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NEW DATA ON STERCORITE ($NaNH_4HPO_4 . 4H_2O$) AND ON ITS ISOSTRUCTURAL ARSENATE

RIASSUNTO. — Si chiarisce che le analisi chimiche riportate in letteratura per la stercorite sono state male interpretate; uno spettro di polvere eseguito su stercorite delle isole Chincha (Perù) indica chiaramente che tale minerale corrisponde al composto artificiale $NaNH_4HPO_4 . 4H_2O$. La stercorite è isostrutturale con $NaNH_4HAsO_4 . 4H_2O$ ed entrambi i composti sono triclini ($P\bar{1}$) con una accentuata pseudosimmetria C2/m che ne spiega l'estesa geminazione {010}. I parametri della cella elementare per il fosfato e per l'arseniato sono rispettivamente:

a = 10,636(2)	b = 6,9187(14)	c = 6,4359(13) Å
α = 90,46(3)	β = 97,87(3)	γ = 109,20(3)°
a = 10,706(6)	b = 7,031(4)	c = 6,592(4) Å
α = 90,10(10)	β = 98,25(10)	γ = 109,15(10)°.

ABSTRACT. — A misinterpretation of chemical analyses of stercorite is pointed out; an X-ray powder spectrum of stercorite from Chincha Islands (Peru) proves clearly that the mineral corresponds to synthetic $NaNH_4HPO_4 . 4H_2O$. Stercorite is isostructural with $NaNH_4HAsO_4 . 4H_2O$ and both the compounds are triclinic ($P\bar{1}$) with a marked C2/m pseudo-symmetry which accounts for their easy {010} twinning. The unit-cell parameters are:

a = 10.636(2)	b = 6.9187(14)	c = 6.4359(13) Å
α = 90.46(3)	β = 97.87(3)	γ = 109.20(3)°
a = 10.706(6)	b = 7.031(4)	c = 6.592(4) Å
α = 90.10(10)	β = 98.25(10)	γ = 109.15(10)°

for the phosphate and the arsenate, respectively.

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Introduction.

Stercorite is a mineral found in guano deposits (PALACHE et al., 1963) and, with some doubts (HINTZE, 1930; PALACHE et al., 1963), it should correspond to sodium ammonium hydrogen phosphate tetrahydrate ($NaNH_4HPO_4 . 4H_2O$), a salt used in blowpipe analysis and present in human urine [microcosmic salt (PASCAL, 1956)]. The artificial product is morphologically described as pseudo-monoclinic by SCHASCHEK (1914) who says also that the corresponding arsenate ($NaNH_4HAsO_4 . 4H_2O$), which is not known as a mineral, is truly monoclinic.

The present work, together with a crystal structure determination of stercorite (FERRRARIS & FRANCHINI-ANGELA, 1974), has been carried out as a part of a programme of structural research on arsenates and phosphates.

Chemical composition.

Correspondence of stercorite with $NaNH_4HPO_4 . 4H_2O$ is based on two chemical analyses published by RAIMONDI (1878) and by HERAPATH (1850) who also provides a value of the density (1.615, the only physical quantity known for the mineral). HINTZE (1930) and PALACHE et al. (1963), possibly following DANA (1875), interpret the figures of the two chemical analyses in terms of $(NH_4)_2O$ and infer that the natural material does not conform closely to $NaNH_4HPO_4 . 4H_2O$. « Does not conform closely » is clearly an euphemism; in fact, according to the quoted interpretation, the analysed content of $(NH_4)_2O$ is about 2/3 of the expected value (Table 1). Table 1 shows that the per cent theoretical composition of $NaNH_4HPO_4 . 4H_2O$ expressed in terms of NH_3 and of total water, instead of $(NH_4)_2O$ and crystallization water, corresponds to the original (HERAPATH, 1850; RAIMONDI, 1878) figures given for chemical analyses of stercorite.

Actually, a fresh reference to the original papers showed that they give percentage of NH_3 and not of $(NH_4)_2O$; that is said explicitly by HERAPATH (1850) who, for the record, used recrystallized material. RAIMONDI (1878) does not write any chemical formula and refers the percentage to « amoniaco » (Spanish) which, however, undoubtedly means NH_3 and not $(NH_4)_2O$; that follows clearly by comparison with other analyses in the same book, e.g. with that of teschemacherite (NH_4HCO_3) which is on the same page of stercorite. The source of the misinterpretation might be DANA (1875) who writes the formula of stercorite in terms of $(NH_4)_2O$ and uses the abbreviation « Am. » beside the value of NH_3 quoted from HERAPATH (1850).

TABLE 1.

Chemical analyses of stercorite. A and D show, in two different ways, the percent theoretical composition of $NaNH_4HPO_4 . 4H_2O$; *B and C show the percentages given by* HERAPATH (1850) (*Ichaboe Island*) *and by* RAIMONDI (1878) (*Guañape Islands*).

A		B	C	D	
Na_2O	14.82	15.75	14.50	14.82	Na_2O
$(NH_4)_2O$	12.45	7.68	8.48	8.15	NH_3
P_2O_5	33.95	34.33	34.54	33.95	P_2O_5
H_2O	38.78	42.24	42.48	43.08	H_2O
Total	100.00	100.00	100.00	100.00	

X-ray powder spectra.

In order to have a sound identification of stercorite, some physical measurements on natural material seemed necessary. An old (about 1900) sample [1] from Peru (Chincha Islands, sample no. 14008 from the collection of the Mineralogical Institute of the University of Turin) supplied enough stercorite for an X-ray powder spectrum which turned out to be identical with that obtained from commercial $NaNH_4HPO_4 . 4H_2O$ [Table 2 and ASTM (1961) card no. 11-358]. Table 3 lists X-ray powder data obtained for $NaNH_4HAsO_4 . 4H_2O$. Indices were assigned on the basis of the unit-cell parameters reported in Table 4 and, for stercorite only, of the intensities measured in view of a crystal-structure determination (FERRARIS & FRANCHINI-ANGELA, 1974).

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(1) The sample contains, together with aphtitalite $K_3Na(SO_4)_2$, a small amount of stercorite embedded in guano; stercorite appears vitreous, colorless and is apparently deliquescent.

TABLE 2.

Observed and calculated data for the X-ray powder spectra of stercorite (N, Chincha Islands) and of $NaNH_4HPO_4 . 4H_2O$ *(A). Camera radius* 71.6 *mm, FeKα radiation* ($\lambda_a = 1.93728$, $\lambda_{a1} = 1.93597$ Å). *Intensities on relative scale: vs = very strong, s = strong, m = medium, w = weak.*

I_o	N d_o(Å)	A d_o(Å)	d_c(Å)		*hkl*	
vs	9.95	9.95	9.93		100	
vs	6.56	6.56	6.54	6.52	$\bar{1}10$	010
mw	—	6.36	6.37		001	
mw	5.78	5.77	5.76		$\bar{1}01$	
w	4.953	4.978	4.967		200	
ms	4.803	4.794	4.796	4.772	$\bar{2}10$	110
ms	4.692	4.653	4.658	4.691	$\bar{1}11$	$0\bar{1}1$
vvw	4.444	4.471	4.473		$1\bar{1}1$	
s	4.227	4.239	4.231		$\bar{2}01$	
s	3.648	3.652	3.662	3.657	201	$2\bar{1}1$
s	3.445	3.440	3.453	3.438	$\bar{3}10$	210
s	3.267	3.274	3.272	3.262	$\bar{2}20$	020
m	3.182	3.181	3.183	3.170	002	$\bar{1}02$
mw	3.037	3.033	3.050	3.028	$1\bar{2}1$	$\bar{1}21$
w	2.966	2.966	2.959	2.971	$\bar{2}21$	$0\bar{2}1$
vs	2.891	2.902	2.909	2.908	$\bar{1}12$	102
ms	2.860	2.874	2.880	2.863	$\bar{2}02$	$2\bar{2}1$
vvw	—	2.767	2.775		301	
mw	2.680	2.687	2.680	2.676	$\bar{1}\bar{2}1$	$\bar{3}21$
vw	2.628	2.623	2.631	2.621	$\bar{4}10$	310
w	2.477	2.485	2.485	2.484	$\bar{3}02$	400
mw	2.388	2.393	2.398	2.386	$\bar{4}20$	220
m	2.324	2.320	2.323	2.322	$\bar{4}21$	$\bar{2}\bar{2}1$
w	2.206	2.209	2.208	2.206	$\bar{3}22$	401

vw	2.175	2.169	2.175	2.174	$\bar{4}12$	030
			2.173	2.172	$\bar{4}21$	$1\bar{3}1$
vvw	2.088	2.088	2.088	2.085	$\bar{5}11$	$\bar{4}\bar{1}1$
vvw	2.037	2.037	2.044	2.038	$3\bar{2}2$	$3\bar{3}1$
vvw	2.019	2.018	2.021	2.016	$\bar{2}\bar{2}2$	$\bar{4}22$
vw	1.992	1.987	1.9868	1.9845	500	013
			1.9817		$\bar{5}01$	
vvw	1.915	1.921	1.9227	1.9219	$\bar{2}\bar{1}3$	$5\bar{1}1$
			1.9200		$3\bar{0}3$	
vvw	1.900	1.896	1.9063	1.8974	$4\bar{1}2$	312
vw	1.810	1.809	1.8098		$\bar{5}02$	
w	1.774	1.772	1.7749	1.7712	$\bar{3}\bar{1}3$	$\bar{4}13$
vw	—	1.746	1.7456	1.7455	$\bar{4}03$	510
w	1.728	1.727	1.7296		$\bar{2}40$	
vw	1.706	1.703	1.7054	1.7025	$\bar{3}40$	$\bar{1}40$
vw	1.661	1.661	1.6634	1.6588	$\bar{6}01$	$1\bar{4}1$
vw	1.625	1.625	1.6244	1.6243	$\bar{5}32$	511
			1.6142		$5\bar{2}2$	
vvw	1.545	1.544	1.5476		601	

Plus the following vvw reflections:

1.491	1.490
1.476	1.478
1.440	1.438
1.429	—
1.394	1.394
1.372	—
1.362	—
1.312	—
1.269	—
1.249	—
1.208	—

TABLE 3.

Observed and calculated data for the X-ray powder spectrum of $NaNH_4HAsO_4 \cdot 4H_2O$; *see Table 2.*

I_o	d_o(Å)	d_c(Å)		*hkl*	
ms	10.10	10.00		100	
vs	6.68	6.63	6.63	010	$\bar{1}10$
w	5.90	5.88		$\bar{1}01$	
mw	5.03	5.00		200	
s	4.861	4.837	4.836	110	$\bar{2}10$
s	4.771	4.766	4.774	$\bar{1}11$	$0\bar{1}1$
vvw	4.529	4.538	4.531	$1\bar{1}1$	011
ms	4.304	4.294		$\bar{2}01$	
s	3.695	3.702	3.694	201	$2\bar{1}1$
ms	3.495	3.476	3.475	210	$\bar{3}10$
m	3.334	3.332		300	
m	3.253	3.257	3.252	002	$\bar{2}\bar{1}1$
		3.249	3.246	$\bar{3}11$	$\bar{1}02$
ms	3.094	3.096	3.091	$1\bar{2}1$	$\bar{1}21$
vw	3.018	3.020	3.016	$0\bar{2}1$	$\bar{2}21$
s	2.952	2.967	2.942	102	$\bar{2}02$
ms	2.894	2.898	2.895	$2\bar{2}1$	021
ms	2.727	2.722	2.719	$\bar{1}\bar{2}1$	$\bar{3}21$
w	2.652	2.646	2.646	310	$\bar{4}10$
vw	2.548	2.550	2.550	$3\bar{2}1$	$\bar{3}12$
		2.548		121	
w	2.506	2.499		400	
vw	2.424	2.418	2.418	220	$\bar{4}20$
w	2.380	2.383		$\bar{2}22$	
mw	2.337	2.339	2.338	$4\bar{1}1$	311
vw	2.263	2.265	2.258	022	$\bar{1}\bar{2}2$
w	2.219	2.223	2.213	401	$\bar{3}\bar{1}2$

mw	2.188	2.190	2.189	$4\bar{2}1$	221
w	2.112	2.118	2.113	$\bar{5}10$	$\bar{2}03$
		2.107		$\bar{4}\bar{1}1$	
w	2.061	2.063	2.061	$3\bar{3}1$	031
vw	1.956	1.961	1.961	$\bar{3}13$	$\bar{3}03$
mw	1.921	1.925	1.924	$4\bar{1}2$	312

Plus the following w and vw reflections:

1.852	1.829	1.807	1.771	1.762	1.679
1.661	1.639	1.590	1.518	1.507	1.484
1.467	1.453	1.422	1.368	1.339	1.325
1.313	1.288	1.273	1.228	1.214	1.202
1.185	1.164	1.115			

Crystal data.

SCHASCHEK (1914), after an extensive crystallographic study of $NaNH_4HPO_4 . 4H_2O$ and of $NaNH_4HAsO_4 . 4H_2O$, concludes that while the phosphate is triclinic but simulates a monoclinic symmetry because of a repeated {010} twinning, the arsenate is truly monoclinic.

Vitreous, colourless crystals of $NaNH_4HPO_4 . 4H_2O$ are commercially available, those of $NaNH_4HAsO_4 . 4H_2O$ were grown at 5°C (about 2 months) following the method of SCHASCHEK (1914) with $(NH_4)_2HAsO_4$ and Na_2HAsO_4 as starting products instead of $(NH_4)_3AsO_4$ and Na_3AsO_4 respectively. Crystals of both the compounds are prismatic [001] and, especially those of the arsenate, can reach several mm across; they deteriorate quickly in air and while the phosphate can be preserved by coating it with a thin plasticizing film, the arsenate must be kept in sealed capillaries.

[001] Weisenberg photographs (CuKα radiation) showed clearly all the available crystals of $NaNH_4HPO_4 . 4H_2O$ to be {010} twinned and the symmetry of individuals to be actually triclinic ($P\bar{1}$) with a marked C2/m pseudo-symmetry. Identification of the same type of twinning in $NaNH_4HAsO_4 . 4H_2O$ was not straightforward and was achieved only through a close comparison of upper-layer Weissenberg photographs of the two compounds. The crystallographic study of

the phosphate was then continued on a single-crystal diffractometer (FERRARIS & FRANCHINI-ANGELA, 1974). Its refined unit-cell parameters are reported in Table 4 together with the crystal data for the arsenate; these have been obtained from Weissenberg photographs.

TABLE 4.

Primitive P and centered C pseudo-monoclinic unit-cell parameters of stercorite and of its isostructural arsenate.

		a(Å)	b(Å)	c(Å)	
$NaNH_4HPO_4 \cdot 4H_2O$	C	20.090(2)	6.9187(14)	6.4359(13)	
	P	10.636(2)	6.9187(14)	6.4359(13)	
$NaNH_4HAsO_4 \cdot 4H_2O$	C	20.20(1)	7.031(4)	6.592(4)	
	P	10.706(6)	7.031(4)	6.592(4)	
		α(°)	β(°)	γ(°)	V(Å³)
$NaNH_4HPO_4 \cdot 4H_2O$	C	90.46(3)	98.50(3)	90.22(2)	884.70
	P	90.46(3)	97.87(3)	109.20(3)	442.52
$NaNH_4HAsO_4 \cdot 4H_2O$	C	90.10(10)	98.77(10)	90.00(10)	926.50
	P	90.10(10)	98.25(10)	109.15(10)	463.25

The transformation matrix from P to C unit cell is 210/010/001; the published morphological data (PALACHE et al., 1963) referred to a C unit cell with a double *c* and the matrix which transforms old to new (P) indices is ½ - ½0/010/00½ .

A structural study of stercorite (FERRARIS & FRANCHINI-ANGELA, 1974) shows that the {010} twinning is made easier by a marked pseudo-monoclinic symmetry of the crystal structure; C2/m symmetry is almost perfectly obeyed with the exception of the ammonium group which is roughly equivalent to a water molecule (on geometrical bases only).

Conclusions.

Criticism of published chemical analyses and new crystallographic data proves the identity between stercorite and $NaNH_4HPO_4 . 4H_2O$. Also, SCHASCHEK's (1914) assertion of different (even if apparently equal) symmetries for $NaNH_4HPO_4 . 4H_2O$ and $NaNH_4HAsO_4 . 4H_2O$, which could leave doubts about the isostructurality of the two compounds, is disproved by the present research; such a property is based on chemical formulae, morphological data (PALACHE et al., 1963), unit-cell parameters and, mainly, on X-ray powder spectra and Weissenberg protographs.

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