Natrophosphate, Arctic Mineral and Nuclear Waste Phase: Structure Refinements and Chemical Variability

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Abstract: The crystal structures of natural (Mt. Koashva, Khibiny alkaline massif, Kola Peninsula, Russian Arctic) and synthetic (obtained from an aqueous solution of sodium phosphate and sodium fluoride (1:1) by evaporation at room temperature (RT)) natrophosphate, Na7(PO4)2F·19H2O, have been investigated using single-crystal X-ray diffraction analysis. Natrophosphate and its synthetic analogue are cubic, Fd-3c, a = 27.6942(3) Å (natrophosphate at RT), a = 27.6241(4) Å (natrophosphate at 100 K), a = 28.1150(12) Å (synthetic analogue at RT), a = 27.9777(7) Å (synthetic analogue at 100 K). The crystal structure is based upon the super-octahedral [Na9(H2O)19]3+ polyacationic complexes consisting of six edge-linked Na3(OH)23F octahedra sharing one common fluorine vertex. The A site is statistically occupied by Na and H2O with the prevalence of H2O with the refined occupancy factors O:Na equal to 0.53:0.47 for natrophosphate and 0.75:0.25 for its synthetic analogue. The coordination of the A site in synthetic natrophosphate is enlarged compared to the natural sample, which agrees well with its higher occupancy by H2O molecules. The general formula of natrophosphates can be written as Na6+xHxF(PO4)2·(19 + x)H2O, where x = 0–1. The chemical variability of natrophosphate allows to explain the discrepancies in its solubility reported by different authors. The information-based parameters of structural complexity are equal to 3.713 bit/atom and 2109.177 bit/cell that allows to classify natrophosphate as a structurally very complex mineral.

Keywords: natrophosphate; structural complexity; structure refinement; chemical variations; solubility; Arctic mineralogy

1. Introduction

The history of the study of the phase with the chemical formula Na7(PO4)2F·19H2O is almost 165 years old. It was first described in 1856 by H. Briegleb [1] as transparent octahedral crystals with the composition NaF·Na3PO4·12H2O. Independently this compound was obtained in the course of soda production by means of the Leblanc process (later replaced by the Solvay process) and was studied in 1865 by Rammelsberg [2], who erroneously assigned to it the chemical formula Na3PO4·20H2O, which was soon corrected by Baumgarten to NaF·2Na3PO4·19H2O [3]. The later composition was confirmed by Thorpe [4] and Baker [5]. In 1933, Neuman [6] reported the results of his single-crystal diffraction study to demonstrate that the compound crystallizes in the space group Fd-3c (in modern notation), a = 27.86 Å. Guiot [7] confirmed these data, whereas Rémy and Guérin [8] proposed the existence of a series of compounds with the general formula M3XO4·xMY·(10 – x)H2O where M = Na, K; X = F, As, V; Y = F, OH, and 0 ≤ x ≤ 2. These authors determined for these compounds the space group Fd-3c and the unit-cell parameters equal to 28.14 Å for [M,X,Y,x] = [Na,As,F,0.5], 28.22 Å for [Na,V,F,0.5], and 28.23 Å for [Na,As,OH,0.5]. The crystal structures of Na7(AsO4)2F·19H2O ([Na,As,F,0.5], a = 28.12 Å) and Na7(PO4)2F·19H2O ([Na,F,F,0.5], a = 27.755 Å) were determined by Baur and Tillmanns [9,10].
The natural analogue of Na₇(PO₄)₂F·19H₂O was reported by Kapustin et al. [11] from pegmatite of Yukspor Mt., Khibiny alkaline massif, Kola peninsula (Russian Arctic). The mineral was named ‘natrophosphate’; its wet chemical analyses revealed considerable deviations from the formula Na₇(PO₄)₂F·19H₂O with the deficiency of Na that allowed the authors to suggest Na₆·H(PO₄)₂F·17H₂O as an alternative composition. Khomyakov and Bykova [12] reported the occurrence of natrophosphate in the Lovozero alkaline massif, Kola peninsula, Russia, and determined its chemical formula as Na₆·94(PO₄)₂F₁.11·18.8H₂O. The mineral was also reported from phonolites of the Aris area (Namibia) [13], Ilimaussaq alkaline complex (South Greenland) [14], and Mont-Saint-Hilaire alkaline massif (Canada) [15,16]. The chemical composition of the Aris natrophosphate corresponded to Na₇·04(PO₄)₁.87(SO₄)₀.09Σ=1.96(F₁.29Cl₀.39)Σ=1.67·19.29H₂O; the cubic unit cell with \( a = 27.93(5) \) Å was determined [13]. Genkina and Khomyakov [17] refined the crystal structure of the Lovozero natrophosphate and found its good agreement with the structure model reported by Baur and Tillmanns [10]; the \( a \) unit-cell parameter was determined to be equal to 27.712(2) Å.

Recently, the interest in natrophosphate has been renewed due to its findings as one of the major salts in alkaline nuclear wastes such as those stored at the Hanford site, near Richland, WA, USA [18–21]. The occurrence of this phase considerably complicates the waste processing, which necessitates detailed studies of its composition and solubility. Previous investigations of the Na₃PO₄–NaF–H₂O system revealed the absence of agreement between different studies [22–24] on the composition of precipitates and equilibrium concentrations as summarized by Felmy and MacLean [25]. Herting and Reynolds [20] re-investigated the composition of synthetic natrophosphate ‘is approximately the same as the composition first reported more than 140 years ago’ (the authors mean the Thorpe’s report published in 1872 [4], which ‘resolves the long-standing controversy in the literature concerning the composition of natrophosphate’. Herein we provide a crystal-structure evidence that the problem is still far from being completely resolved and that natrophosphate may in fact have a variable composition that explains the data discrepancies observed in the previous studies [22–24].

2. Materials and Methods

The sample of natural natrophosphate was taken from the collection of the third author and was found in the central part of the Koashvinskii quarry in a microcline-pectolite-sodalite-aegirine vein in urtites, Kola peninsula, Russia (Figure 1). This vein is traced to the depth of 80 m. Natrophosphate was found as aggregates of transparent cubo-octahedral crystals up to 1 cm in diameter (Figure 2). Association includes fibrous aegirine, delhayelite, fluorapatite, natrolite and pectolite.
Figure 1. Koashvinskii quarry (locality of natrophosphate marked by the star).

Figure 2. Aggregates of natrophosphate crystals from Mt. Koashva, Kola peninsula, Russia: (a) microphoto (field of view = 1.8 × 2 cm²); (b) scanning electron microscopy (SEM) image (field of view = 1.1 × 1.2 mm²).

The composition of natrophosphate [26] was determined using a Cameca MS-46 electron probe micro-analyzer as Na₆.₉₄F₁.₁₁(PO₃.₉₆)₂·18.₁₇H₂O and is in a good agreement with the generally accepted formula. Quantification of elemental compositions was conducted using standard samples of natural and synthetic compounds (lorenzenite(Na), fluorapatite (P) and fluorite (F)).

The Raman spectrum of natural natrophosphate was obtained by means of the Horiba Jobin-Yvon LabRam HR800 spectrometer using Ar+ laser with λ = 532 nm (Figure 3). The high-intensity band at 3362 cm⁻¹ corresponds to OH-stretching region and the bands at 935 cm⁻¹ (ν₁), 545 cm⁻¹ (ν₄) and 412 cm⁻¹ (ν₂) are related with PO₄³⁻ vibrations. The lattice mode corresponds to the band at 181 cm⁻¹ [27].

Figure 3. Raman spectrum of natural natrophosphate.

In order to prepare synthetic natrophosphate, trisodium phosphate (0.1639 g) and sodium fluoride (0.0420 g) were mixed and dissolved in 10 mL of distilled water. The resulting aqueous solution was placed into a watch glass for further evaporation at room
temperature. The crystallization started about 12 h and after 24 h crystals of synthetic natrophosphate were obtained. Synthetic natrophosphate forms colorless, transparent cubooctahedral crystals up to 5 mm in size.

The determination of the exact chemical composition is generally challenging, due to its extreme instability in air and solubility in water. In addition, Na migrates under electron beam, so the electron microprobe analysis of natrophosphate does not provide completely unambiguous results. In an attempt to avoid these problems, the crystal structures of natural and synthetic natrophosphates were refined by means of the X-ray diffraction single-crystal analysis that allowed to refine occupancies of the key structural sites.

For the single-crystal X-ray diffraction experiment, the suitable crystals of natrophosphate and its synthetic analogue were fixed on a micro mount and placed on an Agilent Technologies Excalibur Eos (MoKα radiation) and Agilent Technologies Supernova Atlas (CuKα radiation) diffractometers. The samples were kept at room temperature and at 100 K. The Oxford Cryosystems Cryostream was used for low-temperature measurements. The unit cell parameters were refined by least square technique. The structures have been solved by the direct methods and by means of the SHELXL–97 program [28] incorporated in the OLEX2 program package [29] to $R_1 = 0.043$ (natrophosphate at room temperature), $R_1 = 0.028$ (natrophosphate at 100 K), $R_1 = 0.044$ (synthetic analogue at room temperature), $R_1 = 0.043$ (synthetic analogue at 100 K). Empirical absorption correction was applied in CrysAlisPro [30] program complex using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. In the course of the crystal-structure refinement, the site occupancy of the A site was determined at 100 K using mixed O-Na site-scattering curve and fixed at the obtained value for the room-temperature refinement in order to avoid the problem of correlation between displacement parameters and site occupancies. The crystallographic data and structure refinement details are given in Table 1, the final atomic coordinates, anisotropic displacement, site occupancies and BVS (bond-valence sum) parameters are given in Table 2, selected interatomic distances are provided in Table 3.

Table 1. Crystal data and refinement parameters for natrophosphate (1—room temperature (RT), 2—100 K) and its synthetic analogue (3—RT, 4—100 K).

| Sample | 1 | 2 | 3 | 4 |
|--------|--|--|---|---|
| Crystal system | | | cubic | |
| Space group | | | Fd-3c | |
| Temperature (K) | 293 | 100 | 293 | 100 |
| a (Å) | 27.6942(3) | 27.6241(4) | 28.1150(12) | 27.9777(7) |
| V (Å³) | 21,240.7(6) | 21,079.7(10) | 22,224(3) | 21,899.6(2) |
| Z | 32 | 32 | 32 | 32 |
| Formula weight | 697.63 | 709.70 | 708.63 | 706.60 |
| μ (mm⁻¹) | 1.745 | 1.789 | 1.690 | 1.715 |
| F(000) | 11,386.0 | 11,728.0 | 11,728.0 | 11,714.0 |
| CuKα | CuKα | CuKα | CuKα | |
| 20 range (deg) | 5.096–58.522 | 9.054–152.416 | 8.896–144.738 | 8.94–152.566 |
| Index ranges | −37 ≤ h ≤ 30, −33 ≤ k ≤ 32, 23 ≤ l ≤ 33, −34 ≤ h ≤ 24, −26 ≤ k ≤ 24, −17 ≤ k ≤ 33, −14 ≤ l ≤ 33, −24 ≤ l ≤ 28 |
| Reflections collected | 25,873 | 21,079.7(10) | 11,728.0 | 11,714.0 |
| Independent reflections | 1176 [R(int) = 0.030] | 935 [R(int) = 0.044] | 890 [R(int) = 0.039] | 939 [R(int) = 0.042] |
| R1 = 0.043, wR2 = 0.130 | R1 = 0.028, wR2 = 0.070 | R1 = 0.044, wR2 = 0.109 | R1 = 0.043, wR2 = 0.106 |
| R1 = 0.043, wR2 = 0.130 | R1 = 0.028, wR2 = 0.070 | R1 = 0.044, wR2 = 0.109 | R1 = 0.043, wR2 = 0.106 |
| Goodness-of-fit on F² | 1.106 | 1.131 | 1.118 | 1.122 |
| Final R-indexes (I > 2σ(I)) | 0.38/−0.28 | 0.31/−0.40 | 0.22/−0.33 | 0.44/−0.31 |
Table 2. Atomic coordinates, equivalent isotropic displacement parameters (Å$^2$), occupancies (Occ) and BVS (bond-valence sum) parameters for natrophosphate (1—RT, 2—100 K) and its synthetic analogue (3—RT, 4—100 K).

| Atom | 1                | 2                | 3                | 4                |
|------|------------------|------------------|------------------|------------------|
| Na1  |                  |                  |                  |                  |
|      | $x$              | 0.6654(1)        | 0.6657(3)        | 0.6659(1)        | 0.6662(2)        |
|      | $y$              | 0.2623(1)        | 0.2622(3)        | 0.2629(1)        | 0.2631(1)        |
|      | $z$              | 0.0133(1)        | 0.0136(1)        | 0.0136(1)        | 0.0141(1)        |
|      | $U_{eq}$         | 0.0291(3)        | 0.0151(5)        | 0.0441(4)        | 0.0185(3)        |
|      | $\text{Occ}$    | Na               | Na               | Na               | Na               |
|      | $\text{BVS}^*$  | 1.17             | 1.21             | 1.26             | 1.18             |
| P1   |                  |                  |                  |                  |
|      | $x$              | 5/8              | 5/8              | 5/8              |
|      | $y$              | 1/8              | 1/8              | 1/8              |
|      | $z$              | 1/8              | 1/8              | 1/8              |
|      | $U_{eq}$         | 0.0211(1)        | 0.0091(1)        | 0.0391(1)        | 0.0181(1)        |
|      | $\text{Occ}$    | P                | P                | P                | P                |
|      | $\text{BVS}^*$  | 4.93             | 4.97             | 4.97             | 5.06             |
| O1   |                  |                  |                  |                  |
|      | $x$              | 0.6110(2)        | 0.6102(1)        | 0.6153(3)        | 0.6142(1)        |
|      | $y$              | 0.1708(2)        | 0.1706(1)        | 0.1726(3)        | 0.1726(2)        |
|      | $z$              | 0.0986(2)        | 0.0975(1)        | 0.1011(4)        | 0.1013(3)        |
|      | $U_{eq}$         | 0.0471(1)        | 0.0303(3)        | 0.0757(5)        | 0.0472(7)        |
|      | $\text{Occ}$    | 3/4O             | 1/4O             | 1/4O             |
|      | $\text{BVS}^*$  | 1.23             | 1.24             | 1.24             | 1.26             |
| O2   |                  |                  |                  |                  |
|      | $x$              | 0.6143(1)        | 0.6146(1)        | 0.6146(1)        | 0.6150(1)        |
|      | $y$              | 0.4072(1)        | 0.4073(1)        | 0.4064(1)        | 0.4066(1)        |
|      | $z$              | 0.1692(1)        | 0.1695(1)        | 0.1687(1)        | 0.1692(1)        |
|      | $U_{eq}$         | 0.0251(1)        | 0.0121(1)        | 0.0421(1)        | 0.0171(1)        |
|      | $\text{Occ}$    | O                | O                | O                |
|      | $\text{BVS}^*$  | 1.18             | 1.17             | 1.17             | 1.17             |
| O$_w$|                  |                  |                  |                  |
|      | $x$              | 0.6781(1)        | 0.6782(1)        | 0.6787(1)        | 0.6789(1)        |
|      | $y$              | 0.2474(1)        | 0.2470(1)        | 0.2474(1)        | 0.2468(1)        |
|      | $z$              | 0.0996(6)        | 0.0997(1)        | 0.0955(1)        | 0.0960(1)        |
|      | $U_{eq}$         | 0.0331(1)        | 0.0161(1)        | 0.0501(1)        | 0.0231(1)        |
|      | $\text{Occ}$    | O                | O                | O                |
|      | $\text{BVS}^*$  | 0.43             | 0.44             | 0.41             | 0.42             |
| O$_w$|                  |                  |                  |                  |
|      | $x$              | 0.6795(1)        | 0.6795(1)        | 0.6809(1)        | 0.6815(1)        |
|      | $y$              | 0.3467(1)        | 0.3464(1)        | 0.3471(1)        | 0.3471(1)        |
|      | $z$              | 0.0108(1)        | 0.0109(1)        | 0.0106(1)        | 0.0108(1)        |
|      | $U_{eq}$         | 0.0291(1)        | 0.0141(1)        | 0.0461(1)        | 0.0201(1)        |
|      | $\text{Occ}$    | O                | O                | O                |
|      | $\text{BVS}^*$  | 0.44             | 0.45             | 0.42             | 0.43             |
| O$_w$|                  |                  |                  |                  |
|      | $x$              | 0.5816(1)        | 0.5830(1)        | 0.5862(1)        | 0.5871(1)        |
|      | $y$              | 0.2832(1)        | 0.2844(1)        | 0.2892(1)        | 0.2897(1)        |
|      | $z$              | 0.0363(1)        | 0.0354(1)        | 0.0353(1)        | 0.0347(1)        |
|      | $U_{eq}$         | 0.0591(1)        | 0.0431(1)        | 0.0541(1)        | 0.0221(1)        |
|      | $\text{Occ}$    | O                | O                | O                |
|      | $\text{BVS}^*$  | 0.16             | 0.17             | 0.18             | 0.18             |
| A    |                  |                  |                  |                  |
|      | $x$              | 0.5485(1)        | 0.5475(1)        | 0.5468(1)        | 0.5451(1)        |
|      | $y$              | 0.2015(1)        | 0.2025(1)        | 0.2032(1)        | 0.2048(1)        |
|      | $z$              | 0.0485(1)        | 0.0475(1)        | 0.0467(1)        | 0.0451(1)        |
|      | $U_{eq}$         | 0.0531(1)        | 0.0292(2)        | 0.0721(2)        | 0.0311(1)        |
|      | $\text{Occ}$    | 0.53O + 0.47Na   | 0.53O + 0.47Na   | 0.75O + 0.25Na   | 0.75O + 0.25Na   |
| F    |                  |                  |                  |                  |
|      | $x$              | 3/4              | 3/4              | 3/4              | 3/4              |
|      | $y$              | 3/4              | 3/4              | 3/4              | 3/4              |
|      | $z$              | 3/4              | 3/4              | 3/4              | 3/4              |
|      | $U_{eq}$         | 0.0211(1)        | 0.0091(1)        | 0.0361(1)        | 0.0161(1)        |
|      | $\text{Occ}$    | F                | F                | F                |
|      | $\text{BVS}^*$  | 0.86             | 0.89             | 1.12             | 0.84             |

*Calculated using bond-valence parameters derived by Brese and O’Keeffe [31].
Table 3. Selected bond lengths (Å) in the crystal structures of natrophosphate (1—room temperature, 2—100 K) and its synthetic analogue (3—room temperature, 4—100 K).

| Bond Length | 1     | 2     | 3     | 4     |
|-------------|-------|-------|-------|-------|
| Na1–Ow4     | 2.349(2) | 2.346(2) | 2.405(3) | 2.392(2) |
| Na1–Ow4     | 2.371(2) | 2.367(2) | 2.352(3) | 2.342(2) |
| Na1–Ow3     | 2.373(2) | 2.364(2) | 2.412(2) | 2.398(2) |
| Na1–Ow3     | 2.371(2) | 2.361(2) | 2.370(3) | 2.363(2) |
| Na1–Ow5     | 2.478(2) | 2.441(2) | 2.438(3) | 2.406(2) |
| Na1–F       | 2.395(1) | 2.383(1) | 2.421(1) | 2.405(1) |
| <Na1–O,F>   | 2.390   | 2.377   | 2.399   | 2.384   |
| P1–O1       | 1.516(5)(12x) | 1.528(3)(12x) | 1.524(6)(12x) | 1.517(6)(12x) |
| <P1–O>      | 1.527   | 1.528   | 1.524   | 1.517   |
| P2–O2       | 1.543(4x) | 1.547(1)(4x) | 1.543(2)(4x) | 1.546(2)(4x) |
| <P2–O>      | 1.543   | 1.547   | 1.543   | 1.546   |
| F–Na1       | 2.395(1)(6x) | 2.383(1)(6x) | 2.421(1)(6x) | 2.405(1)(6x) |
| <F–Na>      | 2.395   | 2.383   | 2.421   | 2.405   |
| A–Ow5       | 2.465(1)(3x) | 2.487(1)(3x) | 2.676(1)(3x) | 2.667(1)(3x) |
| A–O1        | 2.376(1) | 2.384(1) | 2.605   | 2.649   |
| <A–O>       | 2.442   | 2.461   | 2.658   | 2.663   |

3. Results

In agreement with the previous studies [9,10,17], the crystal structure of natrophosphate is based upon the super-octahedral [Na₆(H₂O)₁₈F]⁵⁺ polycationic complexes consisting of six edge-linked Na₆(OH₂)₅F octahedra sharing one common fluorine vertex so the F atom is at the center of an octahedron formed by six Na atoms (Figure 4). The Na1 site is fully occupied and the <Na1–Ow> bond lengths vary from 2.349 to 2.478 Å for natrophosphate and from 2.352 to 2.421 Å for its synthetic analogue at room temperature. The <Na1–F> bond lengths in the anion-centered octahedra (FNa₆) range from 2.383 (natrophosphate at 100 K) to 2.421 Å (synthetic analogue at room temperature). Two symmetrically independent P sites are tetrahedrally coordinated by O1 and O2 atoms, respectively. The O1 site is disordered around a threefold axis with the occupancy factor of 0.33.

Figure 4. The super-octahedral [Na₆(H₂O)₁₈F]⁵⁺ polycationic cluster in the crystal structure of natrophosphate: (a) ball-and-stick representation; (b) representation in terms of (NaF₆) octahedra (shown in yellow). Legend: Na, F, O and H atoms are shown as yellow, green, red and black spheres, respectively.
The $A$ site is statistically occupied by Na and H$_2$O with the prevalence of H$_2$O with the refined occupancy factors O:Na equal to 0.53:0.47 for natrophosphate and 0.75:0.25 for its synthetic analogue. The almost equal occupancy of the $A$ site by Na and H$_2$O in natrophosphate is in perfect agreement with the previous structure reports [10,17], where the 0.50:0.50 occupancy was assumed. The $A$ site is in tetrahedral coordination by three O$_w$5 and one O1 atoms. The $A$–O bond lengths for natrophosphate are in good agreement with previous structure reports. In particular, Baur and Tillmanns [10] reported for the $A$ site the $A$–O1 and $A$–O$_w$5 bond lengths of 2.41(1) and 2.512(4) Å, respectively, in accord with the values of 2.376(1) and 2.465(1) Å obtained in this study (room-temperature data). In contrast, the $A$–O1 and $A$–O$_w$5 bond lengths for the synthetic natrophosphate prepared by us are significantly higher, 2.605(1) and 2.676(1) Å, respectively (Figure 5). The enlarged coordination of the $A$ site in the synthetic sample agrees well with its higher occupancy by H$_2$O molecules compared to the natural sample. It seems that there exists a correlation between the site occupancy of the $A$ site and the average $<A$–O$>$ bond length. The deficiency of Na at the $A$ site in synthetic material raises the charge-balance problem, which is discussed in details below.

In order to refine the hydrogen atom positions, the samples of natrophosphate and its synthetic analogue were studied at 100 K. The room-temperature refinement of natrophosphate allowed to locate four hydrogen atom positions around the O$_w$3 and O$_w$4 sites with fixed bond lengths. Seven hydrogen positions where refined for the O$_w$3, O$_w$4 and O$_w$5 sites in the synthetic analogue, where H5 split into H5A, H5B and H5C with the occupancy factors of 2/3 for natrophosphate and 0.65, 0.60 and 0.75 for the synthetic analogue. The O$_w$5–H bond lengths and the H5B isotropic displacement parameters are fixed for natrophosphate. The O$_w$5–H bond lengths for the synthetic natrophosphate were studied at 100 K. The room-temperature refinement made it possible to locate seven hydrogen atom positions for both samples. The H positions around the O$_w$5 site are disordered with the occupancy factors of 2/3 and with fixed isotropic displacement parameter for the H4C site. The low-temperature refinement made it possible to locate seven hydrogen atom positions for both samples. The H positions around the O$_w$5 site are disordered with the occupancy factors of 2/3 for natrophosphate and 0.65, 0.60 and 0.75 for the synthetic analogue. The O$_w$5–H bond lengths and the H5B isotropic displacement parameters are fixed for natrophosphate. The hydrogen atom coordinates and isotropic displacement parameters for samples at 100 K are given in Tables 4 and 5. The hydrogen bonding networks can be described on the basis of H-atom positions located at 100 K and calculation of bond-valence sums (BVS) for oxygen atoms [11] (Tables 6 and 7). The O1 atom acts as an acceptor of hydrogen bonds donated by the H$_2$O$_4$, H$_2$O$_3$ and H$_2$O$_5$ molecules with the O…H distance ranging from 1.874 to 2.192 Å for 100 K. The hydrogen-bond networks description is in a good agreement with the previous structure reports [10,17].
with data obtaining by previous studies for synthetic analogue of natrophosphate where H-positions were taken from the difference synthesis without further refinement.

Table 4. Hydrogen atoms coordinates, occupancies (Occ) and displacement isotropic parameters (Å²) for natrophosphate at 100 K.

| Atom   | Occ | x        | y        | z        | U_eq  |
|--------|-----|----------|----------|----------|-------|
| H3A    | 1   | 0.670(9) | 0.271(9) | 0.1107(9)| 0.034(7) |
| H3B    | 1   | 0.6628(1) | 0.2241(1) | 0.1117(1)| 0.052(8) |
| H4A    | 1   | 0.6693(9) | 0.3589(9) | -0.0163(9)| 0.030(6) |
| H4B    | 1   | 0.6669(9) | 0.3641(9) | 0.0324(1)| 0.033(6) |
| H5A    | 0.6667 | 0.585(1) | 0.3051(9)| 0.0578(9)| 0.012(7) |
| H5B    | 0.6667 | 0.562(1) | 0.270(2) | 0.502(14)| 0.050  |
| H5C    | 0.6667 | 0.572(2) | 0.301(1) | 0.135(13)| 0.05(1)  |

Table 5. Hydrogen atoms coordinates, occupancies (Occ) and displacement isotropic parameters (Å²) for synthetic analogue of natrophosphate at 100 K.

| Atom   | Occ | x        | y        | z        | U_eq  |
|--------|-----|----------|----------|----------|-------|
| H3A    | 1   | 0.671(1) | 0.269(1) | 0.112(1) | 0.030(1) |
| H3B    | 1   | 0.666(2) | 0.225(2) | 0.113(2) | 0.07(2)  |
| H4A    | 1   | 0.669(1) | 0.362(1) | 0.031(1) | 0.028(9) |
| H4B    | 1   | 0.674(1) | 0.358(1) | -0.014(1)| 0.030(1) |
| H5A    | 0.75 | 0.587(1) | 0.306(2) | 0.600(2) | 0.02(1)  |
| H5B    | 0.65 | 0.575(2) | 0.260(2) | 0.042(2) | 0.01(1)  |
| H5C    | 0.60 | 0.574(2) | 0.307(2) | 0.019(2) | 0.01(1)  |

Table 6. Hydrogen bonding geometry (Å, °) for natrophosphate (D = donor; A = acceptor).

| D–H   | d(D–H) | d(H ⋅⋅ ⋅ A) | <DHA | d(D ⋅⋅ ⋅ A) | A   |
|-------|--------|-------------|------|------------|-----|
| O–H3A | 0.814  | 2.075       | 161.15 | 2.858      | O2  |
| O–H3B | 0.869  | 2.107       | 139.52 | 2.852      | O1  |
| O–H3B | 0.869  | 2.135       | 143.07 | 2.877      | O1  |
| O–H3B | 0.869  | 1.963       | 168.89 | 2.821      | O1  |
| O–H4A | 0.872  | 1.946       | 170.75 | 2.810      | O2  |
| O–H4B | 0.839  | 1.987       | 177.14 | 2.826      | O2  |
| O–H5A | 0.846  | 1.884       | 167.57 | 2.717      | O2  |
| O–H5B | 0.801  | 1.921       | 127.06 | 2.487      | O6  |
| O–H5C | 0.809  | 1.926       | 170.34 | 2.726      | O5  |

Table 7. Hydrogen bonding geometry (Å, °) for synthetic natrophosphate.

| D–H   | d(D–H) | d(H ⋅⋅ ⋅ A) | <DHA | d(D ⋅⋅ ⋅ A) | A   |
|-------|--------|-------------|------|------------|-----|
| O–H3A | 0.782  | 2.192       | 156.34 | 2.925      | O2  |
| O–H3B | 0.849  | 2.101       | 134.38 | 2.762      | O1  |
| O–H3B | 0.849  | 1.972       | 175.31 | 2.819      | O1  |
| O–H3B | 0.849  | 2.248       | 143.05 | 2.879      | O2  |
| O–H4A | 0.806  | 2.076       | 173.96 | 2.879      | O2  |
| O–H4B | 0.793  | 2.070       | 175.83 | 2.862      | O2  |
| O–H5B | 0.833  | 1.874       | 174.37 | 2.705      | O2  |
| O–H5C | 0.741  | 1.980       | 164.77 | 2.702      | O5  |

4. Discussion

The key issue observed in the current study is the variable occupancy of the A site by Na and H2O molecules that agrees well with the range of the A–O distances obtained from the crystal-structure study. The enlarged AO4 coordination polyhedron corresponds to its
higher occupancy by H$_2$O molecules. The enlargement of the polyhedron also explains well the values of the $a$ unit-cell parameter that increases from 27.694 for natrophosphate to 28.115 Å for its synthetic analogue, i.e., by ca. 1.5%.

The Na deficiency at the $A$ site requires a mechanism for the charge-balance compensation. Following Kapustin et al. [11], we believe that the most reasonable explanation is the incorporation of additional H atoms into the structure through the protonation of particular anionic sites. There are only two possible O sites prone to the protonation reaction: O sites of the phosphate groups and H$_2$O molecules. Protonation of the former sites results in the formation of acid phosphate groups, (HPO$_4$)$_2^-$, whereas protonation of the latter produces hydronium ions, (H$_3$O)$^+$. In our opinion, the first scenario is more realistic. Khomyakov and Menshikov [32] observed that alteration of natrophosphate under natural conditions is associated with the formation of nahpoite, Na$_2$HPO$_4$ = Na$_2$(PO$_3$OH), and dorfmanite, Na$_3$HPO$_4$·2H$_2$O = Na$_2$(PO$_3$OH)·2H$_2$O, that both contain acid phosphate groups. However, the issue requires further investigation; in order to avoid the final decision, the chemical formulas for the natural and synthetic natrophosphate studied here can be written as Na$_{6.94}$H$_{0.06}$F(PO$_4$)$_2$·19.06H$_2$O and Na$_{6.75}$H$_{0.25}$F(PO$_4$)$_2$·19.25H$_2$O, respectively. The general formula of natrophosphates can therefore be written as Na$_{6+x}$H$_x$F(PO$_4$)$_2$·(19 + $x$)H$_2$O, where $x$ = 0–1.

The chemical variability of natrophosphate allows to explain the discrepancies in its solubility reported by different authors [22–25]. The results of the solubility measurements may be influenced by the different chemical nature of the investigated sample that has to be taken into account in the course of thermodynamic modeling.

From the structural point of view, natrophosphate belongs to the family of minerals containing polyoxometalate clusters as recently reviewed in [33]. The presence of the (FNao$_6$)$_5^+$ units at the core of the clusters allows to suggest that the mineral may serve as a precursor for the formation of antiperovskite structure motifs based upon anion-centered octahedra [34]. The polyoxometalate character of its structure defines its high structural complexity: the information-based parameters [35,36] are equal to 3.713 bit/atom and 2109.177 bit/cell that allows to classify natrophosphate as a structurally very complex mineral. Its complexity is most likely the result of the presence of the super-octahedral [Nao$_6$(H$_2$O)$_{18}$F]$^{5+}$ polycationic complexes in the aqueous solutions, from which the mineral and its synthetic analogue crystallize. One may hypothesize on the possibility of formation of larger polynuclear hydrated Na-F clusters that can be viewed as parts of the NaF structure [37].

**Supplementary Materials:** The following are available online at https://www.mdpi.com/2075-163X/11/2/186/s1, Crystallographic Information Files (CIFs) for the four structures of natrophosphate.

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36. Krivovichev, S.V. Structural complexity of minerals: Information storage and processing in the mineral world. *Miner. Mag.* **2013**, *77*, 277–326. [CrossRef]

37. Miller, T.M.; Lineberger, W.C. Mass spectra and photodetachment of sodium fluoride negative ion clusters. *Int. J. Mass Spectr. Ion Proc.* **1990**, *102*, 239–249. [CrossRef]