

Rietveld Structure Refinement of the Apophyllite Crystals from Deccan Basalt Plateau Using X-ray Powder Diffraction Data

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The crystal structure of a rare sample of natroapophyllite from Pune district (western India) located in the Deccan Basalt Plateau has been refined using X-Ray powder diffraction data and the Rietveld method. The Rietveld refinement was carried out using the computer program Diffracplus TOPAS 4.1. The pseudo-Voigt (pV) profile function was used for the fit of the peaks. The Rietveld refinement of the analyzed sample in space group Pnmm (No.58): $a=8.94771 \text{ \AA}$, $b=8.98013 \text{ \AA}$, $c=15.78878 \text{ \AA}$, $Z=2$, confirm the basic natroapophyllite structure. The chemical composition of the apophyllite crystals from Pune region (India) was determined by EDX analysis. The paper presents a new set of the unit cell parameters and fractional coordinates that define the natroapophyllite crystal structure. The quality of the sample analyzed was pristine, the sample being collected from an association of apophyllite-stilbite crystals of centimetric dimensions.

Keywords: natroapophyllite, crystal structure, X-rays diffraction, EDX, Rietveld method

Pune region is located in Deccan Plateau or Deccan Traps, a large igneous province of about 500,000 km² in western and central India. The Deccan Traps consists of massive tholeiitic basaltic lava flows at the end of Cretaceous period and is one of the largest volcanic areas on Earth. Deccan traps formed flat topped ridges which are due to the presence of more resistant basaltic flow units forming a series of step-like terraces. The basaltic flows contain vesicles, joints and weathered cappings usually filled with secondary minerals, the most encountered minerals being heulandite, then stilbite and (progressively less common) mordenite, apophyllite, mesolite, epistilbite, calcite and chabazite [1, 2]. A zonation of zeolite species was proposed by Sukheswala et al. [1] and subsequently investigated by Jeffery et al. [3] who studied a small area of the Deccan Traps north and south from Bombay, including Pune and Nasik regions.

Apophyllite is fairly widespread and it occurs as a secondary mineral in amygdules or druses in basalts and occasionally in cavities in granites, gneisses, skarns. It is almost always occurs together with zeolites, especially in the trap rock environments. The mineral is transparent to colourless but may be white, pink, pale yellow to green. Apophyllite usually forms aggregates of small to medium sized (0.1 to 10 mm) prismatic or tabular crystals studded over early-formed minerals. The best crystals, up to 10 cm in size, are encountered in the Pune (Poona) and Nasik regions. Striations on prism faces (001) are characteristic. Often crystals in thin sections show sectoral growth and anomalous optical characters due to lattice distortion [1].

The mineral sample used in the study (figure 1) belongs to the collection of Mineralogy Laboratory of the Petroleum-Gas University of Ploiesti. The sample is colourless, vitreous to pearly, macroscopically the crystals being similar with other types of apophyllite (fluorapophyllite). The crystals are tabular to prismatic, forms aggregates of medium to large sized (0.50 to 5 cm) and show (100) prisms truncated by the (111) dipyrramids striated perpendicular to the c axis (001). The cleavage is perfect on (001) and the Mohs hardness is 4 to 5.



Fig. 1. Apophyllite-stilbite association from Pune region (India) in the collection of Mineralogy Laboratory of the Petroleum-Gas University of Ploiesti

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The nomenclature of the apophyllite group is a complicated problem. The term “apophyllite” refers to a specific group of phyllosilicates, a hydrous sheet-structured minerals respectively. Apophyllite term was originally referred to a single mineral, with variable ratio of fluorine to hydroxyl. The International Mineralogical Association (IMA) divided in 1978 the apophyllite group into two distinct minerals: Fluorapophyllite and Hydroxyapophyllite, and in 1981 was added to the group an additional member, called Natroapophyllite [4, 5]. In 2008 a change in the nomenclature system used for this group was approved by the IMA, removing the prefixes from the species names and using suffixes to designate the species for a class of minerals of similar chemical makeup that comprise a solid solution series, and includes the members apophyllite-(KF) (instead of Fluorapophyllite), apophyllite-(KOH) (instead of Hydroxyapophyllite), and apophyllite-(NaF) (instead of Natroapophyllite) [6, 7]. Later propose of IMA regarding members of apophyllite group was to rename these minerals as fluorapophyllite-(K), hydroxyapophyllite-(K), and fluorapophyllite-(Na) [8].

The most common minerals are fluorapophyllite and hydroxyapophyllite, encountered in many places worldwide. Natroapophyllite, also exists but is far less common. Fluorapophyllite and hydroxyapophyllite are different minerals only because of the difference in the percentage of fluorine to hydroxyl ions. They represent the end members of a series that might be called the apophyllite series. The Na-rich apophyllite is invariably orthorhombic and fluorine-rich, while the K-rich apophyllite (fluorapophyllite and hydroxyapophyllite) are tetragonal [5, 7].

Natroapophyllite is an unusual sheet structure with orthorhombic symmetry and *Pnmm* space group. The crystal structure is built of sheets of four-membered rings of alternating Si-O tetrahedra with interleaving sheets containing the Ca and Na atoms. Eight-membered rings of Si-O tetrahedra are also located in this plane, thus forming a layered structure parallel to the perfect (001) cleavage. The unshared oxygens in the adjacent four-fold rings point approximately up and down the *c* axis. The coordination of the interlayer ions is also unusual: the sodium ion is surrounded by eight water molecules, the calcium ion is bonded to two water molecules (shared with Na) and four oxygen ions. The fluorine ion is surrounded by a planar group of four Ca ions. Natroapophyllite is basically isostructural with fluorapophyllite and hydroxyapophyllite, with Na substituted for K and the ion pairs Si, Ca, O(2), O(3), O(4) having two independent sets of coordinates because of the lowering of symmetry from tetragonal to orthorhombic [9-11].

The apophyllite crystal structure aroused a great interest since the beginning of the last century. X-ray diffraction studies of the apophyllite structure were made by several authors. [4-7, 9-18].

The crystal structure of fluorapophyllite was initially solved by Taylor and Naray-Szabo [12], and was refined subsequently in space group *P4/mnc* by Colville et al. [11], Chao [14], and Prince [15]. Later Dunn et al. [16] and Rouse et al. [17] also carried out a refinement of crystal structure of hydroxyapophyllite showing the tetragonal symmetry and belonging to the space group *P4/mnc*. More later, Matsueda et al. [5] and Miura et al. [9] reported identification of a natroapophyllite, a sodium analog of the orthorhombic apophyllite described originally by Sahama [13] and Belsare [19]. According to Matsueda et al. [5] there are a pseudo solid-solution series between natroapophyllite and fluorapophyllite which bridges the orthorhombic-tetragonal symmetry change. Miura et al. [9] reported a refinement of natroapophyllite crystal structure from Sampo mine (Japan) in the *Pnmm* space group using the parameters and atomic coordinates described by Colville et al. [11] and Chao [14].

In our paper we carried out a chemical-mineralogical investigation using X-rays diffraction and EDX analysis and a Rietveld structure refinement on a spectacular apophyllite sample (figure 1) from Pune region located in the famous Deccan Basalt Plateau (western India).

Experimental part

The apophyllite crystals were grinded in an agate mortar with pestle by fine grinding. X-ray powder diffraction data were measured at 24°C using an automated Bruker D8 Advance θ - θ diffractometer, with CuK α radiation ($\lambda = 1.54\text{\AA}$; 40 kV; 40 mA), a LynxEye detector and Bragg-Brentano geometry. K β radiation was eliminated by a Ni filter. Primary and secondary Soller slits were 2.5°. A fixed aperture and divergence slit of 0.6 mm, a 0.6 mm antivergence slit and 0.1 mm width detector slit were used. X-ray diffraction data were obtained using 0.1° 2 θ steps from 10° to 60° 2 θ counting for 10 s per step. The powder was placed into a cavity mount in an attempt to minimize preferred orientation.

The apophyllite sample was also analyzed by SEM/EDX using a Hitachi S3400-N microscope equipped with an Oxford Instruments X-act energy dispersive X-ray (EDX) spectrometer, operated using the Inca software package. The generated spectra were determined and analyzed by an EDX spectrometer, with 125 eV resolutions, and detector active area 10 mm². During tests, the working conditions were kept stable in order to minimize any effect on the statistical nature of the production of radiation.

In table 1 is presented the average chemical composition obtained by EDX analysis carried out on several calcinated powders from the apophyllite sample.

Table 1
AVERAGE CHEMICAL COMPOSITION OF THE APOPHYLLITE CRYSTALS
FROM PUNE REGION (INDIA) (DETERMINED BY EDX ANALYSIS)

Element	Wt%	Standard deviation
Si	29.60	0.20
Ca	21.30	0.10
Na	4.20	0.10
K	0.40	0.20
F	2.60	0.40
O	41.90	0.40
TOTAL	100.00	

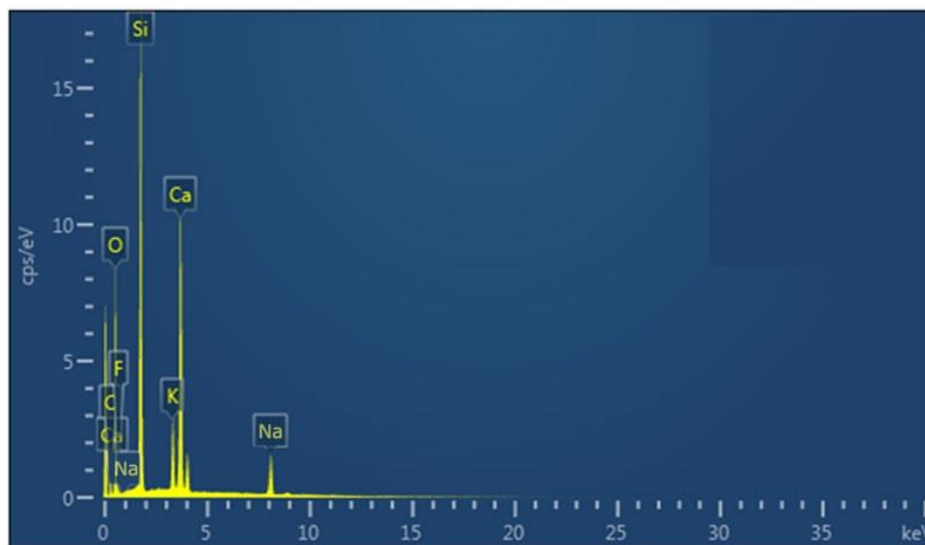


Fig. 2. EDX analysis of the apophyllite sample from Pune region (India)

Results and discussions

The Rietveld refinement was carried out using Diffracplus TOPAS 4.1 software. Pseudo-Voigt (pV) profile function was used for the fit of the peaks; the result of measurement shows that the peaks shape is Lorentzian. Rietveld refinement using X-ray powder diffraction data of apophyllite sample in the space group *Pnmm* (No.58) [20]: $a=8.94771 \text{ \AA}$, $b=8.98013 \text{ \AA}$, $c=15.78878 \text{ \AA}$, $Z=2$, $Rwp=9.67$, $Rexp=8.62$, $Rp=8.75$, confirm the basic natroapophyllite structure. The figures of merit [21-23] represented by goodness-of-fit GOF ($Rwp/Rexp$) and Durbin-Watson d -statistic (DW), were $GOF=1.12$ and $DW=2.08$, both indicating a good refinement. The parameters which represent the quality of the Rietveld refinement are presented in table 2.

Table 2
RIETVELD QUALITY PARAMETERS REFINEMENT OF THE APOPHYLLITE
SAMPLE FROM PUNE REGION (INDIA)

Parameter	Value	2-sigma
a (Å)	8.94771	0.03895
b (Å)	8.98013	0.02264
c (Å)	15.78878	0.06145
Z	2	-
Cry size L (nm)	8988.90	0.04265
Cry density (g/cm ³)	2.322	0.05965
Cell Volume (Å ³)	1268.65504	0.08264
R Bragg	23.843	-
Rwp (%)	9.67	-
Rexp (%)	8.62	-
Rp (%)	8.75	-
GOF	1.12	-
DW	2.08	-

Qualitative analysis was performed using Diffracplus EVA software with Search/Match program and PDF-ICDD 2-2008 database. Identification of crystalline phases (minerals) was made using “best quality marks”: (*) (=high quality), after removing the background and $K\alpha_2$ radiation. Qualitative analysis of the apophyllite sample analyzed is presented in figure 3.

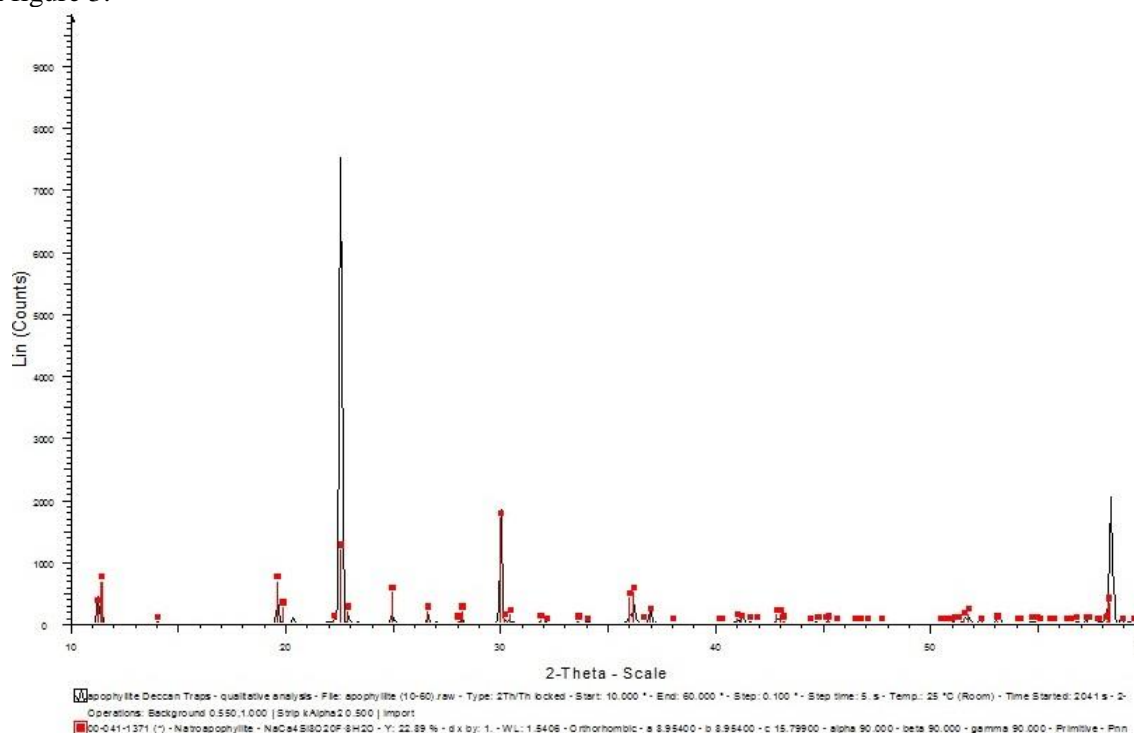


Fig. 3. Qualitative analysis of the apophyllite sample from Pune region (India)

Graphical representation of final Rietveld refinement of the apophyllite sample analyzed showing the observed data (Y_{obs}), the calculated data (Y_{calc}) and the difference between them ($Y_{obs}-Y_{calc}$), is presented in figure 4.

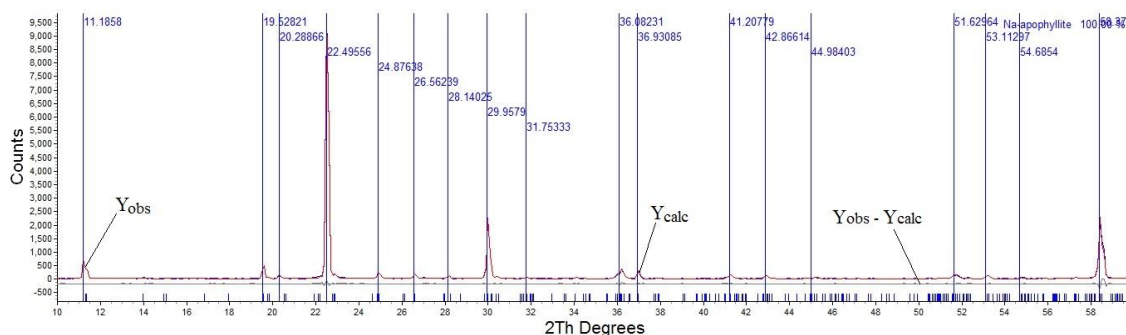


Fig. 4. Final Rietveld refinement of the apophyllite sample from Pune region (India)

Natroapophyllite is less common mineral of the apophyllite group, crystallized in the orthorhombic system ($Pnmm$ space group). The natroapophyllite crystal structure consists of continuous sheets of SiO_4 tetrahedra lying parallel to (001), sheets composed of 4-membered and 8-membered rings pointing up and down the c axis. The sheets are linked together by Ca ions bonded to two oxygens from each of the two adjacent sheets, one (OH,F) and two H_2O molecules. Each (OH,F) ion is coordinated to four coplanar Ca ions, whereas each Na ion is surrounded by eight H_2O molecules [10].

The position of the atoms and the bonds between atoms in refined structure of apophyllite is shown in figure 5. Apophyllite is a sheet structure with the bridging Si-O bond lengths in Si(1)-tetrahedra 1.6285 Å and in Si(2)-tetrahedra 1.6218 Å, while the non-bridging bond length Si-O(3) is 1.5942 Å. Regarding Ca-polyhedron and Na-O polyhedron, the average Ca-O bond length is 2.3956 Å and the average Na-O bond length is 2.8122 Å respectively. Other bond lengths were calculated considering that the fluorine ion is bonded to calcium ion (Ca-F=2.4289 Å) and to H3 atom (F-H=1.1129 Å) and water molecule hydrogen bonded to silicate structure.

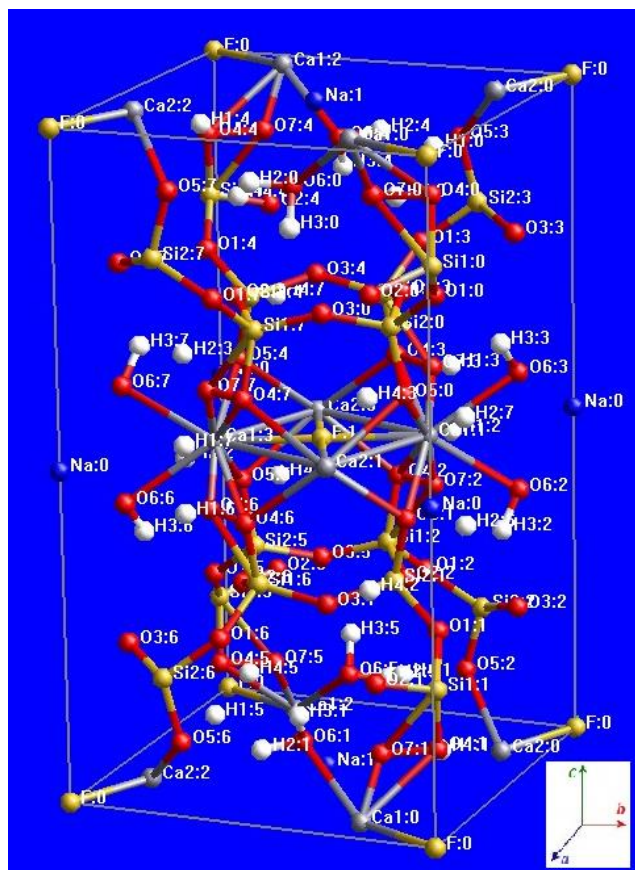


Fig. 5. The position and the bonds between the atoms in the refined structure of the apophyllite sample from Pune region (India)

The atomic positional parameters for the natroapophyllite structure resulted from the Rietveld refinements are presented in table 3. The structure in figure 6 shows a 3D view of the coordination polyhedron in the refined structure of natroapophyllite.

Table 3
ATOMIC POSITIONAL PARAMETERS FOR THE APOPHYLLITE CRYSTAL STRUCTURE FROM PUNE REGION (INDIA) RESULTED FROM RIETVELD REFINEMENT

Atom	Np	x	y	z	Occ	Beq	2-sigma
Na	2	0.00000	0.00000	0.50000	0.9312	0.941	0.0254
K					0.0387		
F	2	0.00000	0.00000	0.00000	1	0.371	0.0367
Si1	8	0.18463	0.03630	0.18914	1	0.774	0.0455
Si2	8	0.42054	0.28196	0.31061	1	0.404	0.0316
Ca1	4	0.07247	0.28868	0.00000	1	1.950	0.0674
Ca2	4	0.75903	0.11451	0.00000	1	1.182	0.0261
O1	8	0.28972	0.09199	0.23667	1	0.183	0.0423
O2	8	0.08674	0.19886	0.20786	1	0.362	0.0158
O3	8	0.26795	0.40741	0.30262	1	-1.510	0.0233
O4	8	0.23864	0.15406	0.15551	1	1.376	0.0856
O5	8	0.39952	0.26608	0.50078	1	1.620	0.0248
O6	8	0.14987	0.28214	0.05513	1	1.251	0.0296
O7	8	0.12998	0.08296	0.08995	1	1.360	0.0249
H1	8	0.52379	0.16377	-0.01096	1	0.935	0.0976
H2	8	0.00551	0.58796	-0.01849	1	0.999	0.0749
H3	8	0.00164	0.32040	0.18091	1	0.999	0.0529
H4	8	0.48229	0.27119	0.16061	1	1.090	0.0679

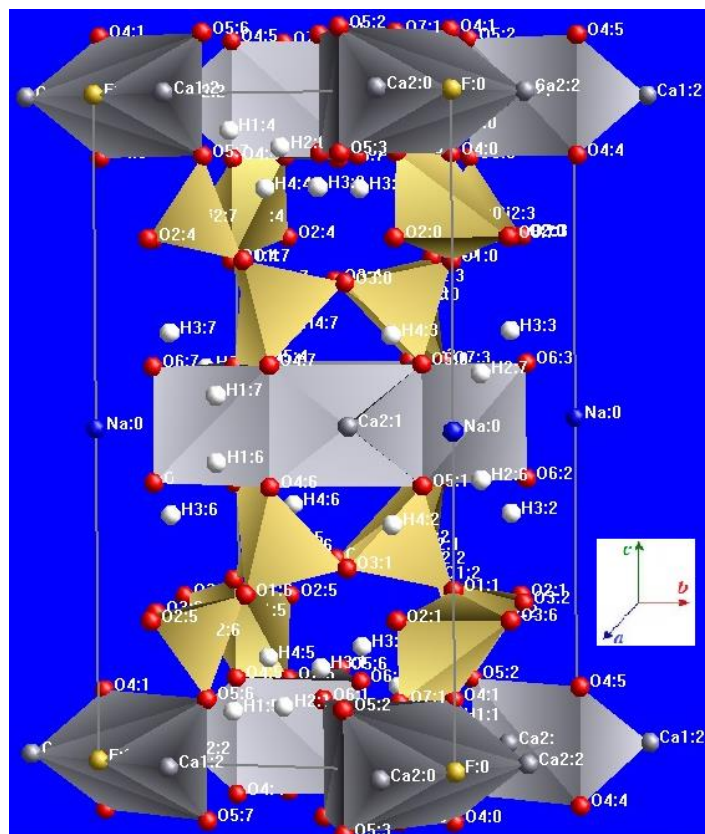


Fig. 6. The natroapophyllite structure of the sample from Pune region (India) resulted from the Rietveld refinement

Conclusions

The crystal structure of apophyllite from Deccan Basalt Plateau (Pune region, India) was refined by the Rietveld method using X-ray powder diffraction data. The results led to the conclusion that the apophyllite sample belongs to space group $Pnmm$ (No.58) and confirmed the basic natroapophyllite structure. The figures of merit were goodness-of-fit $GOF=1.12$ and Durbin-Watson d -statistic $DW=2.08$, both indicating a good refinement. The unit cell parameters resulted from the Rietveld refinement of the natroapophyllite sample were: $a=8.94771 \text{ \AA}$, $b=8.98013 \text{ \AA}$, $c=15.78878 \text{ \AA}$, $Z=2$.

The paper provides a new set of the unit cell parameters and fractional coordinates that define the natroapophyllite structure. We noticed that it is the first time when a Rietveld refinement is carried out on the natroapophyllite crystals from Deccan Basalt Plateau (Pune region, India).

After performing the Rietveld structure refinement and EDX analysis we can give for the natroapophyllite crystals from Pune region (India) the following chemical formula: $(Na_{0.93}K_{0.39})_{0.97}Ca_4Si_8O_{20}F \cdot 8H_2O$.

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