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Larisaite, $Na(H_3O)(UO_2)_3(SeO_3)_2O_2 \cdot 4H_2O$, a new uranyl selenite mineral from Repete mine, San Juan County, Utah, U.S.A.

Nikita V. CHUKANOV[1], Dmitry Yu. PUSHCHAROVSKY[2], Marco PASERO[3], Stefano MERLINO[3], Anna V. BARINOVA[2], Steffen MÖCKEL[4], Igor V. PEKOV[2], Aleksandr E. ZADOV[5] and Viktor T. DUBINCHUK[6]

[1] Institute of Problems of Chemical Physics, Chernogolovka, Moscow region, 142432, Russia
Corresponding author: e-mail: chukanov@icp.ac.ru
[2] Faculty of Geology, Moscow State University, Vorobievy Gory, Moscow, 119992, Russia
[3] Dipartamento di Science della Terra, Universita di Pisa, Via S. Maria 53, I-56126 Pisa, Italy
[4] Alpha-geophysik in Sachsen, Neudorfer Str. 18, D-09629 Burkersdorf, Germany
[5] NPO Regenerator, Skladochnaya 1, Moscow, 127018, Russia
[6] All-Russian Scientific-Research Institute of Mineral Resources (VIMS), Staromonetnyi per., Moscow, 109017, Russia

Abstract: Larisaite, a new uranyl selenite with the idealized formula $Na(H_3O)(UO_2)_3(SeO_3)_2O_2 \cdot 4H_2O$, has been found in a sedimentary rock from Repete mine near Blanding, San Juan Co., Utah, U.S.A., in association with quartz, haynesite, andersonite, wölsendorfite, uranophane, gypsum, calcite and montmorillonite. The mineral is named in memory of Russian mineralogist and crystallographer Larisa Nikolaevna Belova (1923-1998) who made a significant contribution to the knowledge on the uranium minerals. Larisaite forms coarse lamellar crystals up to 1 mm and radial aggregates up to 2 mm. It is transparent or translucent, yellow, lustre vitreous, streak yellow. Fluorescence under the UV light is green (wavelengths of excitation 250 nm). Larisaite is sectile, with Mohs' hardness 1, perfect cleavage on (010) and uneven fracture across the cleavage direction. Calculated density is 4.50 g/cm^3 from the crystal structure refinement and 4.46 g/cm^3 from the empirical formula. Optically biaxial (-), α 1.597(2), β 1.770(5), γ 1.775(5); $-2V \approx 20°$. Dispersion is strong, $r<v$. Orientation: X = *b*, Z coincides with the direction of elongation. Pleochroism: γ (yellow) $\approx$ β (yellow) > α (light greenish-yellow). IR spectrum is given. Average values for 3 point microprobe analyses (wt.%, ranges are given in brackets) are: Na_2O 2.04 (1.82-2.32), K_2O 0.69 (0.62-0.76), CaO 0.23 (0.17-0.30), UO_3 72.19 (71.77-72.64), SeO_2 18.12 (17.83-18.48); H_2O content determined by Penfield method is 7.64; total 100.91 wt.%; contents of Mg, Sr, Ba, Pb, Zn, Mn, Ni, Co, Cu, Fe, Al, Si, S, As, Cl, F are lower than detection limits *i. e.* < 0.02-0.05%. The empirical formula based on $(SeO_3)_2O_2$ is: $Na_{0.81}K_{0.18}Ca_{0.05}(H_3O)_{0.73}(UO_2)_{3.09}(SeO_3)_2O_2 \cdot 4.1H_2O$. $1-(K_P/K_c) = 0.013$ ("superior"). The crystal structure has been determined (R=0.067). Larisaite is monoclinic, space group $P11m$; a = 6.9806(9), b = 7.646(1), c = 17.249(2) Å, γ = 90.039(4)°, V = 920.64 Å^3, Z = 2. The strongest lines in the powder diffraction pattern [*d*, Å (*I*, %) (*hkl*)] are: 8.63 (43) (002), 7.67 (100) (010), 3.85 (40) (-113, 020, 113), 3.107 (77) (211), 2.874 (53) (006, -115). By the U : Se ratio, the values of unit cell parameters and the structure type, larisaite is related to haynesite, guilleminite and piretite. In common with guilleminite, uranium polyhedra and SeO_3 triangles form the sheets, however the distribution of interlayer cations and H_2O molecules is different. Holotype specimen is deposited in the Geoscientific Collections of Freiberg University of Mining and Technology, Faculty of Geosciences, Geotechnics and Mining, Freiberg, Germany (the inventory number 80251).

Key-words: larisaite, new mineral, uranyl selenite, Repete mine, Utah, hydrogen bonds.

Introduction

Among more than 200 uranium minerals, only 6 uranyl selenites have been described. Three of them are characterized by the ratios $SeO_3 : UO_2 \geq 1$ (*i. e.* 3 : 1 for demesmaekerite, 2 : 1 for derriksite and 1 : 1 for marthozite) – see Cesbron *et al.*, 1965, 1969, 1971. The general formula of other three uranyl selenites, guilleminite (Pierrot *et al.*, 1965), haynesite (Deliens & Piret, 1991) and piretite (Vochten *et al.*, 1996) is $M_{0-1}(UO_2)_3(SeO_3)_2(O,OH)_{2-4} \cdot nH_2O$ (n = 3-5). The last three minerals are orthorhombic, with similar unit cell parameters and differing in the prevailing additional cation *M* (Ba, no *M* cations and Ca, respectively). The crystal structure of guilleminite was reported by Cooper & Hawthorne (1995), whereas the crystal structures of haynesite and piretite are not investigated so far. The new mineral larisaite, which was approved by the IMA Commission on New Minerals and Mineral Names, is related to guilleminite, haynesite and piretite (Table 1), but it is monoclinic and contains Na as the prevailing *M* cation. It was named in the memory of Russian mineralogist and crystallographer Larisa Nikolaevna Belova (1923-1998) who gave significant contribution to

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Table 1. Comparative data for larisaite, haynesite, guilleminite and piretite.

Mineral	Larisaite	Haynesite	Guilleminite	Piretite
Formula	$Na(H_3O)(UO_2)_3(SeO_3)_2O_2 \cdot 4H_2O$	$(UO_2)_3(SeO_3)_2(OH)_2 \cdot 5H_2O$	$Ba(UO_2)_3(SeO_3)_2O_2 \cdot 3H_2O$	$Ca(UO_2)_3(SeO_3)_2(OH)_4 \cdot 4H_2O$
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*P*11*m*	*Pnc*2 or *Pncm*	$P2_1nm$	$Pmn2_1$ or *Pmnm*
Unit cell dimensions				
a, Å	6.981	6.935	7.08	7.010
b, Å	7.646	8.025	7.29	17.135
c, Å	17.249	17.43	16.88	17.606
γ, °	90.04			
Z	2	2	2	4
Optical properties				
α	1.597	1.618	1.720	1.54
β	1.770	1.738	1.798	1.73
γ	1.775	1.765	1.805	1.75
Optical sign, 2V, °	-20	-45	-35	-33
References	This work	Deliens & Piret, 1991	Pierrot *et al.*, 1965; Cooper & Hawthorne, 1995	Vochten *et al.*, 1996

Note: unit cell dimensions of orthorhombic minerals are given for the original orientation corresponding to $a < b < c$.

the knowledge of the uranium minerals (Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry of Russian Academy of Sciences, Moscow). A holotype specimen is deposited in the Geoscientific Collections of Freiberg University of Mining and Technology, Faculty of Geosciences, Geotechnics and Mining, Freiberg, Germany (the inventory number 80251).

Occurrence, general appearance and physical properties

Larisaite is a secondary mineral found in a sedimentary rock of Upper Jurassic age in the Repete mine near Blanding, San Juan County, Utah, USA (see Deliens & Piret, 1991). In this work a sample from the collection of S. Mőckel was investigated. It forms coarse lamellar crystals up to 1 mm showing {010} as dominant form and rosettes up to 2 mm (Fig. 1) in cracks, in association with montmorillonite, quartz, haynesite, wölsendorfite, andersonite, uranophane, gypsum and calcite. Crystal faces are rough and usually corrugated.

Crystals of larisaite are transparent or translucent, canary-yellow, lustre is vitreous with pearly sheen on cleavage planes, streak yellow. Fluorescence under the UV light is green (wavelength of excitation 250 nm). Larisaite is sectile, it shows Mohs' hardness 1, perfect cleavage on (010) and uneven fracture across the cleavage direction. Grinding of larisaite leads to its amorphization. Density could not be satisfactorily measured owing to porosity of most crystals. Application of the method of equilibration in heavy liquids would be the only way to measure density for perfect small crystals, but liquids with D > 4.46 g/cm^3 are not available Calculated density is 4.46 g/cm^3 for the empirical formula and 4.50 g/cm^3 for the structural formula and unit cell volume given below. Optically, the new mineral is biaxial (-), α 1.597(2), β 1.770(5), γ 1.775(5); -2V ≈ 20°. Optic angle dispersion is strong, $r < v$. Orientation: X = *b*, Z coinsides with the direction of elongation. Extinction angle with respect to the elongation direction is 1-3°. Pleochroism: γ (yellow) ≈ β (yellow) > α (light greenish-yellow). Twinning was not observed.

IR spectroscopy

Larisaite was mixed with anhydrous KBr, pelletized, and analysed using a Specord 75 IR spectrophotometer. IR spectrum of pure KBr-disk was subtracted from the overall spectrum. In a separate experiment with dry mineral oil as immersion medium, correctness of IR spectrum in the ranges 3000-4000 and 1500-1800 cm^{-1} was proved. Polystyrene and gaseous NH_3 were used as frequency standards; the precision of frequency measurement is ±1 cm^{-1}; the mean resolution for the region 400-1600 cm^{-1} is 0.8 cm^{-1}.

By the overall aspect, IR spectrum of larisaire (Fig. 2) is similar to spectra of haynesite Čejka *et al.*, 1999) and piretite (Vochten *et al.*, 1996), differing in position and/or splitting of some absorption bands. Wavenumbers of the band maxima in the IR spectrum of larisaite are (cm^{-1}, s – strong band, w – weak band, sh – shoulder): 3670 sh, 3600s (O-H stretching vibrations of H_2O molecules forming weak hydrogen bonds), 3320, 2900 sh (O-H stretching vibrations of the ions H_3O^+), 1730 sh (bending vibrations of the ions H_3O^+), 1622 (bending vibrations of H_2O molecules), 1095, 1044 (bending vibrations of the ions H_3O^+), 901s (stretching modes of UO_2^{2+}), 754s, 740s, 730sh (all-stretching modes of SeO_3^{2-}), 592w, 506 (stretching vibrations of non-covalent bonds and libration modes of H_2O), 470s, 380 (bending modes of SeO_3^{2-}). IR spectrum of larisaite differs from that of haynesite by the presence of additional bands at 3600 and 506 cm^{-1} (water molecules forming weak hydrogen bonds) and absence of the band at 820 cm^{-1} (bending vibrations of the OH groups). In the IR spectrum of piretite lower frequencies of Se-O and O-H stretching vibrations are observed (strong band at 732 cm^{-1} and strong broad bands at 2927 and 3303 cm^{-1} respectively).

Čejka *et al.* (1999) assigned very strong band at 1036 cm^{-1} as well as shoulders in the range 1080-1170 cm^{-1} present in IR spectrum of haynesite to "δ UOH or combination bands related to $(SeO_3)^{2-}$ stretching vibrations". This assignment is hardly true, taking into account very high integral absorption intensity in the range 1000-1200 cm^{-1} in the spectrum of haynesite and absence of strong bands in this range for piretite. On the other hand, for the ions H_3O^+ with the symmetry C_{3v} calculated frequencies of normal vibrations are (cm^{-1}; see Čejka *et al.*, 1999; Arkhipenko *et al.*, 1977): $\nu_1(A_1)$ = 3160 (symmetric stretching vibrations); $\nu_2(A)$ = 1050-1140 (bending vibrations); $\nu_3(E)$ = 3320 (doubly degenerate anti-symmetric stretching vibrations); ν_4 = 1730-1740 (doubly degenerate bending vibrations). Both haynesite and larisaite (but not piretite) show absorption of IR radiation in all these ranges, though for haynesite the bands of stretching vibrations of the ions H_3O^+ are concealed by the strong band of H_2O absorbed by the KBr-disk (at 3434 cm^{-1}). Strong bands in the range 1000-1200 cm^{-1} in IR spectra of haynesite and larisaite can not be treated as combination bands of SeO_3^{2-} stretching vibrations because in this case intensities of these bands should be considerably lower. So, presence of very strong bonds in the range 1000-1200 cm^{-1} in IR spectrum of haynesite, less strong bonds in this range for larisaite and absence of strong bonds there for piretite indicates that total amount of the H_3O^+ ions lowers in the order: haynesite → larisaite → piretite. Note that alternative formula, $(H_3O)_2(UO_2)_3(OH)_4(SeO_3)_2 \cdot H_2O$, has been proposed for haynesite by the authors of its first description (Deliens & Piret, 1991).

Chemical data

The electron-microprobe analyses were performed using a CAMEBAX analyser equipped with a Link AN 10000 spectrometer at an operating voltage of 15.7 kV and a beam current of 1.2 nA. The electron beam was rastered over an area 16 × 16 μm^2 to minimize loose Na. The standards used are: albite (for Na), orthoclase (for K), wollastonite (for Ca), UO_2 (for U), Se (for Se). Average values of three point microprobe analyses of the holotype sample (wt.%, ranges are given in brackets) are: Na_2O 2.04 (1.82-2.32), K_2O 0.69 (0.62-0.76), CaO 0.23 (0.17-0.30), UO_3 72.19 (71.77-72.64), SeO_2 18.12 (17.83-18.48); contents of Mg, Sr, Ba, Pb, Zn, Mn, Ni, Co, Cu, Fe, Al, Si, S, As, Cl, F are lower

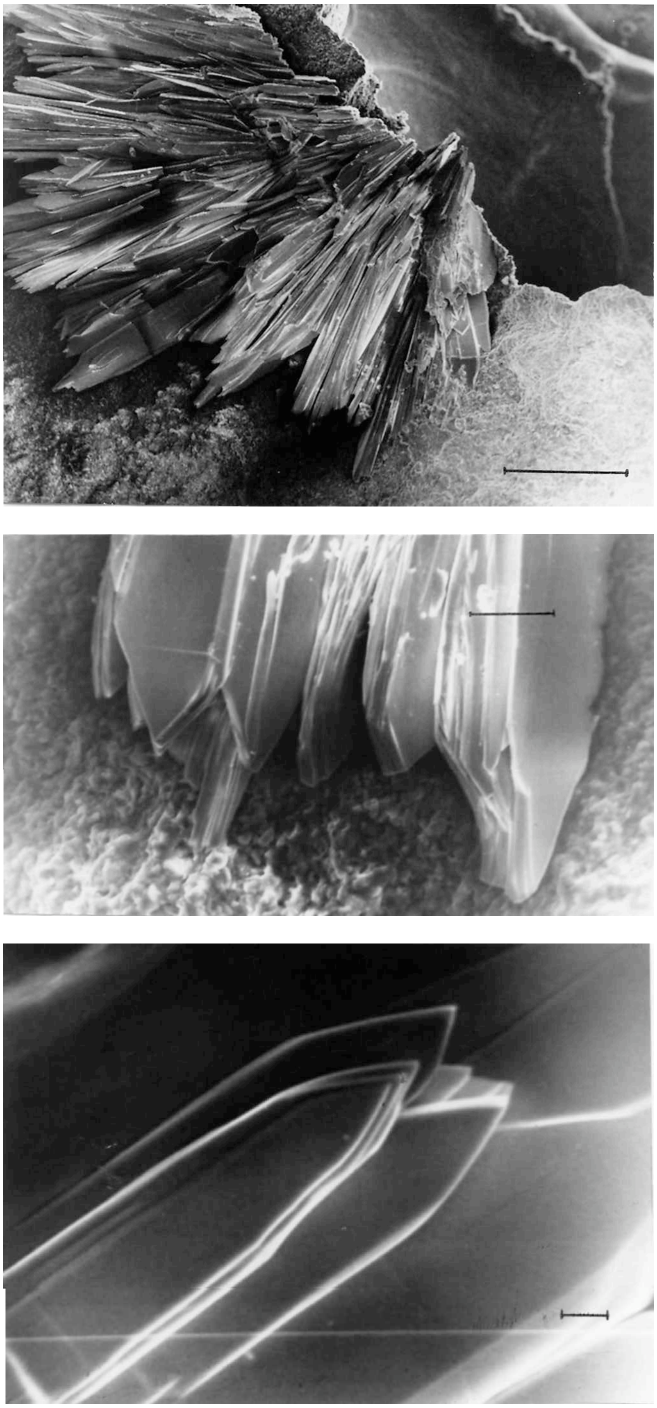

Fig. 1. a,b,c. Aggregates of larisaite. SEM images. Scale section is 50 μm for (a), 5 μm for (b) and 1 μm for (c).

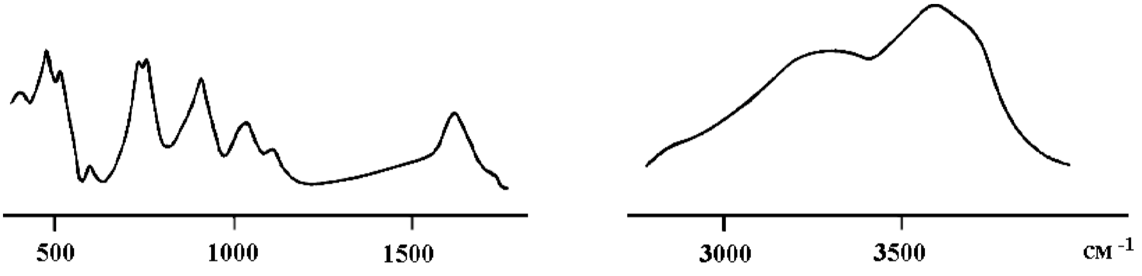

Fig. 2. IR spectrum of larisaite.

Table 2. X-ray powder data for larisaite.

I_{meas}, %	d_{meas}, Å	d_{calc}, Å	*hkl*
43	8.63	8.627	002
100	7.67	7.670	010
33	7.02	7.009	011
		6.968	100
27	5.74	5.751	003
		5.732	012
27	4.45	4.436	103
		4.435	-112
40	3.85	3.845	-113
		3.835	020
		3.834	113
27	3.762	3.760	014
		3.744	021
23	3.499	3.504	022
		3.484	200
23	3.313	3.312	-114
33	3.176	3.178	-210
77	3.107	3.114	211
33	3.050	3.092	105
53	2.874	2.876	006
		2.870	-115
27	2.664	2.658	106
23	2.415	2.410	-125
23	2.105	2.100	-134
		2.095	134
23	2.056	2.060	108
		2.056	230
		2.054	035
25	1.935	1.940	-322
		1.936	233
		1.932	322
22	1.921	1.923	-226
27	1.879	1.882	-323
		1.880	028
20	1.811	1.814	128
		1.810	-142
		1.808	-324
23	1.761	1.762	-143
		1.760	-316
22	1.732	1.733	401
22	1.521	1.523	415
		1.516	-2.1.10
22	1.443	1.445	054
		1.443	-425, -430
30	1.411	1.412	-338
		1.408	1.0.12, 337
19	1.365	1.366	-253, -511
		1.364	-3.1.10
		1.363	434
33	1.342	1.342	338
		1.341	-2.2.11
30	1.333	1.334	418
		1.333	513, 254
		1.332	427
		1.331	-435
23	1.293	1.293	522, -440
		1.292	505
27	1.231	1.232	0.0.14, -3.2.11
		1.231	-158
		1.230	3.2.11, -354, 158

Table 3. Crystal data, structure solution and refinement for larisaite.

Chemical formula	$NaH_3O[(UO_2)_3(SeO_3)_2O_2] \cdot 4H_2O$
Molecular weight	2495.31
Radiation and wavelength	Mo *K*α, 0.71073 Å
Crystal system, space group	Monoclinic, *P*11*m*
Unit cell dimensions (from single-crystal data)	*a* = 6.981 (1) Å *b* = 7.646 (1) Å *c* = 17.249 (2)Å γ = 90.039 (4)°
Volume	920.64 Å^3
Z	2
Density (calculated)	4.50 g/cm^3
Absorption coefficient μ	30.5 mm^{-1}
F(000)	1075.0
Crystal size	0.20 x 0.04 x 0.02 mm
Data collection method	Single crystal diffractometer Nonius Kappa CCD
θ range for data collection	2.91-30.30°
Index ranges	$-9 \leq h \leq 9$, $-10 \leq k \leq 10$, $-24 \leq l \leq 24$
Reflections collected	10106
Unique reflections	4891 (R_{int} = 0.088)
Reflections with F>4σ(F)	2400
Structure solution	Direct methods
Refinement method	Full-matrix least-squares refinement on F^2
Number of refined parameters	216
$R(F)_{obs}$ [F>4σ(F)]	0.067
$Rw(F^2)$ [F>4σ(F)]	
R indices (all data)	R(F) = 0.125, Rw(F^2) = 0.205, S = 0.998
Largest diff. peak and hole	2.41 and -1.27 e/Å^3

than detection limits *i. e.* < 0.05-0.1 %. H_2O content determined by Penfield method is 7.64; total 100.91 wt.%. CO_2 was not determined because the IR spectrum shows absence of carbonate groups. The empirical formula based on $(SeO_3)_2O_2$ is: $Na_{0.81}K_{0.18}Ca_{0.05}(H_3O)_{0.73}(UO_2)_{3.09}(SeO_3)_2O_2 \cdot 4.1H_2O$. The Gladstone-Dale compatibility index for D = 4.46 g/cm^3 calculated from the empirical formula is $1-(K_P/K_c) = 0.013$ ("superior").

The idealized formula is: $Na(H_3O)(UO_2)_3(SeO_3)_2O_2 \cdot 4H_2O$. It requires: Na_2O 2.56, UO_3 70.91, SeO_2 18.34, H_2O 8.19, total 100.00 wt.%.

X-ray crystallography

X-ray powder diffraction data for larisaite (Table 2) were obtained in 114.6 mm Gandolfi camera (CuKα-radiation, Ni-filter). The powder-diffraction pattern of the new mineral has been indexed by considering the cell parameters obtained from the single crystal XRD data. Unit cell dimensions of larisaite refined from powder data are: *a* = 6.968(2), *b* = 7.670(5), *c* = 17.254(6) Å, γ = 90.29(3)°, *V* = 922(1) Å^3, *Z* = 2.

A single crystal with approximate dimensions 0.2 × 0.04 × 0.02 mm was initially tested by optical microscopy and then used for the X-ray data collection at room temperature on a Nonius KappaCCD diffractometer equipped with an ar-

Table 4. Fractional atom coordinates and displacement parameters *Ueq* (in Å^2) for larisaite.

Atom	*x*	*y*	*z*	*Ueq*
U(1)	0.9547(3)	0.5586(4)	0	0.069(1)
U(2)	0.4549(3)	-0.5575(5)	0.5	0.090(1)
U(3)	0.4572(2)	0.5641(2)	0.8934(1)	0.073(1)
U(4)	0.9572(2)	-0.5651(2)	0.3933(1)	0.087(1)
Se(1)	0.9470(5)	0.6047(6)	0.7998(3)	0.088(2)
Se(2)	0.4485(5)	-0.6078(6)	0.2994(2)	0.076(1)
K**	0.74(2)	-0.11(2)	0.5	0.34(6)*
Na**	0.442(8)	0.083(6)	0.878(2)	0.21(2)*
O(1)	0.139(3)	0.624(4)	0.859(1)	0.105(9)
O(2)	0.639(3)	-0.622(4)	0.359(1)	0.094(8)
O(3)	0.992(3)	0.437(2)	0.742(1)	0.104(8)
O(4)	0.489(3)	-0.430(3)	0.243(1)	0.099(8)
O(5)	0.797(3)	0.533(4)	0.867(1)	0.101(9)
O(6)	0.296(3)	-0.521(4)	0.366(1)	0.109(9)
O(7)	0.642(5)	0.528(7)	0	0.119(15)
O(8)	0.148(5)	-0.515(7)	0.5	0.115(14)
O(9)	0.268(4)	0.592(6)	0	0.098(12)
O(10)	0.772(5)	-0.586(7)	0.5	0.116(15)
O(11)	0.980(5)	0.322(1)	0	0.073(10)
O(12)	0.480(5)	-0.321(2)	0.5	0.068(10)
O(13)	0.422(4)	0.328(1)	0.888(1)	0.100(10)
O(14)	0.930(3)	-0.330(1)	0.387(1)	0.064(7)
O(15)	0.926(6)	0.794(2)	0	0.100(13)
O(16)	0.413(5)	-0.792(2)	0.5	0.120(18)
O(17)	0.494(4)	0.797(1)	0.893(1)	0.100(10)
O(18)	0.999(4)	-0.799(1)	0.389(1)	0.119(11)
W(1)	0.795(7)	0.100(1)	0.812(3)	0.26(2)*
W(2)	0.285(6)	-0.109(6)	0.317(2)	0.20(2)*
W(3)	0.660(4)	0.064(5)	0	0.10(1)*
W(4)	0.178(4)	-0.064(4)	0.5	0.10(1)*
W(5)	0.168(9)	0.044(9)	0.816(4)	0.28(3)*
W(6)	0.688(8)	-0.046(7)	0.322(3)	0.23(2)*

*Isotropic displacement parameters

**The site-occupancy factors for K and Na are 0.15 and 0.6, respectively

*** W = (H_2O, H_3O)

ea detector and a X-ray tube operated at 55 kV, 30 mA, producing Mo*K*α radiation ($\lambda = 0.71073$ Å). The data were collected at a crystal-to-detector distance of 40 mm. At first 10 φ-rotation images with frame-widths of 1° were used for the initial orientation matrix and unit cell determination. Then a total of 238 images, with frame-widths of 2° and 600 s time exposure per each frame, were measured to obtain a comprehensive set of three-dimensional data; 74.4% of the reciprocal space was covered. The whole data collection lasted approximately 40 hours, with a resolution up to 0.71 Å ($2\theta_{max} = 60°$).

The three-dimensional data were reduced using the DENZO-SMN program from Nonius which is based on the HKL package. A semi-empirical absorption correction was accomplished in DENZO-SMN using the redundancy of data measurements.

The unit cell dimensions $a = 6.9806(9)$, $b = 7.646(1)$, $c = 17.249(2)$ Å and $\gamma = 90.039(4)°$ were obtained by least square refinement of 3204 reflections in the range $2.91 \leq \theta \leq 30.30°$. The crystal structure was solved by direct methods. The layer fragment formed by U, Se and O atoms is essentially the same as compared with that of guilleminite and initially was refined in the space group $Pn2_1m$ using the SHELX-97 package (Sheldrick, 1997). However the arrangement of the interlayer cations and water molecules indicated the lowering of orthorhombic symmetry to monoclinic one. The transition from orthorhombic symmetry to the monoclinic one, $P11m$, in the course of the refinement was made for the reason that in the orthorhombic space group we obtained an impossible distance between Na and K (~2.5 Å). From the crystal chemical point of view, the short Na-K distance would actually imply the presence of two superimposed coordination polyhedra within the same cage whereas in the space group $P11m$ K and Na are located in neighbour cages.

Although the geometry of the structure was in general well assessed, a few Se-O distances refined to unreliable values. For that reasons, soft metrical constraints were set up to better model the geometry of SeO_3 trigonal pyramids, using the DFIX option of SHELX-97. Those constraints were progressively weakened during the refinement, by reducing their weight, but never removed at all.

The refinement, carried out with anisotropic displacement parameters for all polyhedral sheet (U, Se and O) atoms and with isotropic ones for the interlayer atoms, converged to $R(F) = 0.067$ for 2400 reflections with $F > 4\sigma(F)$. Further details of the X-ray data collection and structure refinement of larisaite are given in Table 3 .

The largest residual electron densities are 2.41 and -1.27 e/Å^3, respectively. Refined atomic parameters, selected interatomic distances and the bond strengths are listed in Tables 4, 5 and 6, respectively. High values of displacement parameters for alkaline cations are related to the problems of refinement of light atoms in the presence of uranium. The high bond valence sums for Na is related to the corresponding odd Na-O distance (1.89 Å) which is merely the result of the difficulties of the refinement (correlations, presence of heavy atoms, *etc.*).

The figures were obtained with the use of the program ATOMS (Dowty, 1995).

The crystal structure: description and discussion

In common with guilleminite the layers $[(UO_2)_3(SeO_3)_2O_2]$ oriented parallel to the (010) plane form the basis of the crystal structure of larisaite (Fig. 3). The layers consist of the columns parallel to [100] where dimers formed by two pentagonal bipyramids UO_7 with shared edge alternate with hexagonal bipyramides UO_8. These columns are linked along [001] into the layers by the SeO_3 trigonal pyramids (Fig. 4). Apart guilleminite (Cooper & Hawthorne, 1995) the topologically similar polyhedral layers were found in the series of uranylphosphates, namely phosphuranylite, upalite, françoisite-(Nd), dewindtite and dumontite, except that in selenites the linkage between U,O columns is provided by SeO_3 trigonal pyramids which are replaced by PO_4 tetrahedra in the structures of uranylphosphates. The cations Na^+, K^+, H_3O^+ and water molecules are located within the inter-

Table 5. Selected interatomic distances in the structure of larisaite (in Å)

U(1)-O(15)	1.81(1)	U(2)-O(16)	1.81(1)	U(3)-O(17)	1.80(1)	U(4)-O(14)	1.81(1)
U(1)-O(11)	1.82(1)	U(2)-O(12)	1.82(1)	U(3)-O(13)	1.82(1)	U(4)-O(18)	1.81(1)
U(1)-O(7)	2.20(3)	U(2)-O(8)	2.16(3)	U(3)-O(7)	2.26(2)	U(4)-O(10)	2.26(2)
U(1)-O(9)	2.21(3)	U(2)-O(10)	2.22(3)	U(3)-O(9)	2.27(2)	U(4)-O(8)	2.31(2)
U(1)-O(5)	2.56(2) x2	U(2)-O(6)	2.59(2) x2	U(3)-O(1)	2.35(2)	U(4)-O(2)	2.34(2)
U(1)-O(1)	2.80(2) x2	U(2)-O(2)	2.80(2) x2	U(3)-O(4)	2.36(1)	U(4)-O(3)	2.35(2)
<U(1)-O>	<2.34>	<U(2)-O>	<2.35>	U(3)-O(5)	2.43(2)	U(4)-O(6)	2.43(2)
				<U(3)-O>	<2.18>	<U(4)-O>	<2.19>
Se(1)-O(3)	1.65(1)	Se(2)-O(2)	1.68(2)	K-O(12)	2.43(13)	Na-O(13)	1.89(5)
Se(1)-O(5)	1.65(2)	Se(2)-O(4)	1.69(1)	K-O(14)	2.86(10) x2	Na-W(5)	2.22(9)
Se(1)-O(1)	1.69(2)	Se(2)-O(6)	1.70(2)	K-W(4)	3.05(12)	Na-O(17)	2.23(5)
<Se(1)-O>	<1.66>	<Se(1)-O>	<1.69>	K-W(6)	3.15(6) x2	Na-W(3)	2.59(5)
				K-O(16)	3.39(13)	Na-W(1)	2.72(8)
				K-O(18)	3.55(12) x2	<Na-O>	<2.32>
				K-O(10)	3.62(15)		
				<K-O>	<3.16>		

Parameters of H-bonds

D-A (Å)		} ADA'	(°)
W(1)-W(5)	2.65(6)		
W(1)-W(6)	2.69(5)	W(5)-W(1)-W(6)	102(2)
W(2)-W(5)	2.69(6)		
W(2)-W(6)	2.85(6)	W(5)-W(2)-W(6)	104(2)
W(3)-O(15)	2.79(4)	O(17)-W(3)-O(11)	138(1)
W(3)-O(17)	2.98(3) x2	O(17)- W(3)- O(17)	76(1)
W(3)-O(11)	2.99(5)	O(15)-W(3)-O(11)	89(1)
W(4)-O(16)	2.64(4)	O(12)- W(4)- O(18)	139(1)
W(4)-O(12)	2.89(4)	O(16)-W(4)-O(12)	95(1)
W(4)-O(18)	3.06(3) x2	O(18)-W(4)-O(18)	78(1)
W(5)-O(13)	3.07(7)		
W(5)-O(17)	3.26(7)	O(13)-W(5)-O(17)	81(2)
W(6)-O(14)	2.99(5)		
W(6)-O(18)	3.09(5)	O(14)-W(6)-O(18)	84(1)

layer space. Both Na and K sites are characterized by the partial occupancies. The K$^+$ cations occupy in minor amounts the same position as Ba^{2+} cations in the crystal structure of guilleminite whereas the Na$^+$ cations are localized in the new site as compared with guilleminite structure, with shorter interatomic distances. Water molecules [H_2O] and hydronium cations [1.25 H_3O^+ per each component layer (3 U + 2 Se + 14 O)] are statistically distributed over 6 sites within the interlayer space, in such a way as to avoid contacts between H_3O^+, K$^+$ and Na$^+$ cations. The partial substitution of H_3O^+ cations for H_2O molecules located in the interlayers was also revealed in the structure of phosphuranylite (Demartin *et al.*, 1991). The crystal chemical formula of larisaite can be written as follows:

$(\square_{0.7}K_{0.3})(Na_{1.2}\square_{0.8})[W^{(1)}{}_1W^{(2)}{}_1W^{(3)}{}_2W^{(4)}{}_2W^{(5)}{}_2W^{(6)}{}_2]_{\Sigma 10}$ $[(UO_2)_6(SeO_3)_4O_4]$,

where $W^{(i)} = (H_2O,H_3O)$, and $\square$ is vacancy.

A set of possible hydrogen bonds has been outlined on the basis of O…O distances between interlayer oxygens (belonging to either H_2O or H_3O^+) and oxygens belonging to the U-centered polyhedra. The O atoms involved as acceptor of hydrogen bonds are those labeled O11 to O18, each linked to one U atom only, and forming the shortest U-O bonds. However, due to the disordered nature of the structure and the difficulty in determining accurate positions for partially occupied oxygen sites in the presence of fully occupied uranium sites, the hydrogen bond scheme, although reliable in its basic features (Fig. 5), was not conclusively set up.

To resume, the basic difference between larisaite and guilleminite lies in the occupancy of the interlayer space: in larisaite, neighbour cavities are alternately occupied by potassium and sodium cations in distinct crystallographic sites, and this implies the lowering of the space group symmetry from *P*2$_1$*nm* to *P*11*m*, whereas in guilleminite those cavities

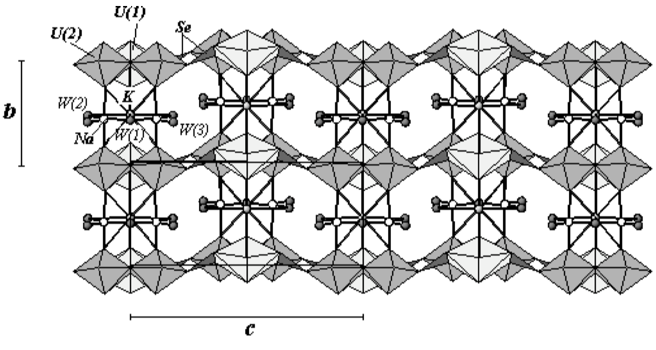

Fig. 3. Crystal structure of larisaite; view along [100].

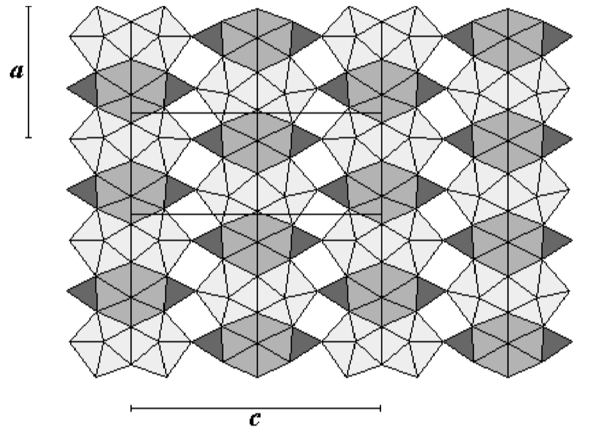

Fig. 4. Polyhedral sheet formed by UO_7 pentagonal bipyramids, UO_8 hexagonal bipyramids and SeO_3 triangles; view along [010].

Table 6. Bond-valence balance calculations for larisaite (in conventional v.u.).

	U1	U2	U3	U4	Se1	Se2	K	Na	H-bonds	$\Sigma_v a$
O1	*0.235		0.565		1.394					2.194
O2		*0.238		0.571		1.421				2.230
O3				0.563	1.541					2.104
O4			0.549			1.376				1.925
O5	*0.377		0.484		1.529					2.390
O6		*0.357		0.478		1.357				2.192
O7	0.752		0.669*							2.090
O8		0.807		0.612*						2.031
O9	0.738		0.666*							2.070
O10		0.725		0.669*			0.018			2.068
O11	1.564								+0.132	1.696
O12		1.561					0.446		+0.156	1.773
O13			1.558					0.790	+0.119	2.151
O14				1.591			*0.139		+0.132	1.765
O15	1.579								+0.186	1.672
O16		1.579					0.033		+0.260	1.719
O17			1.619					0.311	+0.134 +0.095	1.968
O18				1.588			*0.021		+0.120 +0.114	1.768
W1								0.092	-0.256 -0.230	-0.431
W2									-0.231 -0.167	-0.398
W3								0.120*	-0.186 -0.132 *-0.134	-0.287
W4							0.083		-0.156 -0.260 *-0.120	-0.381
W5								0.312	+0.256 +0.231 -0.119 -0.095	+0.460
W6							*0.064		+0.230 +0.167 -0.132 -0.114	0.170
$\Sigma_v c$	5.857	5.862	6.110	6.072	4.464	4.154	1.028	1.625		

Note: Parameters were taken from Brese & O'Keeffe (1991), and from Burns *et al.* (1997) for U^{6+}-O interaction only. Left side asterisks mean two bonds for the cation, right side asterisks mean two bonds for the anion. In the bond valence sums over anions, K-O and Na-O bond valences were computed at 15% and 60% of the given values, respectively, in keeping with the site occupancies. The contribution of the H-bonds have been computed, following Ferraris & Ivaldi (1988), on the basis of the O…O distances. W3 has been considered either a water molecule (H.bonds to O11 and O15) or a hydronium (H-bonds to O11 and O17x2). Similarly, W4 has been considered either a water molecule (H-bonds to O16 and O12) or a hydronium (H.bonds to O16 and O18x2). Hydrogen bond valences were computed accordingly, assuming, for W3 and W4, 50% H_2O and 50% H_3O^+.

are equivalent and are occupied by barium only. The topology of the U-Se layer, apart from the doubling of the parameters due to the lower symmetry, is the same in the two structures.

Along with the above described holotype sample, a hypersodic variety of larisaite has been found among the samples from the Repete mine. Its composition [electron microprobe, mean values over 4 point analyses (wt.%): Na_2O 3.87, K_2O 0.65, UO_3 71.86, SeO_2 18.21, total 94.59] corresponds to the empirical formula $[Na_{1.52}K_{0.17}(H_3O)_{0.19}]_{\Sigma 1.88}(UO_2)_{3.06}(SeO_3)_2O_2 \cdot nH_2O$ (n ≈ 3-4). Taking into account the analytical and structural data, we can assume that in this sample Na^+ not only occupies the Na site, but also can be distributed over the $W^{(i)}$ sites substituting there H_3O^+ ions.

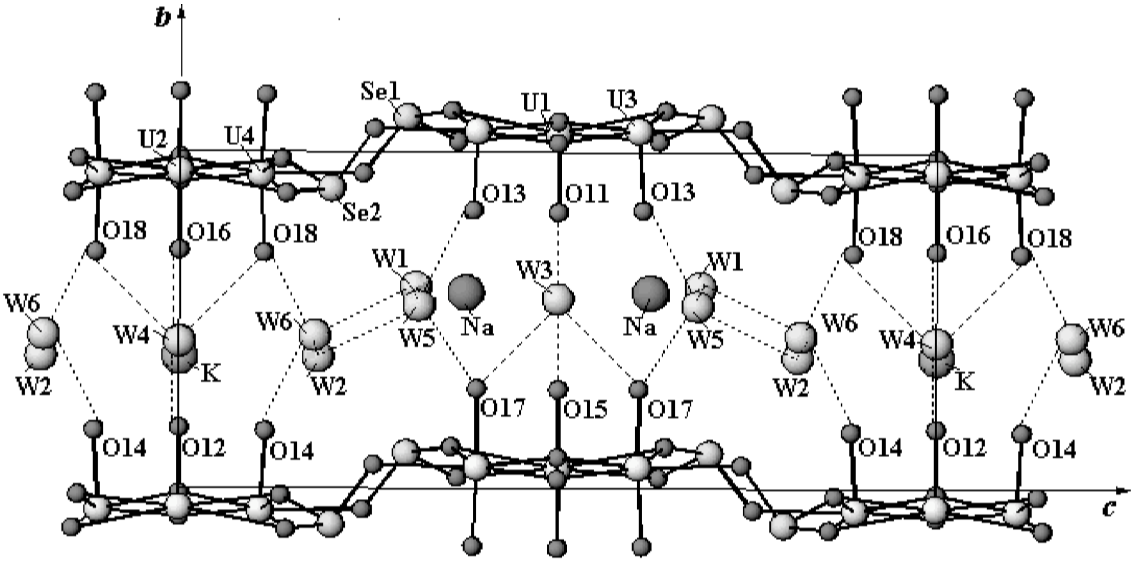

Fig. 5. Hydrogen bonding in larisaite.

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