

FERRIERITE-NH₄, (NH₄,Mg_{0.5})₅(Al₅Si₃₁O₇₂)·22H₂O, A NEW ZEOLITE FROM NORTHERN BOHEMIA, CZECH REPUBLIC

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ABSTRACT

The new zeolite ferrierite-NH₄, ideally (NH₄,Mg_{0.5})₅(Al₅Si₃₁O₇₂)·22H₂O, was discovered in open pits at Libouš and Bílina in the Miocene Most Basin, which is situated in the Czech Republic. The associated minerals are calcite, siderite, whewellite, quartz, opal, baryte, and clay minerals (at Libouš) and marcasite, pyrite, baryte, sphalerite, and gypsum (at Bílina). Ferrierite-NH₄ forms white radiating aggregates up to 2 mm across consisting of thin flattened prismatic crystals. Density calculated from the empirical formula is 2.154 g/cm³. Ferrierite-NH₄ is optically biaxial, positive, $\alpha = 1.518(2)$, $\beta = 1.520(2)$, $\gamma = 1.522(2)$ ($\lambda = 589$ nm). The IR spectrum shows the presence of the NH₄⁺ cation. The chemical composition of the holotype sample is (wt.%; electron microprobe, H and N analyzed by gas chromatography of products of ignition): (NH₄)₂O 2.7, Na₂O 0.24, MgO 1.63, Al₂O₃ 10.48, SiO₂ 69.44, H₂O 14.8, total 99.29. The empirical formula based on 36 Si+Al *pfu* is H_{0.35}[(NH₄)_{2.74}Mg_{1.07}Na_{0.21}](Al_{5.44}Si_{30.56}O₇₂)·21.55H₂O. Ferrierite-NH₄ is orthorhombic, space group *Immm*, with *a* 19.10(1) Å, *b* 14.15(1) Å, *c* 7.489(3) Å, *V* 2024(3) Å³, and *Z* = 1. The strongest lines of the powder X-ray diffraction pattern [*d*, Å (*I*, %) (*hkl*)] are: 9.52 (97) (200), 6.95 (28) (101), 6.60 (19) (011), 3.988 (61) (321, 031, 420), 3.784 (19) (330), 3.547 (73) (112, 040), 3.482 (100) (202), 3.143 (37) (141, 312).

Keywords: ferrierite-NH₄, zeolite, ammonium, new mineral, Libouš, Bílina, Most Basin, Czech Republic.

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INTRODUCTION

This paper describes a new zeolite, ferrierite-NH₄, which was found as a relatively abundant mineral phase in two different areas of the Miocene Most Basin (northern Bohemia), also formerly called the North Bohemian Brown-Coal Basin, in the Czech Republic. The new mineral was named by analogy with other ferrierite-series zeolites: ferrierite-Na, ferrierite-K, and ferrierite-Mg. The suffix modifier -NH₄ indicates that ammonium is the prevailing extra-framework cation.

The mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA no. 2017-099). The holotype specimen of ferrierite-NH₄ is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the registration number 5120/1.

OCCURRENCE

The Miocene Most Basin is the largest of four basins in the Ohře (Eger) graben system in the Czech Republic and is located in the central part of the system. Its total area is about 1400 km² (Rajchl *et al.* 2009) and the basin fill remnants are preserved over an area of about 870 km² (Kvaček *et al.* 2004). The maximum total thickness of the preserved freshwater sediments is 500 m (Grygar & Mach 2013). The majority is composed of clastic sediments (clays and sands), but the economically important part is organic matter in the form of coal seams. The main coal seam, covering more than half of the basin, has a thickness of 20–30 m. In the remaining area of the basin the coal seam is absent or is split into several coal seams by clastic interlayers (Dvořák *et al.* 2012). About 63 mineral species have been described from here (Dvořák *et al.* 2012), including the new minerals humboldtine (Breithaupt 1822), tschermigite (Kobell 1853), and bílinite (Šebor 1913).

Specimens containing the new mineral ferrierite-NH₄ were collected from two large, active open coal pits: the Libouš open pit (the Doly Nástup Tušimice mine, Fig. 1) in the western part of the Most basin, and the Bílina open pit (the Doly Bílina mine) in the eastern part of the basin. The distance between these occurrences is more than 40 km. The first analyzed samples and the holotype were found by Oldřich Janeček in 2004 at the eastern margin of the Libouš open pit (the cadastre of the former village of Krbice, 50.4128500° N, 13.3815036° E). They were collected from the base of the main coal seam and occur there as radiating aggregates of elongated tabular crystals (described below as sample Li1x) or fine fibrous



Fig. 1. Occurrence of ferrierite-NH₄ in the hanging wall of the main coal seam (Li2) at the eastern margin of the Libouš open pit. During coal mining, the occurrences of ferrierite-NH₄ were observed over an area of several thousand m². Photo by T. Novotný, 2017.

aggregates (Li1f) in fractures in abundant pelosiderite nodules in association with calcite, siderite, whewellite, quartz, opal, baryte, and clay minerals. Later, occurrences of ferrierite-NH₄ were also discovered at the eastern margin of the Libouš open pit (50.4252517° N, 13.3812767° E) in the hanging wall of the main coal seam (Li2). Above the coal seam there is a 1.5 m thick layer of dark brown carbonaceous shale with abundant small siderite concretions bearing radiating aggregates of ferrierite-NH₄.

In the southern part of the Bílina open pit (the cadastre of the former village of Jenišův Újezd), ferrierite-NH₄ was found by Roman Gramblička in a somewhat different geological situation. It is found only in the proximity of the Bílina fault, and it is observed in fractures of carbonate concretions, as well as in siderite and sandstone bands in the base of the main coal seam. Associated minerals are marcasite, pyrite, baryte, sphalerite, and supergene gypsum. The analyzed samples were found in 2011 (Bi1), 2012 (Bi2), and 2017 (Bi3) in a line between GPS coordinates 50° 33.09558' N, 13° 43.02042' E and 50° 33.11767' N, 13° 42.85205' E.

GENERAL APPEARANCE AND PHYSICAL PROPERTIES

At the first (holotype, Li1x) occurrence ferrierite-NH₄ forms white radiating aggregates with silky luster up to 1.5 mm across (Fig. 2a, b) consisting of very thin flattened prismatic crystals (Fig. 3) elongated along (001) and growing on pelosiderite rocks consisting of siderite, opal, kaolinite, goethite, and organic matter. Individual brittle to flexible crystals are transparent and exhibit vitreous luster. At the same place, abundant white aggregates of ferrierite-NH₄ (Li1f)



FIG. 2. (a) Radiating aggregate of ferrierite-NH₄ crystals on a rock consisting of siderite, opal, kaolinite, goethite, and organic matter; Libouš open pit (Li1). Photo by A. Kasatkin. Field of view 2 mm. (b) White radiating aggregates of ferrierite-NH₄ crystals in association with tiny grey siderite crystals on pelosiderite; Libouš open pit (Li1). Field of view 5 mm.

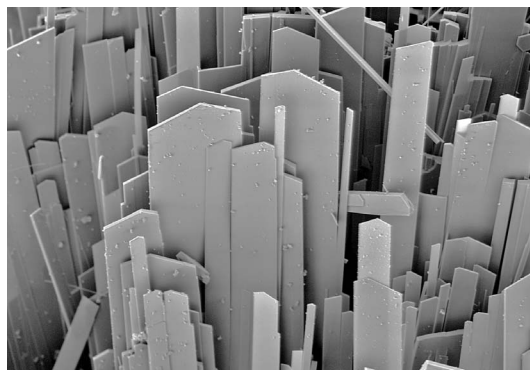


FIG. 3. Elongated flattened prismatic crystals of ferrierite-NH₄; Libouš open pit (Li1x). SEM photo. Field of view 300 μ m.

composed of flexible fibers 1 to 5 μ m thick (Fig. 4) were also observed. In other occurrences in the Libouš (Li2) and Bílina (Bi1–3) open pits, radiating aggregates of ferrierite-NH₄ up to 2 mm across are most common, but there are also random aggregates of thin fibers covering an area of several cm².

Cleavage is not observed. Density calculated using the empirical formula is 2.154 g/cm³. Ferrierite-NH₄ exhibits intense bluish white fluorescence under both short- (254 nm) and long-wave (366 nm) UV radiation; such fluorescence is unusual for zeolite-group minerals.

Ferrierite-NH₄ is optically biaxial, positive, $\alpha = 1.518(2)$, $\beta = 1.520(2)$, $\gamma = 1.522(2)$ ($\lambda = 589$ nm). $2V$ (calc.) $\approx 90^\circ$. The optical orientation is $Z = c$. Under the microscope ferrierite-NH₄ is colorless and non-pleochroic.

INFRARED SPECTROSCOPY

In order to obtain an IR absorption spectrum, ferrierite-NH₄ powder was mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm⁻¹. A total of 16 scans were collected. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

Absorption bands in the IR spectrum of ferrierite-NH₄ (Fig. 5) and their assignments are as follows (cm⁻¹; s – strong band, w – weak band, sh – shoulder): 3610, 3565sh, 3360w (O–H stretching vibrations of H₂O molecules); 3250, 3220sh (N–H stretching vibrations of ammonium cations); 1646 (bending vibrations of H₂O molecules); 1474 (bending vibrations of ammonium cations); 1216s, 1076s, 1060sh (stretching vibrations of the tetrahedral framework); 791, 730, 707, 681, 647w, 564s, 530sh (mixed vibrations of the tetrahedral framework); 474s, 435s

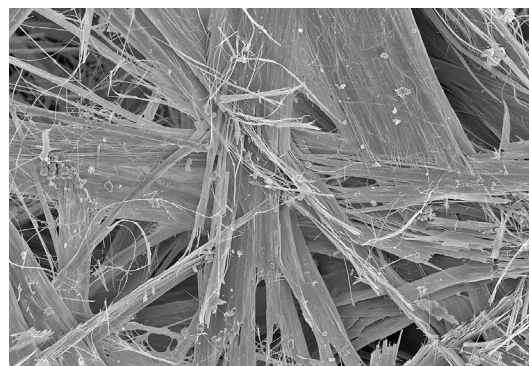


FIG. 4. Bundles of flexible fibers of ferrierite-NH₄; Libouš open pit (Li1f). SEM photo. Field of view 400 μ m.

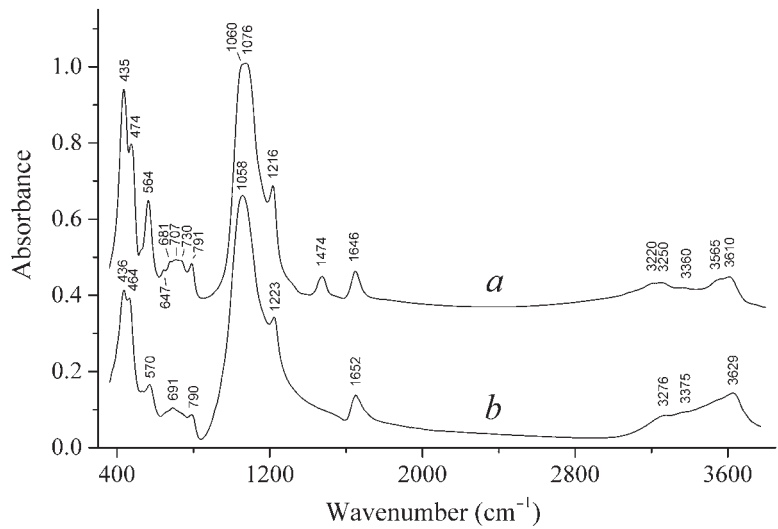


FIG. 5. Powder IR absorption spectra of (a) ferrierite-NH₄ and (b) ferrierite-K, (K_{1.69}Mg_{1.18}Ca_{0.27}Ba_{0.17}Na_{0.13})(Si_{30.92}Al_{5.08}O₇₂)·nH₂O, from a post-magmatic hydrothermal assemblage uncovered near the village of Austa, Kyrdzhali region, Eastern Rhodopes, Bulgaria.

(lattice modes involving predominantly bending vibrations of the tetrahedral framework and librational vibrations of H₂O molecules).

CHEMICAL DATA

Five electron-microprobe compositions of the holotype sample were obtained using a Tescan VEGA-II XMU digital scanning electron microscope with an INCA Energy 450 energy-dispersive spectrometer (EDS) (EDS mode, 20 kV, 600 pA). Hydrogen and N were analyzed by gas chromatography of the products of ignition at 1200 °C in an

TABLE 1. CHEMICAL COMPOSITION OF THE HOLOTYPE SAMPLE OF FERRIERITE-NH₄ (wt.%)

Constituent	Mean	Range	Standard deviation	Probe standard
(NH ₄) ₂ O	2.7 ± 0.2			
Na ₂ O	0.24	0–0.43	0.17	Albite
MgO	1.63	1.52–1.74	0.08	Diopside
Al ₂ O ₃	10.48	10.14–10.79	0.24	Albite
SiO ₂	69.44	69.07–69.81	0.29	SiO ₂
H ₂ O	14.8 ± 0.6*			
Total	99.29			

* This value obtained by subtraction of H₂O formed as a result of oxidation of NH₄⁺ from the total measured water content.

TABLE 2. CHEMICAL COMPOSITION OF FERRIERITE-NH₄ (wt.%) FROM THE MOST BASIN

n*	Libouš			Bílina		
	Li1x 35	Li1f 14	Li2 19	Bi1 15	Bi2 16	Bi3 3
(NH ₄) ₂ O	2.15	2.25	2.35	2.38	2.20	2.18
Na ₂ O	0.34	0.14	0.29	0.07	0.31	0.38
K ₂ O	0.13	0.10	0.00	0.21	0.26	0.17
MgO	1.71	1.74	1.46	1.40	1.41	1.32
Al ₂ O ₃	10.14	10.41	9.64	9.52	9.59	9.35
SiO ₂	71.62	71.52	70.26	72.07	71.88	71.19
H ₂ O**	15.47	15.58	15.11	15.43	15.40	15.23
total	101.56	101.74	99.11	101.08	101.05	99.82
NH ₄	2.14	2.22	2.40	2.37	2.20	2.20
Na	0.29	0.11	0.25	0.06	0.26	0.33
K	0.07	0.06	0.00	0.12	0.14	0.09
Mg	1.10	1.12	0.96	0.90	0.91	0.86
Al	5.15	5.27	5.01	4.85	4.89	4.83
Si	30.85	30.73	30.99	31.15	31.11	31.17
H ₂ O	22.00	22.00	22.00	22.00	22.00	22.00
H***	0.45	0.64	0.45	0.50	0.46	0.48
Si/Al	6.00	5.83	6.18	6.42	6.36	6.46
T _{Si}	0.86	0.85	0.86	0.87	0.86	0.87

Note: * n – number of spot analyses; ** H₂O calculated on the basis of theoretical content of 22 H₂O molecules *pfu*; *** Excessive H calculated for charge balance.

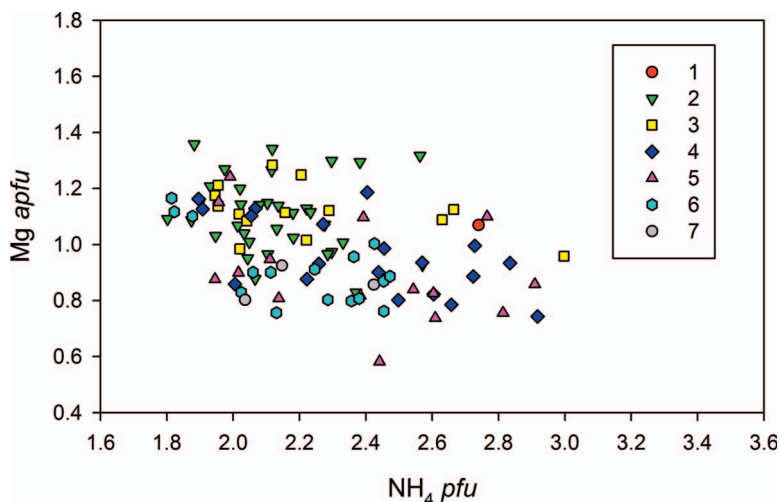


FIG. 6. NH₄ (*pfu*) versus Mg (*apfu*) for studied ferrierite-NH₄ samples from the Libouš and Bílina open pits: 1 – Libouš holotype, 2 – Libouš Li1x, 3 – Libouš Li1f, 4 – Libouš Li2, 5 – Bílina Bi1, 6 – Bílina Bi2, 7 – Bílina Bi3.

oxygen flow. Analytical data are given in Table 1. Contents of other elements with atomic numbers >8 are below detection limits. The Gladstone-Dale compatibility is $1 - (K_p/K_c) = -0.028$ (excellent).

The charge-balanced empirical formula (based on 36 Si+Al *pfu*) is $H_{0.35}[(NH_4)_{2.74}Mg_{1.07}Na_{0.21}](Al_{5.44}Si_{30.56}O_{72}) \cdot 21.55H_2O$. The simplified formula is $(NH_4, Mg_{0.5})_5(Al_5Si_{31}O_{72}) \cdot 22H_2O$.

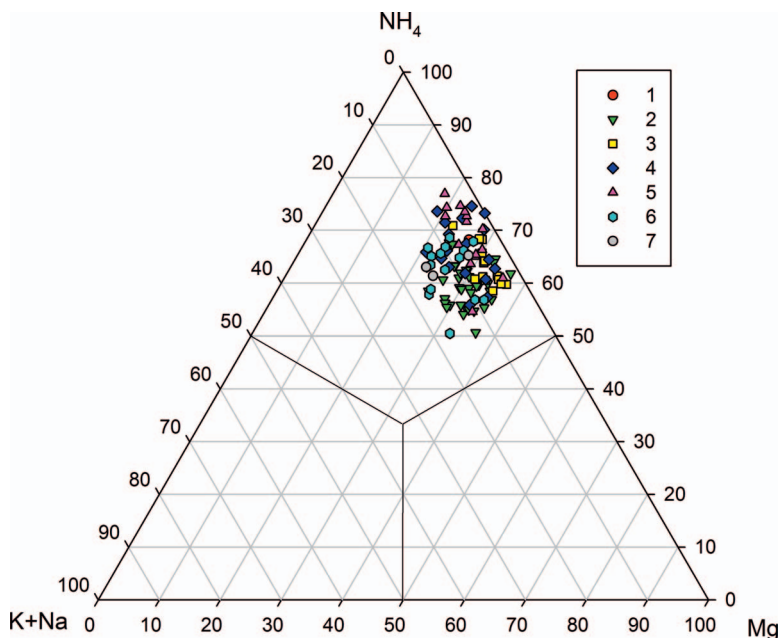


FIG. 7. Ternary graph for extra-framework cations (*pfu*) for studied ferrierite-NH₄ samples from the Libouš and Bílina open pits. Legend as in Figure 6.

TABLE 3. POWDER X-RAY DIFFRACTION DATA FOR FERRIERITE-NH₄ FROM LUBOUŠ AND FERRIERITE-K FROM AUSTA, KYRDZHALI REGION, EASTERN RHODOPES, BULGARIA (OUR DATA)

Ferrierite-NH ₄				Ferrierite-K	
<i>I</i> _{meas} , %	<i>d</i> _{meas} , Å	<i>d</i> _{calc} , Å	<i>hkl</i>	<i>I</i> _{meas} , %	<i>d</i> _{meas} , Å
7	11.34	11.370	110	11	11.36
97	9.52	9.550	200	100	9.54
28	6.95	6.972	101	30	7.01
19	6.60	6.619	011	16	6.61
8	5.79	5.806	310	18	5.80
n/d	n/d	n/d	220	9	5.68
10	4.960	4.966	121	5	4.962
2	4.835	4.851	301	4	4.840
61	3.988	4.001, 3.991, 3.958	321, 031, 420	55	3.985
16	3.864	3.872	411	18	3.873
19	3.784	3.790	330	48	3.789
14	3.741	3.744	002	n/d	n/d
17	3.680	3.682	231	26	3.690
73	3.547	3.557, 3.538	112, 040	84	3.541
100	3.482	3.486	202	62	3.484
9	3.396	3.403	501	13	3.405
8	3.315	3.317, 3.310	240, 022	18	3.317
37	3.143	3.155, 3.145	141, 312	25	3.145
10	3.062	3.067, 3.062	521, 431	24	3.067
6	2.949	2.966, 2.947	530, 402	7	2.949
9	2.899	2.903, 2.899	620, 132	10	2.898
2	2.861	2.858	341	n/d	n/d
6	2.719	2.720	422	10	2.720
4	2.649	2.647	051	8	2.648
n/d	n/d	n/d	350	7	2.584
4	2.571	2.572, 2.564	042, 701	5	2.571
4	2.483	2.489, 2.483, 2.475	631, 242, 103	6	2.483
4	2.423	2.425	602	5	2.424
2	2.361	2.366, 2.362	640, 730	8	2.365
1	2.317	2.315	451	3	2.316
2	2.264	2.264	442	1	2.262
2	2.245	2.246	811	2	2.244
2	2.184	2.186, 2.179	413, 712	1	2.185
5	2.150	2.150	233	2	2.150
2	2.118	2.121, 2.115	361, 460	5	2.115
2	2.037	2.042, 2.035	901, 651	2, 2	2.043, 2.033
8	2.004	2.010, 2.004, 2.000, 1.998	170, 523, 642, 732	8	2.002
3	1.952	1.952, 1.946	071, 613	3	1.952
4	1.932	1.935, 1.927	930, 370	5, 7	1.934, 1.927
12	1.873	1.872, 1.872	004, 053	7	1.872
3	1.840	1.842, 1.841, 1.837, 1.837	703, 462, 204, 253	2, 2	1.847, 1.839
5	1.782	1.787, 1.782, 1.782, 1.778	570, 723, 314, 224	7, 6	1.785, 1.774
1	1.743	1.743, 1.740	453, 752	1	1.741
1	1.716	1.719, 1.714, 1.713, 1.713	932, 181, 372, 813	1, 1	1.723, 1.714
2	1.678	1.679, 1.678	334, 860	1	1.678
2	1.669	1.669	514		n/d
3	1.658	1.655, 1.654	044, 10.2.2	3	1.659
2	1.631	1.634, 1.630, 1.624	743, 11.3.0, 770	2	1.628
2	1.616	1.617, 1.614, 1.614	903, 604, 653	2	1.617
2	1.587	1.592, 1.584	12.0.0, 534	2, 1	1.595, 1.583
2	1.565	1.569, 1.564, 1.564	581, 563, 444	1	1.565

TABLE 3. CONTINUED.

Ferrierite-NH ₄				Ferrierite-K	
<i>I</i> _{meas} , %	<i>d</i> _{meas} , Å	<i>d</i> _{calc} , Å	<i>hkl</i>	<i>I</i> _{meas} , %	<i>d</i> _{meas} , Å
2	1.552	1.556, 1.553, 1.550, 1.549	154, 12.2.0, 273, 10.5.1	2	1.551
2	1.493	1.494, 1.492, 1.490, 1.490	11.3.2, 473, 772, 015	4	1.496
3	1.468	1.471, 1.467, 1.466, 1.465	943, 734, 064, 491	2, 5	1.473, 1.467
2	1.442	1.445, 1.444, 1.442	192, 10.3.3, 824	2, 1	1.446, 1.440
8	1.429	1.429, 1.428	682, 325	7	1.428
3	1.418	1.421, 1.415	880, 0.10.0	3	1.416
1	1.397	1.397, 1.394	11.2.3, 505	1	1.400

Note: *hkl* indices were chosen taking into account intensities of reflections of the calculated powder XRD patterns based on the structure data for samples of K-enriched ferrierite (orthorhombic, *Immm*) reported by Alberti & Sabelli (1987) and Pickering *et al.* (1989). n/d = not detected.

All other studied samples were analyzed using a Cameca SX-100 electron microprobe (National Museum, Prague) operating in the wavelength-dispersion mode with an accelerating voltage of 15 kV, a beam current on the specimen of 10 nA, and a beam diameter of 5 µm. We also attempted analytical conditions as mild as 1 nA current and 20 µm beam diameter with the same results; the analytical conditions were verified using analyses of ferrierite-Mg from Kamloops Lake, Canada (Graham 1918). The following lines and standards were used: *Kα*: albite (Na), BN (N), hematite (Fe), sanidine (Al, Si, K), diopside (Mg), rhodonite (Mn), wollastonite (Ca); *Lα*: Cs glass (Cs), Rb glass (Rb); *Lβ*: baryte (Ba), celestine (Sr); and *Mα*: vanadinite (Pb). Peak counting times (CT) were 20 s for the main elements and 60 s for the minor elements; CT for each background was one-half of the peak time. The raw intensities were converted to concentrations using the PAP (Pouchou & Pichoir 1985) matrix-correction software. The elements Ba, Cs, Fe, Mn, Rb, and Sr were sought, but found to be below the detection limit (about 0.01–0.03 wt.%).

Chemical composition of all studied samples from both occurrences do not show significant differences (Table 2); NH₄ content varies in the range 1.8–3.0 *pfu* and ammonium and NH₄ as extra-framework cations predominate over Mg (0.6–1.4 *apfu*, Fig. 6) and minor Na + K (up to 0.6 *apfu*, Fig. 7). The calculated values of *T*_{Si} = Si/(Si + Al) (Table 2) agree very well with those published for ferrierite series minerals (0.80–0.87) by Coombs *et al.* (1997).

The Gladstone-Dale compatibility index (Mandarino 1981) calculated for the holotype sample is excellent: $1 - (K_p/K_c) = -0.028$.

X-RAY DIFFRACTION DATA

Powder X-ray data were obtained using a Rigaku R-Axis Rapid II single-crystal diffractometer

equipped with a cylindrical image plate detector using the Debye-Scherrer geometry (*d* = 127.4 mm). Data (in Å for CoK α) are given in Table 3.

The obtained diffraction pattern was indexed with an orthorhombic unit cell (space group *Immm*, by analogy with ferrierite-K). Unit-cell parameters of the holotype sample refined from the powder data are as follows: *a* 19.10(1) Å, *b* 14.15(1) Å, *c* 7.489(3) Å, *V* 2024(3) Å³, *Z* = 1.

A crystal fragment of ferrierite-NH₄ (0.166 × 0.070 × 0.043 mm in size) was selected using an optical microscope and mounted for single-crystal X-ray study using an Oxford Diffraction Gemini single-crystal diffractometer equipped with an Atlas CCD detector using monochromated MoK α radiation from a sealed X-ray tube. According to the single-crystal X-ray diffraction data, ferrierite-NH₄ is orthorhombic with unit-cell parameters *a* 19.1444(18) Å, *b* 14.1633(13) Å, *c* 7.4905(5) Å, *V* 2031.0(2) Å³ (at room temperature, from 1353 observed reflections) and *a* 19.0973(6) Å, *b* 14.1333(5) Å, *c* 7.4719(2) Å, *V* 2016.72(11) Å³ (at 120 K). The crystal structure could not be solved because of the poor quality of the available crystals.

DISCUSSION

Orthorhombic symmetry was chosen for ferrierite-NH₄ by analogy with ferrierite-K, taking into account the crystal-chemical similarity of K⁺ and NH₄⁺. Powder X-ray diffraction data for ferrierite-NH₄ (Table 3) are in agreement with this assumption. Alberti *et al.* (1998) also chose orthorhombic symmetry (space group *Immm*) for synthetic NH₄-exchanged ferrierite. Properties of synthetic analogues of ferrierite-NH₄ have been studied in numerous works (Fjellvåg *et al.* 1989, Sobalik *et al.* 1998, Datka *et al.* 2003, Peixoto *et al.* 2003). These compounds are

TABLE 4. COMPARATIVE DATA FOR FERRIERITE-SERIES MINERALS

	Ferrierite-NH ₄	Ferrierite-Na	Ferrierite-K	Ferrierite-Mg
Formula	(NH ₄ ,Mg _{0.5}) ₅ (Al ₅ Si ₃₁ O ₇₂)·22H ₂ O	(Na,K,Mg _{0.5}) ₅ (Al ₅ Si ₃₁ O ₇₂)·nH ₂ O	(K,Na,Mg _{0.5}) ₅ (Al ₅ Si ₃₁ O ₇₂)·nH ₂ O	(Mg _{0.5} ,K,Na) ₇ (Al ₇ Si ₂₉ O ₇₂)·nH ₂ O
Crystal system	Orthorhombic	Orthorhombic or monoclinic (pseudo-orthorhombic)	Orthorhombic	Orthorhombic
Space group	<i>Immm</i>	<i>Immm</i> or <i>P2₁/n</i>	<i>Immm</i>	<i>Immm</i>
<i>a</i> , Å	19.10	18.886	18.973	19.187–19.231
<i>b</i> , Å	14.15	14.182	14.140	14.145–14.161
<i>c</i> , Å	7.489	7.470	7.478	7.498–7.499
β, °	90	≈90	90	90
<i>V</i> , Å ³	2024	2000.8	2006.2	2037.3–2039.9
<i>Z</i>	1	1	1	1
Strong lines of the powder X-ray diffraction pattern: <i>d</i> , Å (<i>I</i> , %)	9.52 (97) 6.95 (28) 6.60 (19) 3.988 (61) 3.864 (16) 3.784 (19) 3.680 (17) 3.547 (73) 3.482 (100)	9.60 (100) 5.84 (18) 4.01 (21) 3.974 (28) 3.797 (20) 3.708 (31) 3.535 (26) 3.493 (22)	9.54 (100) 7.01 (30) 3.985 (55) 3.789 (48) 3.690 (26) 3.541 (84) 3.484 (62) 3.145 (25) 3.067 (24)	No data
IR absorption bands	3610, 3565sh, 3360w, 3250, 3220sh, 1646, 1474, 1216s, 1076s, 1060sh, 791, 730, 707, 681, 647w, 564s, 530sh, 474, 435s	No data	3629, 3375sh, 3276sh, 1652, 1223s, 1058s, 790, 730sh, 691, 655sh, 570, 464s, 436s	3625, 3500, 3270sh, 1700sh, 1645, 1220s, 1060s, 785sh, 740sh, 714, 572, 462s, 442s
Optical data	Biaxial (+) α = 1.518 β = 1.520 γ = 1.522	Biaxial (+) α = 1.473 β = 1.474 γ = 1.477	Biaxial (+) α = 1.489 β = 1.489 γ = 1.492	Biaxial (+) α = 1.487 β = 1.489 γ = 1.491
Density, g·cm ⁻³	2.154 (calc.)	2.06–2.23 (meas.) 2.13 (calc.)	2.16 (calc.)	2.21 (meas.) 2.136
Sources	This work	Wise & Tschernich (1976), Gramlich- Meier <i>et al.</i> (1985), Gottardi & Galli (1985)	Wise & Tschernich (1976), Yajima & Nakamura (1971), Chukanov (2014), our PXRD data	Alietti <i>et al.</i> (1967), Alberti & Sabelli (1987), Deer <i>et al.</i> (2004), Passaglia (1978), Chukanov & Chervonnyi (2016)

medium pore-size catalysts with strong shape-selective properties.

Ferrierite-NH₄ differs from ferrierite-Na, ferrierite-K, and ferrierite-Mg by exhibiting significantly higher refractive indices (Table 4). This is evidenced by a very high Gladstone-Dale constant *k* for (NH₄)₂O of

0.483 (for comparison: for Na₂O *k* = 0.190, for K₂O *k* = 0.196, and for MgO *k* = 0.200 – see Mandarino 1981).

Ammonium-bearing aluminosilicates are very rare in nature. Ferrierite-NH₄ is the second (after ammonioleucite, Hori *et al.* 1986) natural ammonium-

dominant zeolite and the first hydrous zeolite-group mineral with species-defining ammonium. Two other NH₄-dominant aluminosilicate minerals are budding-tonite (NH₄-analogue of sanidine) and tobelite (NH₄-analogue of muscovite).

The formation mechanism of ammonioleucite is presumed to be related to a low-temperature hydrothermal reaction of the solution containing ammonium ions with analcime (Hori *et al.* 1986). Buddingtonite at its type locality, the Sulfur Bank mine, California, USA (Erd *et al.* 1964), formed *via* low-temperature replacement of plagioclase by ammonia-bearing hot springs. Buddingtonite from the the Condor oil-shale deposit near Proserpine, Queensland, Australia (Loughnan *et al.* 1983), is concluded to be of diagenetic origin; it developed in an ammonium-rich environment. Tobelite from its type locality, the Ohgidani pottery stone deposit near Tobe, Japan (Higashi 1982), is a product of hydrothermal alteration of a biotite andesite dike; the source of the ammonium is unknown.

An interesting hydrothermal assemblage of nitrogen-bearing aluminosilicate minerals was described from alpine-type veins in the headwaters of the Shchugor river, near Man'-Khambo Ridge, Northern Urals, Russia. These minerals are represented by tsaregorodtsevite, N(CH₃)₄(AlSi₅O₁₂), a sodalite-group member with tetramethylammonium as a species-defining cation (Pautov *et al.* 1993), and an NH₄-enriched variety of chabazite-Ca (Karpenko *et al.* 2001b). As shown by geochemical study, nitrogen was probably mobilized during the formation of alpine-type veins from host mica-chlorite schists which contain ammonium-bearing muscovite (Karpenko *et al.* 2001a, b).

All studied occurrences of ferrierite-NH₄ in the Libouš and Bílina open pits are situated in immediate proximity to the coal seam. This mineral was formed in a sedimentary environment by low-temperature diagenesis after formation and cracking of carbonate concretions; there is no evidence of hydrothermal processes. Most probably, organic matter in the Miocene coal sediments was the source of the ammonium. It has been shown experimentally (Townsend & Loizidou 1984) that natural K- and Mg-bearing ferrierite-Na readily reacts with solutions of ammonium salts to form the NH₄-dominant analogue of ferrierite-Na. The exchange was found to be ternary in nature, involving sodium, ammonium, and potassium. Therefore, it is possible to assume that natural ferrierite-NH₄ formed either directly from fluids with increased ammonium ion contents or as a result of ion exchange reactions involving ferrierite-Na or ferrierite-K.

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