

# Crystal structure of trisodium iron diphosphate, $\text{Na}_{2.88}\text{Fe}(\text{PO}_4)_2$ , a synthetic phosphate with hannayite-type heteropolyhedral chains

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## Abstract

$\text{FeNa}_{2.88}\text{O}_8\text{P}_2$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 5.3141(6)$  Å,  $b = 8.5853(9)$  Å,  $c = 8.7859(8)$  Å,  $\alpha = 114.429(9)^\circ$ ,  $\beta = 92.327(9)^\circ$ ,  $\gamma = 106.08(1)^\circ$ ,  $V = 345.1$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{\text{gt}}(F) = 0.028$ ,  $wR_{\text{ref}}(F^2) = 0.087$ ,  $T = 293$  K.

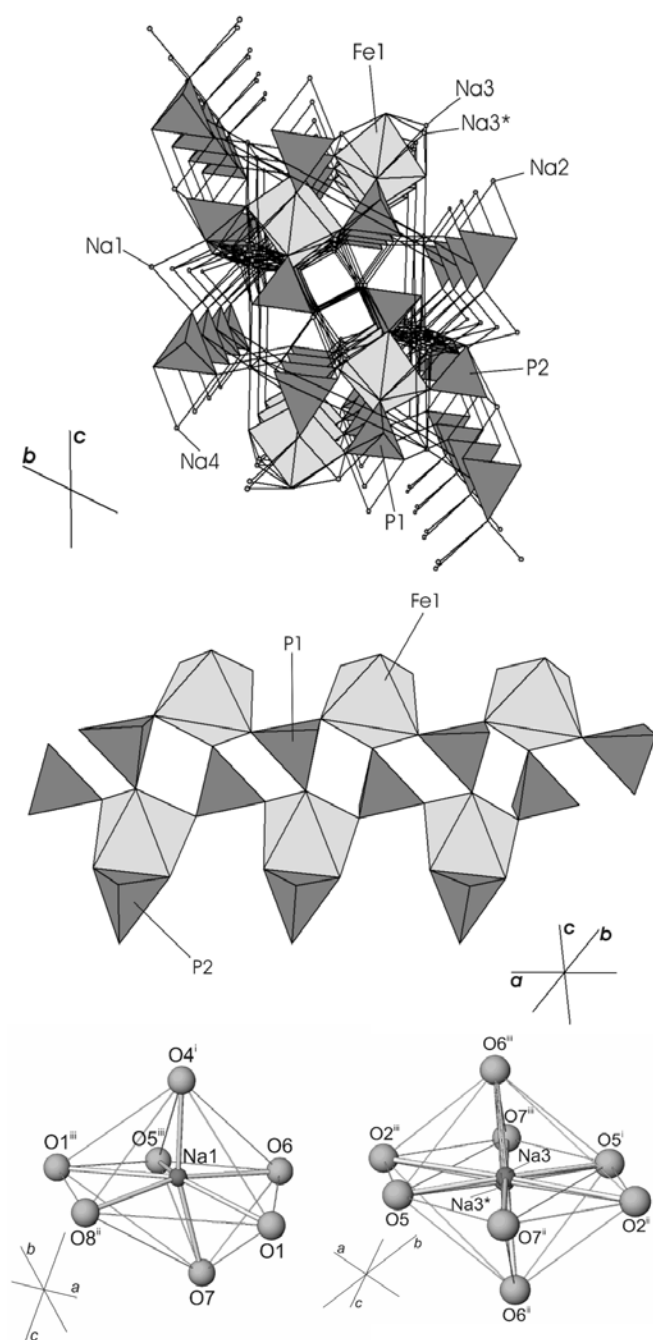
## Source of material

The title compound was synthesized under hydrothermal conditions. The starting material was prepared by mixing  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  in proportions 2:1:1:½. About 25 mg of the homogenized mixture was sealed into a gold tube with an outer diameter of 2 mm and a length of 25 mm, containing 2 mg of distilled water. The gold capsule was then inserted in a Tuttle-type pressure vessel [1] and maintained at a temperature of 700 °C and a pressure of 0.1 GPa. After 3 days the sample, still in the gold tube in the autoclave, was quenched to room temperature in a stream of cold air. Elongated grey crystals of the title compound were associated with large colorless crystals of maricite,  $\text{NaFe}(\text{PO}_4)$ , with  $\text{Na}_2\text{HPO}_4 \cdot n\text{H}_2\text{O}$  and magnetite,  $\text{Fe}_3\text{O}_4$ . A chemical analysis of the title compound has been performed with a CAMEBAX SX-50 electron microprobe (15 kV acceleration voltage, 20 nA beam current, analyst H.-J. Bernhardt, Ruhr-Universität Bochum, Germany). The standard used were graptolite from Kabira [2] (P, Fe) and jadeite (Na). The average of 8 point analyses gives  $\text{P}_2\text{O}_5$ , 44.9(4) wt. %;  $\text{Fe}_2\text{O}_3$ , 26.2(11) wt. %;  $\text{Na}_2\text{O}$ , 28.3(3) wt. %; total 99.4 wt. %. The chemical composition, calculated on the basis of 16 positive charges, is  $\text{Na}_{2.89}\text{Fe}^{3+}_{1.04}(\text{PO}_4)_2$ .

## Discussion

In the natural geological environment of granitic pegmatites, Na-Fe-Mn-bearing phosphates play important geochemical and petrological roles. The alluaudite group of minerals, with an idealized chemical composition  $\text{Na}_2(\text{Mn}, \text{Fe}^{2+})_2\text{Fe}^{3+}(\text{PO}_4)_3$ , constitutes a good example of primary phosphates which can be used as geothermometer, or to constrain the oxygen fugacity which prevailed in granitic pegmatites [3]. In order to better understand the crystallization conditions of iron-rich alluaudites in pegmatites, we decided to investigate the Na-Fe<sup>2+</sup>-Fe<sup>3+</sup> (+PO<sub>4</sub>) ternary system by hydrothermal methods [4]. These experiments produced several new phosphates, which crystallized in the Na-rich part of the system and were investigated by single-crystal X-ray diffraction techniques.

The crystal structure of the title compound does not correspond to that of any other natural or synthetic phosphate. The fundamental structural unit is constituted by a chain running along [100], a chain which is similar to that occurring in hannayite,  $(\text{NH}_4)_2[\text{Mg}_3\{\text{PO}_3(\text{OH})\}_4(\text{H}_2\text{O})_8]$  [5]. The parallel chains, which are linked together by large sodium cations (figure, top), are formed by Fe1 octahedra linked via corner-sharing to the P1 tetrahedra (figure, middle), and decorated by the edge-sharing P2 tetrahedra. The chains can be described as two connected single



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chains, which show a regular alternation of Fe1 octahedra and P tetrahedra in a 1:1 ratio. They can also be decomposed in tetramers constituted by two octahedra linked by two tetrahedra, aligned along the [010] axis. These tetramers can be considered as fragments of kröhnkite-type chains, which are common among sulfates, arsenates and phosphates [6,7]. Topologically, the chains described herein are of c1/1b type, according to the classification of Krivovichev [8]. They have been reported in many synthetic sulfates, chromates and selenates, but in these compounds, the chains generally show an alternation of tetrahedra and UO<sub>7</sub> pentagonal bipyramids [8]. Only the compounds [H<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>][FeF<sub>3</sub>(SO<sub>4</sub>)] [9] and VO(HPO<sub>4</sub>)(H<sub>2</sub>O)<sub>4</sub> [10] really show c1/1b-type tetrahedral/octahedral chains. Among phosphate minerals, heteropolyhedral chains similar to those occurring in the title compound were reported in hannayite, but in this mineral, the chains are not isolated but linked to other chains [5,11]. The sodium sites are connected with the Fe1 site via corner-sharing (Na2-Fe1 and Na3/Na3\*-Fe1), edge-sharing (Na4-Fe1) or face-sharing (Na1-Fe1). These sites also share one corner (Na4-P1-Na3/Na3\* and Na4-P1) or one edge (Na2-P1 and Na3/Na3\*-P2) with the P1 and P2 tetrahedra. The Fe1 (2.011 Å – 2.262 Å), Na2 (2.429 Å – 2.798 Å) and Na4 sites (2.473 Å – 2.659 Å) show topologies of weakly distorted octahedra, whereas the 7-coordinated Na1 site (2.222 Å – 2.812 Å) shows a topology of distorted pentagonal bipyramid (figure, bottom). One sodium

was split into two distinct Na3 and Na3\* positions, and the site occupancy factors have been constrained to 0.25 in order to take into account this disordered cationic distribution. The coordination polyhedra of the Na3/Na3\* site (2.19 Å – 2.94 Å) can be described as a 8-coordinated hexagonal bipyramid (figure, bottom), produced by the fusion of two distorted octahedra. The first octahedron contains Na3 bonded to O5, O5<sup>i</sup>, O6<sup>ii</sup>, O6<sup>iii</sup>, O7<sup>ii</sup> and O2<sup>ii</sup>, and the second octahedron contains Na3\* bonded to O5, O5<sup>i</sup>, O6<sup>ii</sup>, O6<sup>iii</sup>, O7<sup>iii</sup> and O2<sup>iii</sup>. The idealized formula of the title compound, calculated from the structural data, is Na<sub>2.88</sub>Fe(PO<sub>4</sub>)<sub>2</sub>, in good agreement with the chemical analysis.

**Table 1.** Data collection and handling.

|                                                         |                                                           |
|---------------------------------------------------------|-----------------------------------------------------------|
| Crystal:                                                | gray, elongated,<br>size 0.025 × 0.050 × 0.180 mm         |
| Wavelength:                                             | Mo K <sub>α</sub> radiation (0.71073 Å)                   |
| μ:                                                      | 28.50 cm <sup>-1</sup>                                    |
| Diffractometer, scan mode:                              | Xcalibur with Sapphire2 CCD, φ/ω                          |
| 2θ <sub>max</sub> :                                     | 82.78°                                                    |
| N(hkl) <sub>measured</sub> , N(hkl) <sub>unique</sub> : | 5417, 3193                                                |
| Criterion for I <sub>obs</sub> , N(hkl) <sub>gt</sub> : | I <sub>obs</sub> > 2 σ(I <sub>obs</sub> ), 2436           |
| N(param) <sub>refined</sub> :                           | 138                                                       |
| Programs:                                               | SHELXS-97 [12], SHELXL-97 [13],<br>ATOMS [14], WinGX [15] |

**Table 2.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

| Atom   | Site | Occ.     | x          | y          | z           | U <sub>11</sub> | U <sub>22</sub> | U <sub>33</sub> | U <sub>12</sub> | U <sub>13</sub> | U <sub>23</sub> |
|--------|------|----------|------------|------------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Fe(1)  | 2i   |          | 0.09311(5) | 0.74752(3) | 0.26905(3)  | 0.0110(1)       | 0.0094(1)       | 0.0104(1)       | 0.00292(8)      | 0.00277(8)      | 0.00350(8)      |
| P(1)   | 2i   |          | 0.37109(9) | 1.20034(6) | 0.48461(5)  | 0.0110(2)       | 0.0082(2)       | 0.0096(2)       | 0.0023(1)       | 0.0016(1)       | 0.0036(1)       |
| P(2)   | 2i   |          | 0.11493(9) | 0.70244(6) | -0.06014(5) | 0.0122(2)       | 0.0083(2)       | 0.0105(2)       | 0.0025(1)       | 0.0028(1)       | 0.0046(1)       |
| Na(1)  | 2i   |          | -0.2761(2) | 0.9777(1)  | 0.2513(1)   | 0.0303(5)       | 0.0277(4)       | 0.0357(5)       | 0.0108(4)       | 0.0089(4)       | 0.0224(4)       |
| Na(2)  | 2i   | 0.881(4) | 0.3076(2)  | 1.1428(1)  | 0.1247(1)   | 0.0286(6)       | 0.0249(5)       | 0.0181(5)       | 0.0127(4)       | 0.0032(4)       | 0.0100(4)       |
| Na(3)  | 2i   | 0.25     | 0.503(6)   | 0.507(4)   | 0.022(2)    | 0.007(4)        | 0.009(3)        | 0.032(6)        | 0.000(2)        | -0.003(4)       | 0.001(4)        |
| Na(3*) | 2i   | 0.25     | 0.469(5)   | 0.480(3)   | -0.059(2)   | 0.007(4)        | 0.009(3)        | 0.032(6)        | 0.000(2)        | -0.003(4)       | 0.001(4)        |
| Na(4)  | 1g   |          | 0          | ½          | ½           | 0.0303(7)       | 0.0478(8)       | 0.0351(7)       | 0.0225(6)       | 0.0157(6)       | 0.0297(7)       |
| O(1)   | 2i   |          | 0.2317(3)  | 1.0197(2)  | 0.3297(2)   | 0.0305(8)       | 0.0103(5)       | 0.0148(6)       | -0.0006(5)      | -0.0031(5)      | 0.0036(5)       |
| O(2)   | 2i   |          | -0.0523(3) | 0.4837(2)  | 0.2123(2)   | 0.0305(8)       | 0.0137(6)       | 0.0148(6)       | 0.0053(5)       | 0.0062(5)       | 0.0020(5)       |
| O(3)   | 2i   |          | 0.3471(3)  | 1.3452(2)  | 0.4274(2)   | 0.0270(8)       | 0.0130(6)       | 0.0213(7)       | 0.0039(5)       | -0.0009(6)      | 0.0100(5)       |
| O(4)   | 2i   |          | 0.2155(3)  | 0.8492(2)  | -0.1165(2)  | 0.038(1)        | 0.0224(7)       | 0.0333(9)       | -0.0001(7)      | 0.0044(7)       | 0.0211(7)       |
| O(5)   | 2i   |          | 0.3230(3)  | 0.7212(2)  | 0.0819(2)   | 0.0142(7)       | 0.0237(7)       | 0.0188(6)       | 0.0088(5)       | 0.0000(5)       | 0.0076(5)       |
| O(6)   | 2i   |          | -0.1259(3) | 0.7217(2)  | 0.0291(2)   | 0.0139(6)       | 0.0197(6)       | 0.0209(7)       | 0.0077(5)       | 0.0057(5)       | 0.0065(5)       |
| O(7)   | 2i   |          | -0.2380(3) | 0.7830(2)  | 0.3619(2)   | 0.0236(7)       | 0.0286(7)       | 0.0191(6)       | 0.0178(6)       | 0.0119(6)       | 0.0142(6)       |
| O(8)   | 2i   |          | 0.3343(3)  | 0.7787(2)  | 0.4737(2)   | 0.0120(6)       | 0.0240(7)       | 0.0251(7)       | 0.0065(5)       | 0.0034(5)       | 0.0095(6)       |

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