20	260, 610	1.6802	1.6805, 1.6793	20
213	2.703	2.703	5	611, 523	1.6561	1.6562, 1.6554	15
040	2.669	2.670	20	450	1.6381	1.6375	5
041	2.580	2.580	40	451	1.6165	1.6151	1
400	2.551	2.551	5	621, 541	1.5997	1.5995, 1.6004	1
232	2.522	2.522	10	612, 262	1.5927	1.5922, 1.5932	1
141	2.501	2.501	10	514	1.5647	1.5649	5
410	2.482	2.481	5	362	1.5039	1.5042	1
104	2.430	2.432	5	171	1.4920	1.4920	10
411	2.409	2.408	10	172, 461	1.4444	1.4447, 1.4444	5
331	2.388	2.388	10	046, 552	1.4152	1.4156, 1.4153	5
240	2.367	2.365	10	712	1.3878	1.3877	5

The relative intensities in Table 1 were averaged from three different packings of both Mono Lake and Skipton Cave newberyites in flat, shallow specimen holders. The perfect (010) cleavage of newberyite makes it difficult to obtain a random orientation of grains in normal diffractometer and powder-camera mounts, so the intensities are quite likely biased. Nonetheless they are consistently reproducible and can be relied on for identification of well-crystallized newberyite. The relative intensities listed on ASTM card no. 1-0597 may represent a random grain orientation, although we were unable to duplicate them with natural newberyite.

For comparison purposes the unit cell parameters of newberyite from Skipton Caves, Victoria (UCLA MS #1765) were determined using CuK_α radiation and quartz as an internal standard. The data in Table 2 show them to be in excellent agreement with the Mono Lake specimen. In addition, Miller indices were assigned to the powder pattern published by McKie (1955) for newberyite from Tanganyika. McKie's sample was reported to have been of high chemical purity (Bassett, 1954), but our refinement of his measured peaks shows substantially larger cell dimensions than the Mono Lake and Skipton Caves newberyites. McKie does not report the use of an internal standard, and it is assumed that his d-spacings were subject to a systematic error. Pollman (1961) used single crystal rotation photographs to determine the cell constants of the Mejillones newberyite, but his values of a and b do not agree with the axial ratio $a:b$ which he reports (second footnote, Table 2).

Dehydration of newberyite. Thermogravimetric analysis of the Mono Lake newberyite revealed no distinct temperature with which loss of water could be associated. At a heating rate of 3° C./min. for unsized crystals the weight loss curve is a smooth function of temperature. Loss of H_2O began at 125° C. and at 260° C. the weight loss exceeded 31% ($-3H_2O$). The sample suffered a total weight loss of 36.1$_4$% ($-3\frac{1}{2}H_2O$) at 575° C., leaving the decomposition product, $Mg_2P_2O_7$.

Equilibrium was obviously not attained at this rapid heating rate, and for that reason a prolonged study of the dehydration was undertaken, using a small oven open to the atmosphere. Unsized crystals maintained at 95° C. for 24 hours showed less than 0.4% weight loss; however, a 26% weight loss was measured after heating for 250 hours at 110° C. Gradual weight loss was still being registered when heating was discontinued. These results are in accord with those of vom Rath (1879) who reported that newberyite "loses its water" at 110° C. A sample of newberyite ground for x-ray analysis showed no change after heating 24

TABLE 2. CELL CONSTANTS AND AXIAL RATIOS FOR NEWBERYITE

Locality	a	b	c	$a:b:c$	Source
Mono Lake, Calif.	10.203±.005	10.679±.005	10.018±.006	0.9554:1:0.9381	Present investigation
Skipton Caves, Victoria	10.213±.003[1]	10.680±.003	10.017±.004	0.9563:1:0.9379	Present investigation
Pare Mtn. District, Tanganyika	10.24 ±.02	10.74 ±.02	10.06 ±.03	0.9534:1:0.9367	McKie (1955), indexed and refined in present investigation
Mejillones, Chile	10.29 ±.01[2]	10.69 ±.01	9.99 ±.01	0.9567:1:0.9344[2]	Pollmann (1961)
Mejillones, Chile	—	—	—	0.9548:1:0.9360	Schmidt (1883), morphological
Skipton Caves, Victoria	—	—	—	0.9435:1:0.9299	vom Rath (1880), morphological

[1] The barely significant increase in a for the Skipton Caves newberyite is quite likely due to a replacement of Mg ($r=0.78$ Å) by 0.36 wt. % Mn ($r=0.91$ Å). Mn analysis was made by electron microprobe. There was no detectable Fe (*contra* MacIvor, 1887).

[2] If Pollmann's axial ratio $a:b=0.9567:1$ and value for b (in good agreement with our results) are assumed correct, this value becomes $a=10.23±.01$ Å, which is in reasonable agreement with the Mono Lake and Skipton Caves newberyites. Otherwise his reported axial ratio is incorrect and should read $a:b:c=0.9626:1:0.9344$.

hours at 95° C., but after 12 hours at 110° C. gave an x-ray pattern characteristic of amorphous material.

An x-ray study of unsized material removed at intervals during the 250 hour heating experiment showed a progressive decrease in the intensity of the newberyite peaks, with the relative intensities remaining constant. No line broadening or shift in peak positions was noted, although specifically sought. With time all peaks disappeared, attesting to the gradual formation of more and more amorphous $MgHPO_4 \cdot xH_2O$ at $\sim$110° C. Formation of the amorphous phosphate was easily observed on a microscope heating stage. As expected, the smaller particles lost birefringence sooner than large crystals. No change of the newberyite morphology was observed during the loss of the waters of crystallization, but a dramatic recrystallization was observed when at higher temperatures $Mg_2P_2O_7$ formed.

Discussion

Dehydration of newberyite. Our data suggest that crystal size and heating rate are controlling factors in the rate of water loss for newberyite and are consequently essential parameters in any analytical method employing programmed temperature rise. Garn and Kessler (1960) also stress the importance of controlling the atmosphere over hydrous phosphates during differential thermal analysis and thermogravimetric analysis. Manly (1950) noted that synthetic $MgHPO_4 \cdot 3H_2O$ produced a strong endothermic DTA peak at 255° C. with a "fine-grained powder" but at an unspecified heating rate. Since more than two thirds of the water in newberyite is evolved into a dry oven at 110° C., it is probable that Manly's endothermic peak at 225° C. is a non-equilibrium effect and will be found to be a function of heating rate, grain size and atmosphere. Additional evidence that Manly's (1950) DTA analysis was of metastable material may be found in Kiehl and Hardt's (1933) observation that $MgHPO_4 \cdot 3H_2O$ decomposes to the pyrophosphate above 158° C.

Decomposition of struvite to newberyite. The identity of the crystal relics in which monetite and newberyite were found was established by determining their symmetry point group (*mm*2) and checking a list of minerals crystallizing in this class. Struvite, $MgNH_4PO_4 \cdot 6H_2O$, was immediately suspect. Struvite has been found in guano at Saldanha Bay, South Africa, and Skipton Caves, Victoria, as large, distinct crystals often twinned on {001} with deep re-entrant angles (Fig. 1 and Goldschmidt, 1922).

That the chemical and x-ray investigations failed to indicate the presence of struvite in the specimens is not surprising: struvite can decom-

pose in subaerial or subaqueous environments (see below). Our crystal relics give evidence that the decomposition

$$MgNH_4PO_4 \cdot 6H_2O = MgHPO_4 \cdot 3H_2O + NH_3 + 3H_2O$$

did progress at normal earth-surface temperatures. To confirm this reaction we measured the volume and weight of a sized piece of polycrystalline newberyite, having carefully removed the encasing layer of monetite.[1] The following calculations show excellent agreement of the observed and theoretical weight loss given in the formula above.

(a)	vol. of polycrystalline newberyite	1.92 cc
(b)	density of struvite	1.705 g/cc
(a) × (b) = (c)	wt. of original struvite crystal	3.27 g
(d)	wt. of polycrystalline newberyite	2.37 g
(c) − (d) = (e)	difference in weight	0.90 g
(e)/(c)	wt. loss during decomposition	28%
	expected wt. loss, struvite-newberyite	29%

Whether this decomposition took place in a subaerial or a subaqueous environment is the subject of considerable interst. Hutchinson (1950, p. 474) states, " . . . it would seem from MacIvor's account of the Skipton Cave that over long periods in dry guano only newberyite and perhaps bobierrite are stable." MacIvor (1887) in fact reported that he found struvite forming in "wet" guano ($>30\%$ H_2O) but newberyite only in drier guano ($<20\%$ H_2O). Occurring with newberyite but distinct from it in this guano, MacIvor found white "indistinctly crystalline" nodules which he considered to be altered struvite. In his 1887 paper he calls these nodules "amorphous magnesium ammonium phosphate," remarking on their similarity to a white crust that formed on struvite crystals left exposed to air in the laboratory. In a later note (1902) he calls them $Mg_3(PO_4)_2 \cdot xH_2O$ (not "bobierrite," as did Hutchinson). Either or both of these alteration products are likely in a dry environment, as was demonstrated by Kiehl and Hardt (1933).

During a careful experimental investigation of the thermal decomposition of struvite, Kiehl and Hardt measured vapor pressures and compositions above $MgNH_4PO_4 \cdot 6H_2O$. They concluded that the reaction

$$MgNH_4PO_4 \cdot 6H_2O = MgNH_4PO_4 \cdot H_2O + 5H_2O$$

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[1] The importance of the dense veneer of monetite in preserving the relic struvite morphology should be emphasized. Without it the minute crystals of newberyite would most likely have been dispersed by normal weathering processes and this unique occurrence gone unrecognized. That monetite, $CaHPO_4$ was originally deposited as brushite, $CaHPO_4 \cdot 2H_2O$, can only be surmised from the facts that brushite is a very common constituent of guano, crystallizing below 25 C. at pH<6.4, and that it decomposes readily to monetite (Hutchinson, 1950, p. 464).

would proceed at 50° C. or below if water vapor were removed as it was liberated; only above 60° C. did they detect ammonia.[1] Thus for lack of water, it seems that a subaerial decomposition of struvite to newyberite and/or bobierrite is unlikely.

Recent studies of the aqueous chemistry of struvite and newberyite were undertaken by Johnson (1959) and Taylor *et al.* (1963). The former found the solubility product of struvite to be $10^{-13.20}$ at 38° C.; the latter determined it to be $10^{-13.15}$ at 25° C. The agreement of these values indicates that solubility is relatively unaffected by slight temperature changes. Both investigations showed that solutions which were saturated with respect to struvite were also super-saturated with either newberyite or bobierrite ($Mg_3(PO_4)_2 \cdot 8H_2O$). Johnson stated that in his experiments $Mg_3(PO_4)_2$ precipitated from a solution saturated with struvite above pH 6.87–6.88 and that $MgHPO_4$ precipitated below this pH. Taylor *et al.* showed that when $MgNH_4PO_4 \cdot 6H_2O$ dissolves in water or a weakly buffered solution such that the value of $a_{Mg}a^2_{OH}$ rises above 10^{-15}, hydrolysis of the magnesium ammonium salt will cause precipitation of $MgHPO_4 \cdot 3H_2O$ (newberyite) if ammonia is allowed to escape. A further decomposition of newberyite to the more stable bobierrite was suggested from the experimental data.

From the experimental viewpoint it seems that a subaqueous replacement of struvite by newberyite is more likely than a subaerial decomposition. Evidence other than experimental supports this conclusion. First, the struvite relics—now newberyite coated with monetite—are found in a diatomaceous ashy mudstone which is overlain by water-deposited ash and diatomite layers (Calvert, private comm.). The original guano horizon(s) in which the struvite crystals grew was thus undoubtedly submerged for a considerable length of time. Either submergence, or another cause of removal of the guano, would be equivalent to lowering the activity of ammonia in the environment, thereby allowing newberyite to crystallize. Secondly, the growth pattern of newberyite crystals in the monetite envelope indicates crystallization from solution. The thin, bladed crystals have their long axes normal to the encasing surfaces in a typical replacement pattern. Concentric rings parallel to the relic crystal surfaces can be clearly seen in sections cut through the newberyite, indicating different stages in the replacement history.

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[1] Roy *et al.* (1948) performed an ambiguous thermal analysis of $MgNH_4PO_4 \cdot 6H_2O$: their starting material was calcined at 110° C. before determining the DTA curve. At this temperature struvite had most certainly decomposed to $MgNH_4PO_4 \cdot O.xH_2O$ and/or $MgHPO_4 \cdot O.xH_2O$, and it is not surprising that their weight loss on ignition to $Mg_2P_2O_7$ was less than 25%, against an expected value of 54.7%.

CONCLUSIONS

Struvite once crystallized in or immediately below a guano deposit on Paoha Island, Mono Lake, California. Subsequent submergence and removal of the source of ammonia permitted the replacement of struvite by newberyite in a subaqueous environment. The struvite crystals were originally coated by monetite which preserved their morphology during recrystallization and a later exposure to weathering processes.

As for the guano—Mark Twain (1872) commented about the "millions of wild ducks and seagulls" that swam about the lake during his visit. Even today Paoha Island is a seasonal resting place for many gulls that feed on brine shrimp in the alkaline waters of Mono Lake. We now have evidence that Paoha Island was a popular rookery during the early stages of its elevation, since the struvite relics are found very near the summit of the island.

ACKNOWLEDGMENTS

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