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Nickeltalmessite, $Ca_2Ni(AsO_4)_2 \cdot 2H_2O$, a New Mineral Species of the Fairfieldite Group, Bou Azzer, Morocco[1]

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Abstract—Nickeltalmessite, $Ca_2Ni(AsO_4)_2 \cdot 2H_2O$, a new mineral species of the fairfieldite group, has been found in association with annabergite, nickelaustinite, pecoraite, calcite, and a mineral of the chromite–manganochromite series from the dump of the Aït Ahmane Mine, Bou Azzer ore district, Morocco. The new mineral occurs as spheroidal aggregates consisting of split crystals up to 10 × 10 × 20 μm in size. Nickeltalmessite is apple green, with white streak and vitreous luster. The density measured by the volumetric method is 3.72(3) g/cm^3; calculated density is 3.74 g/cm^3. The new mineral is colorless under a microscope, biaxial, positive: $\alpha = 1.715(3)$, $\beta = 1.720(5)$, $\gamma = 1.753(3)$, $2V_{meas} = 80(10)°$, $2V_{calc} = 60.4$. Dispersion is not observed. The infrared spectrum is given. As a result of heating of the mineral in vacuum from 24° up to 500°C, weight loss was 8.03 wt %. The chemical composition (electron microprobe, wt %) is as follows: 25.92 CaO, 1.23 MgO, 1.08 CoO, 13.01 NiO, 52.09 As_2O_5; 7.8 H_2O (determined by the Penfield method); the total is 101.13. The empirical formula calculated on the basis of two AsO_4 groups is $Ca_{2.04}(Ni_{0.77}Mg_{0.13}Co_{0.06})_{\Sigma 0.96}(AsO_4)_{2.00} \cdot 1.91H_2O$. The strongest reflections in the X-ray powder diffraction pattern [*d*, Å (*I*, %) (*hkl*)] are: 5.05 (27) (001) $(\underline{1}00)$, 3.57 (43) $(\underline{0}11)$, 3.358 (58) (110), 3.202 (100) (020), 3.099 (64) $(0\bar{2}1)$, 2.813 (60), $(\bar{1}\underline{2}1)$, 2.772 (68) $(2\bar{1}0)$, 1.714 (39) $(\bar{3}31)$. The unit-cell dimensions of the triclinic lattice (space group $P1$ or $P\bar{1}$) determined from the X-ray powder data are: $a = 5.858(7)$, $b = 7.082(12)$, $c = 5.567(6)$ Å, $\alpha = 97.20(4)$, $\beta = 109.11(5)$, $\gamma = 109.78(5)°$, $V = 198.04$ Å^3, $Z = 1$. The mineral name emphasizes its chemical composition as a Ni-dominant analogue of talmessite. The type material of nickeltalmessite is deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia, registration number 3750/1.

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INTRODUCTION

The Aït Ahmane cobalt deposit (Ni, Ag, and Au are by-products) is located in the eastern part of the Bou Azzer ore district situated in the central Anti-Atlas in Morocco. The Bou Azzer deposits attributed to plutonogenic hydrothermal arsenopyrite–glaucodot–cobaltite assemblage are confined to the contact between hydrothermally altered serpentinite and host rhyolite along the Main Fault of the Anti-Atlas (Boroshanskaya et al., 1981).

The unusual mineral diversity of this ore district is largely related to he pronounced supergene zone of the primary arsenide ore. Two hundred fifteen mineral species have been identified therein. All six new mineral species discovered in Bou Azzer belong to arsenates. These are irhtemite, arhbarite, nickelaustinite, wendwilsonite, bouazzerite, and maghrebite (Favreau et al., 2007). Nickeltalmessite, a new member of the fairfieldite group, described in this paper, is an arsenate as well. The mineral is named by analogy with isostructural talmessite, emphasizing its compositional feature (significant prevalence of Na over Mg).

The type material of nickeltalmessite is deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia, registration number 3750/1; and in the Mineralogical Collection of Technische Universität Bergakademie Freiberg, Germany, inventory number 82195.

MODE OF OCCURRENCE AND PHYSICAL PROPERTIES

Nickeltalmessite was identified in the dump of the Aït Ahmane Mine, Bou Azzer ore district. The new mineral occurs as apple green spheroidal aggregates up to 0.5 mm in diameter composed of small (up to 10 × 10 × 20 μm) split crystals (Fig. 1). Other supergene Ni

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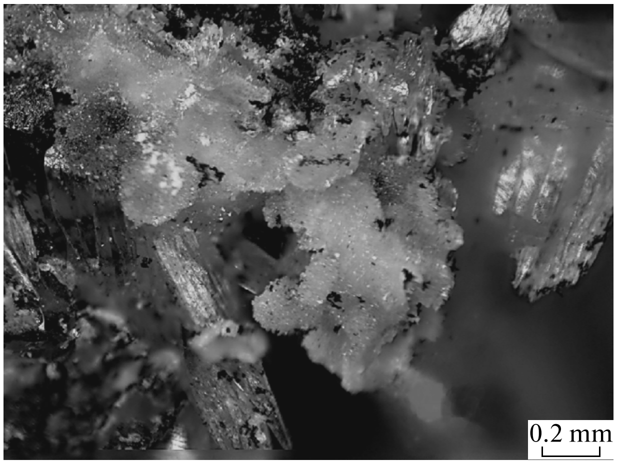

Fig. 1. Aggregate of nickeltalmessite

minerals (nickelaustinite, annabergite, and pecoraite), calcite, and relics of the mineral attributed to the chromite–manganochromite series are associated with nickeltalmessite. Some spherulites of nickeltalmessite contain nickelaustinite as inclusions (Fig. 2).

The new mineral is brittle; the Mohs hardness is about 4. Cleavage is perfect parallel to {010}. The density measured by the volumetric method is 3.72(3) g/cm^3; the calculated density is 3.74 g/cm^3.

The new mineral is colorless in transmitted light under a microscope, biaxial, positive: α =1.715(3), β = 1.720(5), γ = 1.753(3), $2V_{meas}$ = 80(10)°, $2V_{calc}$ = 60.4°. The angle between axis X and elongation of separate crystals is 25°. Dispersion and twinning are not observed.

The wavenumbers of absorption bands in the IR spectrum of nickeltalmessite and their assignment are as follows (cm^{-1}; s is strong band; w is weak band; sh is shoulder; Fig. 3a): 3100sh and 2885s (O–H stretching vibrations); 2410, 2300sh, and 1760w (vibrations of acid OH groups); 1540 (bending vibrations of H_2O molecules); 977, 910sh, 865s, 844s, and 803s (stretching vibrations of AsO_4^{3-} ions); 530w and 434s (bending vibrations of AsO_4^{3-} ions, Ni–O stretching vibrations, and librational vibrations of H_2O molecules). Relatively weak bands of acid groups (in the range of 1700–2500 cm^{-1}) have been identified in the IR spectra of all fairfieldite-group minerals (Fig. 3b, 3c). It has been suggested that strong hydrogen bonds formed in the minerals by water molecules give rise to partial protonization of arsenate anions in compliance with acid–base equilibrium (Pekov et al., 2001): $H_2O + AsO_4^{3-} \longleftrightarrow OH^- + HAsO_4^{2-}$.

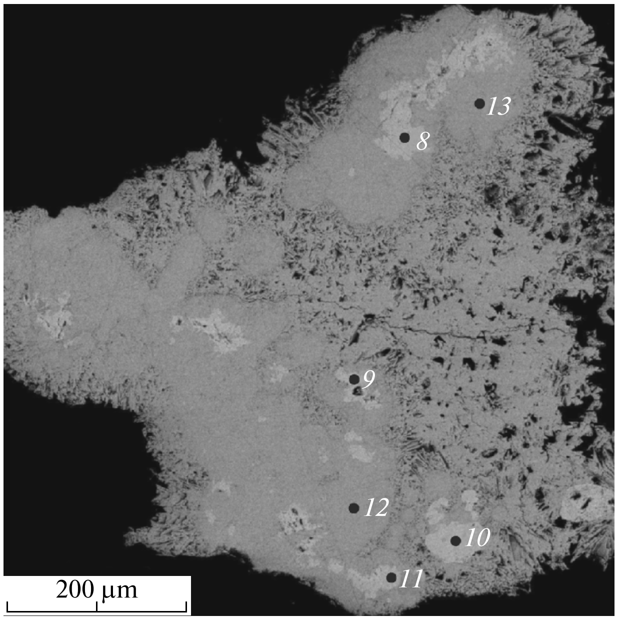

Fig. 2. Nickelaustinite cores (points 8, 9, 10, 11) in aggregate of nickeltalmessite (12, 13). BSE image.

Thermogravimetric data were obtained with an ATV-10 thermobalance. As a result of heating of the mineral in vacuum from 24 to 500°C at a constant rate of 4 °C/min, weight loss is 8.03 wt %.

CHEMICAL COMPOSITION

The chemical composition was determined with a Tescan Vega II XMU SEM equipped with an INCAx-site EDS operating at 20 kV on a tungsten cathode, current 0.3 nA on Co, takeoff angle 35°, and a distance between sample and detector of 25 mm. The chemical composition (average of five-point analyses) is given in

Table 1. Chemical composition of nickeltalmessite, wt %

Component	Average content	Range	Standard
CaO	25.92	25.50–26.33	Wollastonite
MgO	1.23	0.74–1.73	MgO
CoO	1.08	0.49–1.75	Co
NiO	13.01	11.59–14.74	Ni
As_2O_5	52.09	51.88–52.69	InAs
H_2O	7.8(1)		
Total	101.13		

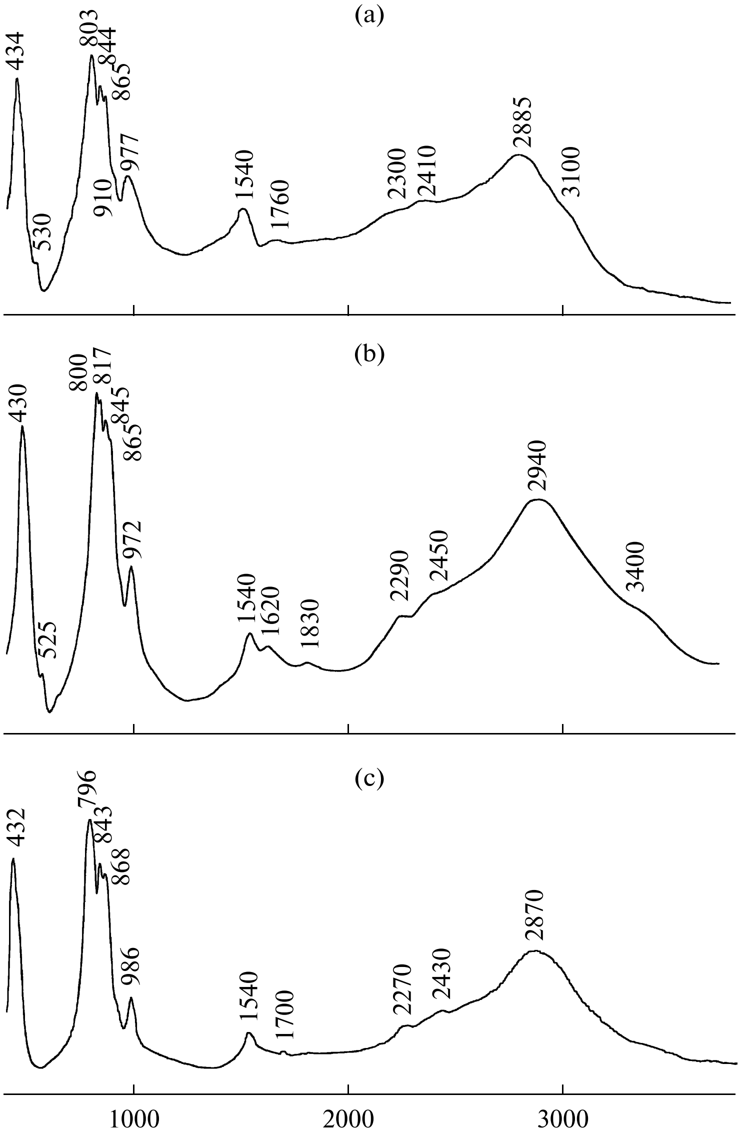

Fig. 3. IR spectra: (a) nickeltalmessite, (b) talmessite, and (c) roselite-beta.

Table 1. Water content was measured by the Alimarin method in an oxygen flow at 1000°C using absorbing tubes filled with burnt $Mg(ClO_4)_2$. The empirical formula calculated on the basis of $(AsO_4)_2$ is $Ca_{2.04}(Ni_{0.77}Mg_{0.13}Co_{0.06})_{\Sigma 0.96}$ $(AsO_4)_{2.00} \cdot 1.91H_2O$. A similar formula was calculated on the basis of ten oxygen atoms: $Ca_{2.057}(Ni_{0.775}Mg_{0.136}Co_{0.064})_{\Sigma 0.975}$ $(AsO_4)_{2.007} \cdot 1.926H_2O$. The simplified formula is $Ca_2Ni(AsO_4)_2 \cdot 2H_2O$. The composition calculated from this formula is as follows, wt %: 24.77 CaO, 16.50 NiO, 50.77 As_2O_5, 7.96 H_2O; the total is 100.00.

The compatibility of chemical composition, optical parameters, and density is good: $1 - (K_p/K_C) = -0.015$ (for calculated density) and $1 - (K_p/K_C) = -0.029$ (for measured density).

CRYSTALLOGRAPHY

X-ray single crystal study was unsuccessful because of the small size and block structure of individual crystals.

X-ray powder diffraction pattern of nickeltalmessite was recorded with a Rigaku D/MAX-2200 diffractometer, $CuK_{\alpha 1}$ radiation (Table 2). According to the strongest reflections, the mineral is close to other fairfieldite-group members. In analogy to other minerals of this group, the probable space group of the new mineral is $P1$ or $P\bar{1}$.

The unit-cell dimensions of the triclinic lattice of nickeltalmessite refined from the X-ray powder diffraction pattern are: $a = 5.858(7)$, $b = 7.082(12)$, $c =$

Table 2. X-ray powder diffraction data on nickeltalmessite

I_{meas}, %	d_{meas}, Å	d_{calc}, Å	*hkl*	I_{meas}, %	d_{meas}, Å	d_{calc}, Å	*hkl*
18	6.38	6.42	010	20	2.439	2.437	0.21
27	5.05	5.07, 5.06	001, 100	7	2.339	2.342	$1\bar{3}0$
19	4.62	4.62, 4.61	$0\bar{1}1$, $\bar{1}01$	21	2.162	2.160	$\bar{1}\bar{2}2$
9	4.36	4.37	110	19	2.128	2.125	$2\bar{2}1$
7	4.00	3.99	$\bar{1}11$	19	2.105	2.109	$2\bar{3}0$
43	3.57	3.55	011	24	2.077	2.084	210
18	3.42	3.41	$1\bar{2}0$	17	2.020	2.020	$\bar{1}22$
58	3.358	3.368	110	19	1.897	1.897	$\bar{3}21$
16	3.295	3.300	$1\bar{1}1$	10	1.782	1.774	022
100	3.202	3.212	020	39	1.714	1.714	$\bar{3}31$
5	3.118	3.113	$0\bar{2}1$	15	1.602	1.606	040, $\bar{3}\bar{1}2$
64	3.099	3.113	$0\bar{2}1$	18	1.587	1.586	$3\bar{2}1$
60	2.813	2.809	$1\bar{2}1$	16	1.543	1.544, 1.541	$\bar{2}\bar{2}3$, $0\bar{3}\bar{3}$
68	2.772	2.767	$\bar{2}10$	14	1.461	1.461	122, $\bar{3}22$
20	2.587	2.588	$\bar{1}\bar{1}2$	14	1.404	1.405, 1.404, 1.403	$\bar{2}42$, $\bar{4}31$, $1\bar{5}1$
14	2.506	2.491	$\bar{1}2\bar{1}$	12	1.350	1.349	$4\bar{1}0$

5.567(6) Å, α = 97.20(4), β = 109.11(5), γ = 109.78(5)°, $V = 198.04$ Å^3, $Z = 1$.

DISCUSSION

The results of investigation show that nickeltalmessite is a Ni-dominant arsenate member of the fairfieldite group (Table 3) and an arsenic analogue of cassidyite $Ca_2Ni(AsO_4)_2 \cdot 2H_2O$. The minerals of the talmessite–roselite-beta isomorphic series, including Ni-bearing varieties, are abundant in the Bou Azzer ore district (Permingeat, 1956; Cesbron et al., 1972; Pekov et al., 2001; Favreau et al., 2007). Earlier, the highest Ni content (7.3 wt % NiO corresponding to atomic ratio Ni : Mg = 0.8) was identified in a talmessite sample of the Aghbar Mine (Cesbron et al., 1972).

The crystal chemistry of fairfieldite-group minerals has been studied in detail (Fanfani et al., 1970; Cattietal., 1977; Keller et al., 1981; Yakubovichetal., 2003). In the structures of these minerals, Ca atoms occupy independent sites with coordination number 8. Distorted PO_4 or AsO_4 tetrahedrons are vertex-shared with MO_6 octahedrons, where M represents divalent cations with an ionic radius of 0.80 ± 0.06 Å (Mg, Mn, Fe, Co, Ni, or Zn).

Two vertices of each MO_6 octahedron are occupied by H_2O molecules forming strong hydrogen bonds with oxygen atoms in the pendant of tetrahedron vertices. It is evident that these hydrogen bonds give rise to partial protonization of the AsO_4 groups recorded in the IR spectra of arsenate members pertaining to the fairfieldite group.

Thus, the crystal structure of fairfieldite-group minerals predetermines a wide range of isomorphic substitutions of M-cations. The prevalence of a particular cation in the mineral is related not so much to crystallochemical causes as to mineral-forming conditions. Obviously, in Bou Azzer primary ore minerals, largely arsenides (skutterudite- and löllingite-group minerals, safflorite, and clinosafflorite (Borishanskya et al., 1981)), were a source of Ni for nickeltalmessite and Ni-bearing varieties of talmessite and roselite-beta. In general, the deposits of this region are clearly specialized in cobalt: the annual cobalt production is 10–12 times higher than that of nickel as a by-product. Local Ni concentrations, however, are rather high as a result of later-stage ore deposition. Elevated Ni contents have been noted in the eastern Bou Azzer, where the Aït Ahmane Mine is located (Favreau et al., 2007) and in the central part of this ore district. Nickeline, pararammelsbergite, and gersdorffite (the latter

Table 3. Comparative characteristics of nickeltalmessite and related minerals of the fairfieldite group

Mineral	Nickeltalmessite	Talmessite	Roselite-beta	Parabrandtite	Gaitite	Cassidyite
Formula	$Ca_2Ni(AsO_4)_2 \cdot 2H_2O$	$Ca_2Mg(AsO_4)_2 \cdot 2H_2O$	$Ca_2Co(AsO_4)_2 \cdot 2H_2O$	$Ca_2Mn(AsO_4)_2 \cdot 2H_2O$	$Ca_2Zn(AsO_4)_2 \cdot 2H_2O$	$Ca_2Ni(PO_4)_2 \cdot 2H_2O$
Symmetry	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P1$ or $P\bar{1}$	$P\bar{1}$	$P1$ or $P\bar{1}$	$P1$?	$P\bar{1}$	$P1$ or $P\bar{1}$
a, Å	5.858	5.784	5.88	5.89	5.899	5.71
b, Å	7.082	6.943	7.67	7.03	6.890	6.73
c, Å	5.567	5.537	5.58	5.64	5.578	5.41
α, degree	97.20	97.3	112.3	97.77	97.38	96.8
β, degree	109.11	108.7	71.3	109.32	109.07	107.3
γ, degree	107.78	108.1	119.7	108.47	108.06	104.6
Z	1	1	1	1	1	1
Strong reflections of X-ray diffraction pattern, d, Å–I, %	5.05–27 3.57–43 3.358–58 3.202–100 3.099–64 2.813–60 2.772–68 1.714–39	5.09–60 4.62–40 3.56–60 3.21–80 3.07–100 2.77–100 1.717–60	3.98–40 3.59–60 3.22–40 3.08–90 2.75–100 1.894–40 1.719–40	5.11–40 3.64–70 3.37–40 3.231–50 3.090–80 2.811–100 2.778–50	5.05–40 3.350–50 3.208–50 3.080–80 2.781–100 2.750–70 1.721–60	3.49–38 3.23–65 3.13–48 3.03–95 2.70–100 2.67–79 1.660–46
Optical parameters						
Optical sign	(+)	(–)	(–)	(+)	(–) or (+)	No data
$2V_{meas}$, degree	80	~90	80–90	79.9	88	not measured
α, degree	1.715	1.672	1.723	1.701	1.713	1.64–1.65
β, degree	1.720	1.685	1.737	1.721	1.730	not measured
γ, degree	1.735	1.698	1.756	1.751	1.748	1.67–1.68
Density, g/cm^3	3.741 (calc.) 3.72 (meas.)	3.57 (calc.) 3.421 (meas.)	3.77 (calc.) 3.71 (meas.)	3.60 (calc.) 3.55 (meas.)	3.82 (calc.) 3.81(meas.)	3.1–3.2 (calc.) (calc.)
Mohs hardness	4	5	3.5–5	3–5	~5	not measured
Source	This study	Bariand and Herpin, 1960; Yakhontova (1968); Catti et al., 1977	Frondel, 1955; Pierrot, 1964	Dunn et al., 1987	Sturman and Dunn, 1980; Keller et al., 1981	White et al., 1967

occurs as crystals up to 4 cm in size in the Aït Ahmane Mine) are characteristic minerals of this stage.

REFERENCES

1. P. Bariand and P. Herpin, "Un arséniate de calcium et de magnésium, isomorphe de la β-roselite," Bull. Miner **83**, 118–121 (1960).
2. S. S. Borishanskaya, R. A. Vinogradova, and G. A. Krutov, *Minerals of Nickel and Cobalt* (Moscow State Univ., Moscow, 1981) [in Russian].
3. M. Catti, G. Ferraris, and G. Ivaldi, "Hydrogen Bonding in the Crystalline State. Sructure of Talmesiite, $Ca_2(MgCo)(AsO_4)_2 \cdot 2H_2O$, and Crystal Chemistry of Related Minerals," Bull. Miner. **100**, 230–236 (1977).
4. F. Cesbron, G. Pallix, F. Permingeat, and H. Vachey, "Une nouvelle variété de Talmessite: la talmessite nickelifére d'Aghbar (district de Bou-Azzer, Anti-Atlas)," Notes et Mémoires du Service Géologique du Maroc **32** (241), 67–72 (1972).
5. P. J. Dunn, D. R. Peacor, S.-C. Du, et al. "Parabrandtite, the Manganese Analog of Talmessite, from Sterling Hill, Ogdensburg, New Jersey," Neues Jahrb. Mineral. Abh. **157**, 113–119 (1987).
6. L. Fanfani, A. Nunzi, and P. F. Zanazzi, "The Crystal Structure of Fairfieldite," Acta Crystallogr. **26**, 640–645 (1970).

7. G. Favreau, J. E. Dietrich, N. Meisser, and J. Brugger, Ait Haddouch, and L. Maacha, "Famous Mineral Localities: Bou Azzer, Morocco," Mineral. Record, **38** (5), 345–407 (2007)
8. C. Frondel, "Neomesselite and Beta-Roselite: Two New Members of the Fairfieldite Group," Am. Mineral. **40**, 828–833 (1955).
9. P. Keller, H. Hess, and H. Riffel, "Die Kristallstruktur von Zwei Neuen Calcium-Zink-Arsenat-Mineralien von Tsumeb/Namibia," Zeitschr. Krist. **156**, 70–71 (1981).
10. I. V. Pekov, R. A. Vinogradova, N. V. Chukanov, and I. M. Kulikova, "Magnesium and Cobalt Arsenates of the Fairfieldite and Roselite Groups," Zap. Vseross. Mineral. O-va **130** (4), 10–23 (2001).
11. F. Permingeat, "Beta-roselite de Bou-Azzer," Notes et Mémoires du Service Géologique du Maroc **14** (133), 141–142 (1956).
12. R. Pierrot, "Contribution á la Minéralogie des Arséniates et calcomagnésiens naturels," Bull. Soc. Fr. Minér. **87**, 169–211 (1964).
13. B. D. Sturman and P. J. Dunn, "Gaitite, $H_2Ca_2Zn(AsO_4)_2(H_2O)$, a New Mineral from Tsumeb, Namibia (South West Africa)," Can. Mineral. **18**, 197–2000 (1980).
14. J. S. White, Jr., E. P. Henderson, and B. Mason, "Secondary Minerals Produced by Weathering of the Wolf Creek Meteorite," Am. Mineral. **52**, 1190–1197 (1967).
15. L. K. Yakhontova, "Mg–Ca and Ca Arsenates from Oxidizing Zone of Arsenide Deposit," Tr. Miner. Muzeya AN SSSR, No. 18, 154–167 (1968) [in Russian].
16. O. V. Yakubovich, W. Massa, R. P. Liferovich, et al., "Hillite, a New Member of the Fairfieldite Group: Its Description and Crystal Structure," Can. Mineral. **41**, 981–988 (2003).