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NAHPOITE Na_2HPO_4, A NEW MINERAL FROM THE BIG FISH RIVER AREA, YUKON TERRITORY

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Abstract

Nahpoite Na_2HPO_4, a new mineral, occurs as a fine grained, earthy white material in marićite nodules in the Big Fish River area, Yukon. Microscopically, individual grains are somewhat elongate, up to 4 μm long, and exhibit nearly parallel extinction. Nahpoite is colorless with n_{min} 1.490 and n_{max} 1.505. The strongest six lines in the X-ray powder-diffraction pattern [*d* in Å (I)(*hkl*)] are 3.97(45)(110,011), 3.84(55)(111), 3.41(25)(020), 2.868(30)(10$\bar{1}$), 2.803(100)(120,021), 2.720(70) (201,102). It is monoclinic with *a* 5.47(1), *b* 6.84(1), *c* 5.45(1) Å, β 116°20(5)′, *V* 182.75 Å³, *Z* = 2; on the basis of the ideal formula, it has a calculated density of 2.58 g/cm³. Its possible space groups are $P2_1/m$ or $P2_1$. Nahpoite appears to have formed from marićite $NaFePO_4$ by alteration. This study shows that dorfmanite $Na_2HPO_4 \cdot 2H_2O$ and an additional hydrated orthophosphate $Na_2HPO_4 \cdot 7H_2O$ could also be products of alteration of marićite. The name is mnemonic.

Keywords: new mineral, sodium, phosphate, Big Fish River, Yukon, marićite alteration.

Sommaire

La nahpoïte $NaHPO_4$, espèce nouvelle, se présente en un enduit terreux blanc, finement grenu, dans les nodules de marićite de la région de la rivière Big Fish (Yukon). Au microscope, on l'observe en cristaux légèrement allongés, atteignant 4 μm et montrant l'extinction quasi-parallèle. Incolore, d'indices n_{min} 1.490 et n_{max} 1.505. Les six raies les plus intenses dans le cliché de poudre [*d* en Å(I)(*hkl*)] sont: 3.97(45)(110,011), 3.84 (55)(111), 3.41(25)(020), 2.868(30)(10$\bar{1}$), 2.803 (100)(120,021), 2.720(70)(201,102). La nahpoïte est monoclinique, *a* 5.47(1), *b* 6.84(1), *c* 5.45(1) Å, β 116°20(5)′, *V* 182.75 Å³ pour *Z* = 2. La densité calculée (pour la formule idéale) est de 2.58; groupes spatiaux possibles: $P2_1/m$ ou $P2_1$. La nahpoïte serait un produit d'altération de la marićite $NaFePO_4$, comme le seraient aussi un orthophosphate hydraté $Na_2HPO_4 \cdot 7H_2O$ et la dorfmanite $Na_2HPO_4 \cdot 2H_2O$. Le nom choisi est mnémonique.

(Traduit par la Rédaction)

Mots-clés: nahpoïte, minéral nouveau, sodium, phosphate, rivière Big Fish, Yukon, altération, marićite.

Introduction

Nahpoite Na_2HPO_4 is a new mineral that occurs in phosphate nodules in phosphatic ironstones in the northern Richardson Mountains, Yukon. The type locality, 68°28′N, 136°29′W, is on the Big Fish River where the new minerals marićite (Sturman *et al.* 1977) and satterlyite (Mandarino *et al.* 1978) were discovered. The new minerals kulanite (Mandarino & Sturman 1976), barićite (Sturman & Mandarino 1976) and penikisite (Mandarino *et al.* 1977) were discovered in stratigraphically equivalent phosphatic ironstones that crop out near Rapid Creek, 15 km to the northwest.

It should be noted that nahpoite has also been reported recently as an unnamed mineral by Khomyakov & Menschikov (1979) in samples from the Khibina and Lovozero massifs, Kola Peninsula.

The mineral and name, after its composition, were approved by the Commission on New Minerals and Mineral Names, I.M.A. Type material is preserved in the collection of the Department of Geological Sciences, University of Saskatchewan (12504).

Occurrence

The phosphatic ironstones of the northern

Richardson Mountains are noted for the presence of coarsely crystalline segregations of a number of rare phosphates. These rocks occur in the lower portion of a Lower Albian (upper Lower Cretaceous) sequence described by Young (1972, 1977). Their stratigraphy and the rare phosphates that occur in them have been described in some detail by Robertson (1980). The principal occurrences of macroscopically visible phosphates at Rapid Creek are in veins occupying dilational features; however, in the Big Fish River, where nahpoite has been found, phosphates also occur in ellipsoidal and disc-shaped nodules up to 25 cm in diameter. These nodules, some of which appear to be recrystallized replacements of ammonites and pelecypods, occur in specific horizons of a sequence of interbedded ferruginous shales and sideritic mudstones in the lower portion of the Lower Albian section. The principal constituents of these nodules are wolfeite, satterlyite and marićite, which occur together or alone in coarsely crystalline radiating aggregates, finely crystalline pyrite and vivianite–barićite. Pyrite nodules dominate the lowest part of the sequence, with phosphates becoming more prominent upward.

A brief study of compositions of nodules observed *in situ* suggests that 39% are composed primarily of pyrite, 58% of wolfeite, 2% of satterlyite and 1% of marićite. Nodules composed of vivianite–barićite were not observed *in situ*. Similar nodules have been observed in abundance in an ironstone section that crops out along Boundary Creek, 5 km to the northwest. At that locality the approximate proportions of *in situ* nodules, in terms of their dominant constituent, are 5% pyrite, 85% wolfeite and 10% satterlyite. Marićite nodules were not observed, and vivianite–barićite nodules were not observed *in situ*.

Nahpoite has been found in four nodules from the Big Fish River area in which marićite appears to be the only other constituent. To date, nahpoite has not been observed in any of the Boundary Creek nodules, perhaps owing to the absence of marićite at that locality.

Appearance and Physical Properties

Nahpoite occurs as a fine grained, earthy white fracture-filling in marićite, from which it appears to have formed by alteration. Its grain size is too small to permit single-crystal study and makes direct determination of its optical and other properties, such as cleavage and crystal form, impossible. It appears to be very soft, but its actual hardness could not be tested. It is extremely soluble in water and, to a much lesser degree, in concentrated HCl. The rate of dissolution of nahpoite in the latter is estimated to be about 1/200th that in water.

Nahpoite occurs in somewhat elongate grains that exhibit slightly irregular edges and have a maximum dimension of 4 μm. Optically they appear to be length fast, to exhibit nearly parallel extinction and to have minimum and maximum indices of refraction of about 1.490 and 1.505, respectively.

X-ray Data

The initial identification of nahpoite was based on X-ray powder-diffraction studies. Data obtained from the natural material was used in a search of the X-ray Powder Data Files, which indicated Na_2HPO_4. This was substantiated by obtaining a diffractogram from synthetic Na_2HPO_4 (Baker's Analyzed Reagent) and comparing it with the one obtained from the natural material. In Table 1, X-ray powder data obtained from the type material are compared with those obtained from synthetic Na_2HPO_4 and those listed for Na_2HPO_4 in the Powder Data File (card 10–184). Data for the natural and synthetic materials were obtained from both diffractograms and powder photo-

TABLE 1. X-RAY POWDER-DIFFRACTION DATA

Nahpoite			Synthetic Na_2HPO_4		X-ray Powder Data File No. 10-184		
I[1]	d(Å)[1]	hkl[2]	I	d(Å)	I	d(Å)	hkl
12	4.86	001,100	9	4.85	9	4.90	101,10$\bar{1}$
7	4.62	101	7	4.61	5	4.64	200
45	3.97	011,110	45	3.95	45	3.98	111,11$\bar{1}$
55	3.84	110	55	3.815	55	3.84	2$\bar{1}$0
25	3.41	020	25	3.40	20	3.42	020
30	2.868	10$\bar{1}$	33	2.866	40	2.880	002
100	2.803	021,120	100	2.789	100	2.805	121,12$\bar{1}$
70	2.720	201,102	55	2.713	50	2.730	30$\bar{1}$
15	2.650	11$\bar{1}$	15	2.642	25	2.720	301
					20	2.655	012
10	2.527	112,211	5	2.525	8	2.537	31$\bar{1}$
					4	2.528	311
15	2.440	002,200	12	2.438	18	2.453	20$\bar{2}$
					8	2.442	202
12	2.319	202			8	2.320	400
			9	2.301	8	2.309	21$\bar{2}$
					6	2.300	212
					8	2.205	022
12	2.194	212	13	2.192	10	2.197	410
			2	2.121	6	2.129	321
5	2.058	130,031	5	2.061	8	2.068	13$\bar{1}$,131
6	2.040	131	5	2.042	8	2.047	230
15	1.998	220,022	13	1.985	16	1.994	22$\bar{2}$
					8	1.988	222
15	1.913	222	12	1.913	18	1.921	420
					plus 8 other indexed lines and 6 unindexed lines		

1) Intensities obtained from diffractogram, *d* values from Debye-Scherrer photographs. 2) Values for (*hkl*) based on reindexing the data from PDF 10-184 to a unit cell with *a* 5.47, *b* 6.84, *c* 5.45 Å, β 116°20', *Z* = 2.

graphs using Cu $K\alpha$ radiation. The diffractograms were obtained using smear mounts with a Philips wide-angle diffractometer, and the powder photographs using a 57.3 mm diameter Debye–Scherrer camera. Diffraction intensities were estimated from the relative heights above background of the corresponding peaks on diffractograms. On the basis of the reported indexing (PDF 10-184), the unit-cell parameters refined by least squares from the powder data are *a* 9.26(1), *b* 6.82(1), *c* 5.75(1) Å, *β* 90.3, *V* 363.13 Å^3, $Z = 4$. Its calculated density on the basis of the ideal and empirical formula is 2.60 g/cm^3.

The indexing given on PDF 10–184 is for a *B* lattice. If a simpler primitive cell is adopted, as appears to be preferable, its unit-cell parameters are *a* 5.47(1), *b* 6.84(1), *c* 5.45(1) Å, *β* 116°20(5)′, *V* 182.75Å^3, $Z = 2$. Its calculated density on the basis of the ideal and empirical formula is 2.58 g/cm^3; $P2_1/m$ or $P2_1$ are the possible space groups.

Chemistry

Since the physical nature of nahpoite makes it unsuitable for electron-microprobe analysis, other methods were used to obtain its chemical composition and confirm its identity. Preliminary atomic-absorption spectrometric analysis, which was qualitative in nature, was performed on a 2-mg sample. Subsequently, 13 mg of nahpoite were separated from one nodule and analyzed by E.C. Bailey, Department of Chemistry, University of Saskatchewan. P was analyzed by colorimetry and Na by atomic absorption spectrometry. The results of these analyses are presented in Table 2. An analysis of some of the synthetic Na_2HPO_4 performed at the same time as a control yielded essentially identical results.

TABLE 2. PARTIAL ANALYSIS OF NAHPOITE COMPARED WITH STOICHIOMETRIC Na_2HPO_4

	Nahpoite wt.%	Stoichiometric Na_2HPO_4 wt.%
Na_2O	43.67	43.66
P_2O_5	49.54	49.99
H_2O	6.32*	6.35
Total	99.53	100.00

*Calculated on the basis of assuming sufficient H to produce neutrality.

Associated Minerals

During the initial attempt to identify nahpoite by X-ray methods, a diffraction pattern

TABLE 3. X-RAY DATA FOR $Na_2HPO_4 \cdot 7H_2O$

Natural material I	Natural material d(Å)	$Na_2HPO_4 \cdot 7H_2O$ (file no. 12-445) I	$Na_2HPO_4 \cdot 7H_2O$ (file no. 12-445) d(Å)
20	6.65	50	8.35
10	5.98	30	6.03
20	5.43	30	5.47
20	5.15	70	5.21
60	4.67	100	4.65
		5	4.37
100	4.21	100	4.21
		10	3.91
		5	3.78
		10	3.63
10	3.42	10	3.43
		70	3.34
30	3.26	70	3.24
		10	3.13
50	3.03	50	3.01
40	2.91	70	2.91
70	2.85	70	2.866
80	2.81	70	2.813
30	2.73	50	2.739
		5	2.667
50	2.57	30	2.585
15	2.53	10	2.528
15	2.47	30	2.462
		5	2.321
		20	2.248
10	2.18	20	2.191
10	2.12	10	2.118
		20	2.067
30	2.03	50	2.027
10	1.98	20	1.961
		plus 9 other unindexed lines to 1.640	

was obtained (Table 3) that corresponds with data listed for $Na_2HPO_4 \cdot 7H_2O$ (PDF 12–445) rather than Na_2HPO_4. However, subsequent investigation of the same sample under the same operating conditions produced data corresponding only to Na_2HPO_4, as did diffractometry of all other samples containing nahpoite. It was observed that synthetic material, when left exposed to air for a period of several weeks, showed a tendency to gain water of hydration and to change to dorfmanite $Na_2HPO_4 \cdot 2H_2O$ (Kapustin *et al.* 1980). On the other hand, natural Na_2HPO_4, nahpoite, exposed to air in the same laboratory exhibited no such tendency. The reason for this difference in behavior between the synthetic and natural materials is neither known nor understood.

This study indicates that nahpoite, the anhydrous orthophosphate, is a stable alteration product of marićite. Our results suggest that $Na_2HPO_4 \cdot 7H_2O$ can be produced by the alteration of marićite under conditions similar to those that produce nahpoite. Whereas dorfmanite was not found in the material studied, its formation also appears to be a likely consequence of the alteration of marićite.

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