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Crystal symmetry and chemical composition of yukonite: TEM study of specimens collected from Nalychevskie hot springs, Kamchatka, Russia and from Venus Mine, Yukon Territory, Canada

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ABSTRACT

Yukonite, a rare arsenic-bearing hydrous mineral, the crystal symmetry and variety in chemical composition of which have so far been insufficiently studied, has been found in the modern deposit of Nalychevskie hot springs in Central Kamchatka, Russia. This is the first finding of yukonite in Eastern Eurasia and Siberia. Yukonite specimens from Nalychevskie hot springs and from Venus Mine in Yukon Territory, Canada, have been investigated using an analytical transmission electron microscope (TEM). Yukonite is a crystalline substance with extremely thin (~5 nm) platy morphology. Yukonite from Venus Mine forms brittle aggregates in which grains are irregularly bent and randomly distributed. At Nalychevskie hot springs, yukonite occurs as single plates, coexisting with some amorphous material of similar composition. Intensity distributions in electron diffraction indicate that most plates of yukonite at Nalychevskie hot springs have orthorhombic symmetry, but some are hexagonal with a_{hex} = 11.3 Å. The orthorhombic cell is C-centred with $a_{orth} = \sqrt{3}a_{hex}$, $b_{orth} = a_{hex}$. High-resolution images of edge-on mounts indicate that the periodicity normal to the planes is d_{001} = 11.2 Å. Yukonite from Nalychevskie hot springs contains anomalously high Si relative to that in yukonite from Venus Mine and that reported previously. Strong negative correlation between As and Si indicates that Si substitutes for As in the structure.

KEYWORDS: yukonite, arsenic mineral, TEM, crystal symmetry, chemical composition.

Introduction

YUKONITE is a rare Ca ferric-Fe arsenate hydrous mineral. Yukonite has been reported only at a few localities in North America and Europe (Dunn, 1982; Ross and Post, 1997; Pieczka *et al*., 1998) since the first finding in Yukon Territory, Canada by Tyrrell and Graham (1913). Yukonite tends to occur in Ca^{2+}-rich oxidizing conditions as an alteration product of other As minerals, such as arsenopyrite (Pieczka *et al*., 1998), koettigite and parasymplesite (Dunn, 1982).

Yukonite is currently approved by the International Mineralogical Association as a species described before 1959 and 'grandfathered-in'. However, yukonite has not been thoroughly characterized as a mineral to date. The X-ray diffraction (XRD) patterns obtained so far have not provided sufficient information for determination of unit-cell dimensions or symmetry, and yukonite has been regarded as amorphous or imperfectly crystalline. Many reported compositions (Table 1) deviate significantly from the

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formula $Ca_3Fe_7(AsO_4)_6(OH)_9.18H_2O$ given for type-locality yukonite (PDF35-0553 of ICDD, 2002).

There are hot springs with large As contents in active geothermal areas in Kamchatka Peninsula, Far East Russia (e.g. Masurenkov *et al*., 1978, 1991; Okrugin and Zelensky, 2004; Cleverly *et al*., 2004). Nalychevskie hot springs are located in the Eastern-Kamchatskii volcanic belt in south-eastern Kamchatka and emit waters with high As content (Masurenkov *et al*., 1978, 1991; Okrugin and Zelensky, 2004; Fig. 1). Numerous As-rich calcareous deposits have accumulated around the hot springs. In autumn 2003, a field survey and sample collection of the deposits were carried out at Nalychevskie hot springs to explore minerals generated in the As-rich environment (Saji *et al*., 2004). Yukonite was found in the collected samples. This is the first find of yukonite in Russia and Eastern Eurasia.

In this study, yukonite specimens from both the Nalychevskie hot springs and Venus Mine in Yukon Territory, Canada, were examined in order to clarify the crystal symmetry and chemical composition. Transmission electron microscopy (TEM) was used to analyse the very small crystallites of yukonite.

TABLE 1. Chemical composition (wt.%) of yukonite from the literature.

	(1)	(2)	(3)	(4)
K_2O			0.2	
CaO	11.9	10.4	12.1	12.86
MgO	0.3	0.6	0.4	0.41
MnO	0.4	2.2		0.44
ZnO	0.5	3.8		0.56
Fe_2O_3	36.9	28.8	31.5	39.68
Al_2O_3	tr.	0.8	1.0	0
As_2O_5	36.8	32.1	38.5	39.68
P_2O_5	0.9	0.0		0.22
SiO_2	0.6	2.2		0.21
SO_3	0.2	0.2		0.12
H_2O	11.5	19.7	16.3	15.25
Total	100	100	100	100

(1) Yukon, Dunn (1982), sample no. R5783
(2) New Jersey, Dunn (1982), sample no. 146880
(3) Saalfeld, Ross and Post (1997)
(4) Redziny, Pieczka *et al*. (1998)

Nalychevskie hot springs

The Nalychevskaya geothermal system is located within the Avachinsko-Zhupanovskaya graben of eastern Kamchatka. The Nalychevskaya geothermal system consists of the Nalychevskie, Zhyoltorechenskie, Goryacherechenskie, Kraevedcheskie, Talovskie, and Shaibnye hot springs. At Nalychevskie hot springs, a travertine crust of 150 m × 200 m surrounds a series of pots and active vents. In 1959–1960, four boreholes for geological-structural study were drilled to a maximum depth of 217 m. The boreholes opened thermal reservoirs at depths of 25–117 m in the zone of contact between Pliocene-Pleistocene volcanic rocks with subvolcanic diorite. An active vent (Ivanov's gryphon) formed in the deepest borehole with a temperature of the emerging water of 75.6ºC. This is a small thermal pool of 5 m × 6 m in size. Silica and carbonate have precipitated over a period of 44 y to form >5000 m^2 of yellow-brown travertine ground on the shore of the pool. Thermal waters are NaCl type (Saji *et al*., 2004) and slightly enriched in As, B and Si. They belong to one specific water type called 'Nalychevskii balneological water type'. Minerals in travertine

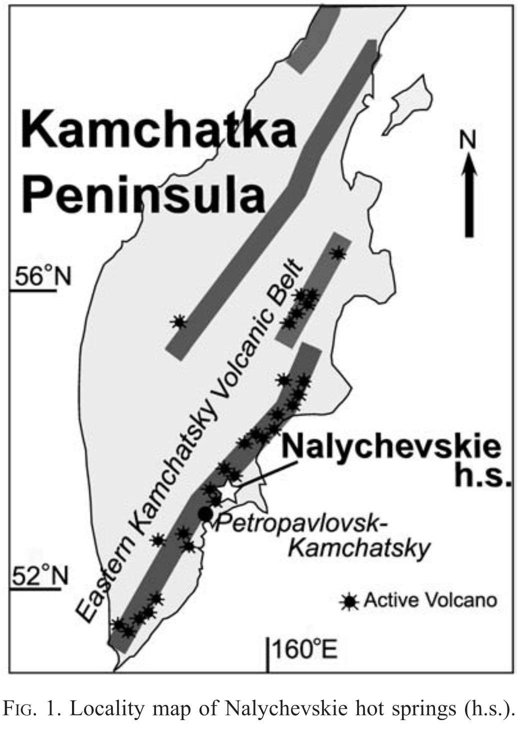

FIG. 1. Locality map of Nalychevskie hot springs (h.s.).

reported previously are calcite, quartz, opal, scorodite, manganoan calcite, aragonite, jarosite, limonite and goethite (Vasilevskii *et al*., 1977*a*,*b*; Masurenkov *et al*., 1978; Litvinov *et al*., 1999).

Samples and methods

An unconsolidated reddish-brown deposit that collapses easily in air was collected near the shore in the thermal water pool around the deepest borehole of Nalychevskie hot springs. According to Saji *et al*. (2004), water temperature, pH, electrical conductivity (EC) and oxidation-reduction potential (Eh) are 64ºC, 6.3, 6.3 mS/cm and −10 mV, respectively, at the sampling point. Na^+ and Cl^- are the main cation and anion in the sampled thermal water (937 and 1454 mg/l, respectively). Anomalous contents of As (6.4 mg/l), Li (4.2 mg/l), H_3BO_3 (401 mg/l), and SiO_2 (388 mg/l) were also detected in the water with the other constituents: Ca^{2+} (232 mg/l), Mn (0.6 mg/l), Sr (2.3 mg/l), Fe (0.9 mg/l), Rb (0.8 mg/l), Cs (0.8 mg/l), Sb (0.1 mg/l), and total dissolved inorganic carbon (498 mg/l), SO_4^{2-} (456 mg/l), Br^- (4.6 mg/l) and F^- (1.0 mg/l).

For analysis, the deposit was washed three times with distilled water and then centrifuged to remove halite and to separate it from relatively larger particles such as calcite grains. Saji *et al*. (2004) reported that the deposit was mainly composed of aggregated spherical particles 1−100 μm in size. The chemical composition of the deposit was measured by energy-dispersive X-ray fluorescence spectrometry (ED-XRF; JEOL JSX-3201), using Rh-*K*α radiation at an accelerating voltage of 30 kV, under vacuum. The deposit contained 14.9 wt.% Ca, 37.6 wt.% Fe, 43.9 wt.% As and 2.6 wt.% Si with trace amounts of K and Mn. X-ray diffraction (XRD) analysis was conducted using a Rigaku MultiFlex diffractometer with Cu-*K*α radiation at 40 kV and 30 mA and a scan speed of 1º/min. The XRD pattern obtained shows seven broad but distinct peaks. The positions and relative intensities of the peaks are in fairly good agreement with those of yukonite (Table 2).

For TEM observation, deposit samples were suspended in distilled water and dropped on copper grids coated by a thin carbon film. For edge-on observation of platy minerals, we also prepared thin sections, which were embedded in epoxy resin and thinned by ion milling. Observation and chemical analysis were carried out with TEM at 200 kV in Akita University (JEOL JEM-2010 equipped with energy-dispersive X-ray spectrometry; Norlan EDS) and in Kanazawa University (JEOL JEM-2010FEF). The camera constant was calibrated using Debye rings from the Au coating on the sample grids. Since analysed samples were sufficiently thin, the standardless thin-film approximation was applied for quantitative chemical analysis (Cliff and Lorimer, 1975).

Yukonite collected at Venus Mine in Yukon Territory, Canada (specimen donated by A. Gomi to the Mineral Industry Museum of Akita University; No.14266) is a lustrous brittle solid, dark brown to dark purple in colour. The Venus Mine workings are in the same veins as the older Daulton Mine, which is the type locality of yukonite (see the Mineral Database, 2005). Therefore, yukonite from Venus Mine can be regarded as a topotype specimen. This specimen was also confirmed to be yukonite by XRD analysis (Table 2). Since separation of the yukonite block into individual crystal grains was not possible, this material was finely crushed and sedimented onto a grid. In order to estimate water contents, thermogravimetry analysis (TG; Rigaku TG8120) was performed for both specimens.

Results and discussions

Morphology and crystal symmetry of yukonite

Using TEM, the major constituent of Nalychevskoe deposit was found to be spherulitic aggregates of thin flakes, which were amorphous under electron diffraction (Fig. 2; Amorphous). Thin plates of <3 μm in maximum dimensions, which were proved to be crystalline, were also found. Lattice spacings obtained from electron diffraction patterns (Fig. 4) agree with published XRD data for yukonite (Table 2) and were hence labelled ‘Yukonite’ in Fig. 2.

Normal-incidence diffraction patterns from the platy crystals indicated two distinct types of crystal symmetry. One type of pattern showed *6mm* plane symmetry (Fig. 3*a*), suggesting that the plates belonged to a hexagonal system with d_{100} = 9.8 Å, a_{hex} = 11.3 Å. Reflections were systematically strong for *hkl* that were multiples of {300} and {220}. This implies the presence of well-developed substructures with pseudotranslations of the type $\langle \tfrac{1}{3},y,z \rangle$ and $\langle x,\tfrac{1}{2}-x,z \rangle$. Hexagonal patterns were obtained from a minority of the plates. The second, more abundant type of diffraction patterns showed a net of

TABLE 2. XRD data for yukonite shown by spacings (Å) and *hkl* indices.

From the literature			This study		*hkl*
(1)	(2)	(3)	(4)	(5)	
	14.1 (100)		15.7 (100)	14.2 (52)	
5.6 (80)	5.58 (37)	5.61 (82)	5.65 (90)	5.61 (72)	110
3.25 (100)	3.25 (57)	3.243 (100)	3.26 (97)	3.26 (100)	300
2.79 (80)	2.79 (60)	2.778 (80)	2.80 (76)	2.80 (85)	220
2.52 (30)	2.61 (20)	2.513 (31)			
2.33 (30)	2.33 (3)				
2.23 (30)	2.24 (11)	2.226 (22)	2.23 (46)	2.24 (24)	320
	2.14 (3)		2.14 (39)		410
1.97 (10)					
1.83 (5)			1.82 (31)		420
1.76 (5)	1.76 (9)	1.767 (5)	1.75 (52)	1.76 (20)	510
1.63 (40)	1.63 (20)	1.632 (35)	1.63 (49)	1.63 (23)	600
1.51 (20)	1.51 (6)				

Numbers in parentheses are relative intensities (%) of reflections.
hkl indices are indicated for hexagonal cell
(1) PDF35-0553 (type yukonite), ICDD (2002)
(2) PDF51-1416, ICDD (2002)
(3) Pieczka *et al*. (1998)
(4) Venus Mine
(5) Nalychevskie hot springs

reflections with the same geometry but a different distribution of intensity. The point symmetry was *mm2*, compatible with orthorhombic symmetry (Fig. 3*b*). The relationship between hexagonal and orthorhombic indexing is $300_{\mathrm{hex}} = 600_{\mathrm{orth}}$, $220_{\mathrm{hex}} = 620_{\mathrm{orth}}$. Hence, the orthorhombic cell is C-centred with $a_{\mathrm{orth}} = [210]_{\mathrm{hex}}$, $b_{\mathrm{orth}} = b_{\mathrm{hex}}$, $a_{\mathrm{orth}} = \sqrt{3}a_{\mathrm{hex}} = 19.6$ Å. The orthorhombic mesh showed systematically strong reflections for $h = 6n$ and $k = 2n$, implying the existence of pseudorepeats $\langle \frac{1}{6},y,z \rangle$ and $\langle x,\frac{1}{2},z \rangle$ in the structure. The minor occurrence of hexagonal symmetry in yukonite diffractions may indicate the orientationally disordered stacking of orthorhombic layers.

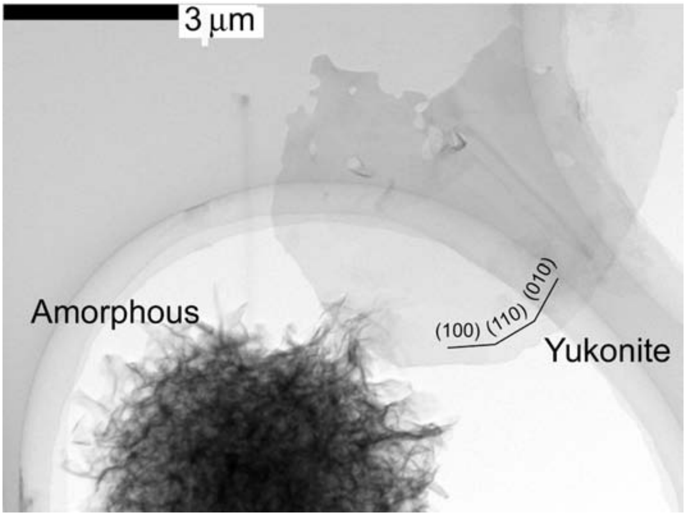

FIG. 2. TEM image of a yukonite grain and an amorphous spherule from the deposit at Nalychevskie hot springs.

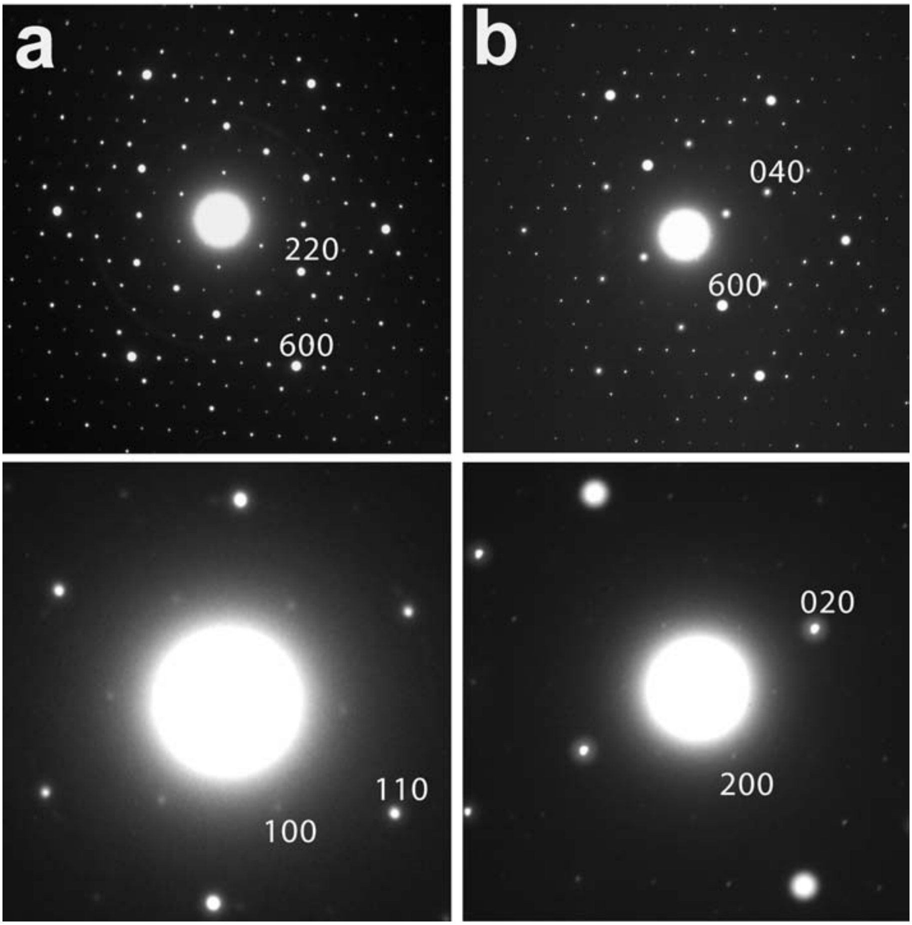

FIG. 3. Selected area electron diffraction patterns of yukonite from Nalychevskie hot springs: (*a*) hxagonal *6mm* symmetric pattern; (*b*) orthorhombic *2mm* symmetric pattern.

High-resolution TEM (HRTEM) images of yukonite from Nalychevskie hot springs are shown in Fig. 4*a*,*b*. In the image taken with [001] as the incident beam direction, lattice fringes with $d_{\text{hex }110}$ = 5.7 Å and $d_{\text{hex }300}$ = 3.3 Å are prominently developed (Fig. 4*a*). In the cross-section cut normal to the plane, lattice fringes with 11.2 Å period are observed parallel to the plane of the dominant platy face (Fig. 4*b*). Single yukonite grains are ~5 nm thick and therefore typically contain only a few repeats of the 11.2 Å lattice sheet stacking. This extremely thin crystal habit of yukonite prevents observation of $l \neq 0$ reflections. Consequently, it was not possible to determine unit-cell angles α and β which are useful for confirmation of yukonite crystal symmetries. The face of the plate is parallel to (001). The thin (001) plates of yukonite are not uniform in shape but are sometimes bounded by {100} and smaller {110} faces (Fig. 2).

Transmission electron microscopy was also used to examine the specimen from Venus Mine. The yukonite was found to be an aggregate of thin platy crystals, which were irregularly bent and randomly oriented (Fig. 4*c*). Plane spacings obtained from ring radii of diffraction pattern agree well with those of the yukonite single crystals from Nalychevskie hot springs. Regions where the incident beam was normal to the plates show perpendicular sets of $d_{\text{hex }110}$ = 5.7 Å and $d_{\text{hex }300}$ = 3.3 Å lattice fringes, while regions where the beam was parallel to plates show $d_{\text{hex }001}$ = 11.2 Å layer spacing. Comparing with *hkl* indices and lattice spacings for yukonite

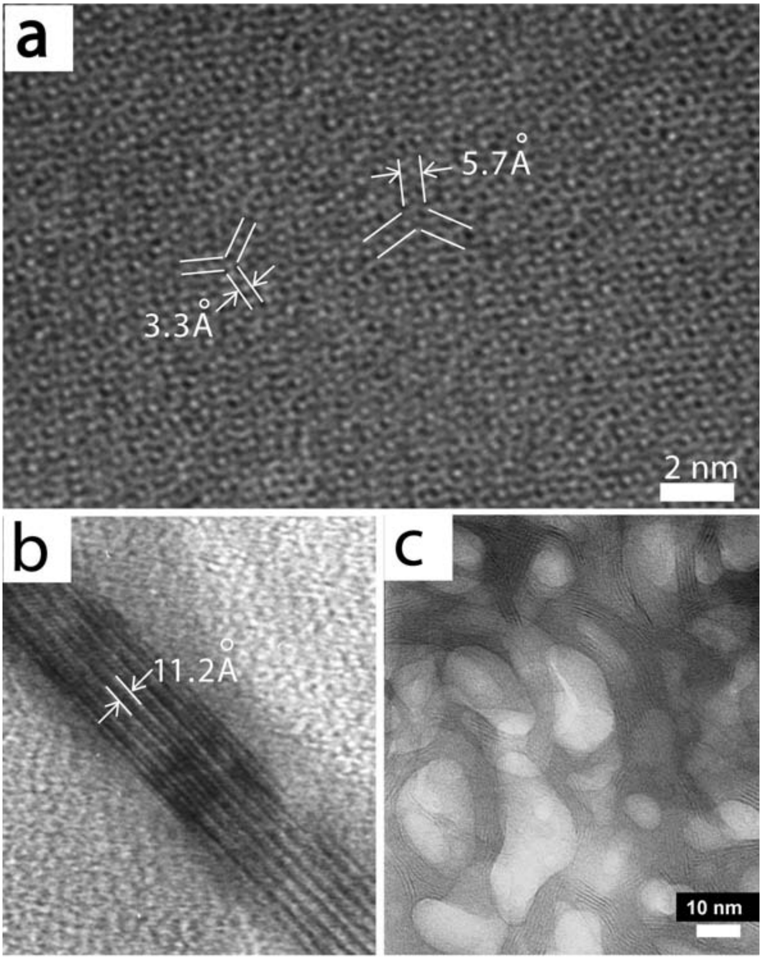

FIG. 4. (*a*) [001] incident HRTEM image of yukonite from the Nalychevskie hot springs. Note the {200} (5.7 Å) and {420}(3.3 Å) lattice fringes. (*b*) Crosscut of the plate of a yukonite grain from Nalychevskie hot springs. 11.2 Å lattice fringes can be seen. (*c*) HRTEM image of yukonite aggregate from Venus Mine.

determined by electron diffraction analyses, most *d*-spacing data obtained by XRD were indexed (Table 2).

Chemical compositions

The TEM-EDS analysis was performed on 20 yukonite crystal plates and four amorphous spherulites from Nalychevskie hot springs and on eight points in a yukonite crystalline aggregate from Venus Mine (Table 3). Here, cation totals are normalized to give 100 wt.%, and oxygen is not included in the stoichiometry.

The contents of the major elements, Ca, Fe, As and Si, range from 13.3 to 16.1 wt.%, 36.0 to 39.3 wt.%, 45.8 to 47.7 wt.% and 0.3 to 1.8 wt.%, respectively, in yukonite from Venus Mine. Yukonite from Nalychevskie hot springs shows more variation in terms of chemical composition. Ca, Fe, As and Si contents range from 17.2 to 22.3 wt.%, 33.9 to 43.7 wt.%, 27.6 to 41.7 wt.% and 3.9 to 8.7 wt.%, respectively. Amorphous spherulites were similar in composition to crystalline yukonite but with less variability: from 15.3 to 16 wt.% Ca, 36.0 to 36.4 wt.% Fe, 40.6 to 42.3 wt.% As and 4.9 to 6.3 wt.% Si. Both materials contain trace amounts of K and Mn (<1.5 wt.%). It is notable that yukonite from Nalychevskie hot springs has greater Ca and Si contents and

TABLE 3. Chemical data* for yukonite measured using TEM-EDS.

Sample	Si	Ca	Fe	As	K	Mn
Venus Mine, aggregate						
V1	0.4 (0.8)	14.0 (21)	39.3 (42)	45.8 (36)	n.d.	0.5 (0.2)
V2	1.1 (2.3)	16.1 (23.5)	38.0 (39.5)	44.3 (34.5)	n.d.	0.5 (0.2)
V3	0.3 (0.5)	14.8 (22)	36.4(39)	47.6 (38)	0.5 (0.3)	0.5 (0.2)
V4	0.3 (0.6)	14.6 (21.6)	36.7 (38.9)	47.3 (37.4)	0.6 (0.9)	0.56 (0.5)
V5	0.6 (1.3)	14.5 (21.4)	36.2 (38.3)	47.4 (37.3)	0.8 (1.1)	0.58 (0.6)
V6	0.7 (1.4)	14.1 (20.8)	36.5 (38.7)	47.7 (37.7)	0.4 (0.7)	0.63 (0.7)
V7	1.3 (2.7)	13.6 (19.9)	37.6 (39.6)	46.4 (36.4)	0.6 (0.9)	0.55 (0.6)
V8	1.8 (3.7)	13.3 (19.5)	36.0 (37.9)	47.8 (37.4)	0.7 (1)	0.41 (0.4)
Nalychevskie h.s., crystalline						
Nc1	5.4 (10.4)	17.2 (23.5)	36.7 (36)	40.5 (29.6)	0.4 (0.5)	n.d.
Nc2	8.7 (15.9)	19.9 (25.4)	39.2 (36)	31.2 (21.4)	1.0 (1.3)	n.d.
Nc3	6.7 (12.8)	18.9 (25.2)	34.8 (33.3)	38.8 (27.7)	0.6 (1.1)	0.2 (0.2)
Nc4	4.9 (9.6)	17.8 (24.4)	35.7 (35.1)	41.1 (30.1)	0.5 (0.8)	n.d.
Nc5	5.5 (10.4)	20.5 (27)	42.0 (39.7)	31.3 (22)	0.7 (0.9)	n.d.
Nc6	5.5 (10.2)	21.5 (28)	40.8 (38.3)	30.8 (21.6)	1.4 (1.9)	n.d.
Nc7	3.9 (7.7)	19.2 (26.3)	37.7 (37)	38.7 (28.3)	0.5 (0.8)	n.d.
Nc8	4.5 (8.6)	19.1 (26)	37.7 (36.8)	38.2 (27.8)	0.5 (0.8)	n.d.
Nc9	4.7 (8.9)	21.8 (28.8)	41.2 (39.1)	31.3 (22.1)	1.0 (1.2)	n.d.
Nc10	5.9 (10.9)	22.2 (28.6)	43.7 (40.5)	27.6 (19.1)	0.6 (0.8)	n.d.
Nc11	4.1 (7.9)	19.1 (26.2)	36.5 (35.9)	39.7 (29.1)	0.6 (0.7)	n.d.
Nc12	5.0 (9.3)	22.3 (29.3)	41.7 (39.2)	30.4 (21.4)	0.6 (0.8)	n.d.
Nc13	8.2 (15.3)	19.8 (25.9)	33.9 (31.9)	37.6 (26.3)	0.5 (0.6)	n.d.
Nc14	4.7 (9.3)	18.4 (25.1)	35.8 (35.2)	40.4 (29.6)	0.5 (0.6)	0.28 (0.2)
Nc15	6.9 (13.2)	18.1 (24.1)	36.1 (34.6)	38.6 (27.6)	0.4 (0.5)	n.d.
Nc16	4.1 (8.2)	18.2 (25.2)	35.2 (35)	41.7 (30.1)	0.5 (0.6)	0.3 (0.2)
Nc17	6.6 (12.2)	20.7 (26.9)	41.6 (38.8)	30.4 (21.1)	0.4 (0.6)	0.3 (0.3)
Nc18	4.9 (9.3)	20.6 (27.4)	41.0 (39.1)	33.0 (23.5)	0.5 (0.7)	n.d.
Nc19	7.8 (14.3)	22.0 (28.2)	38.6 (35.6)	31.3 (21.5)	0.3 (0.4)	n.d.
Nc20	6.3 (11.8)	20.5 (26.9)	38.9 (36.7)	33.8 (23.9)	0.5 (0.6)	n.d.
Nalychevskie h.s., amorphous						
Na1	4.9 (9.5)	15.5 (21.3)	36.3 (36)	42.3 (31.2)	0.5 (0.6)	0.5 (0.4)
Na2	5.3 (10.5)	15.3 (21.2)	36.4 (36.2)	42.1 (31.2)	0.4 (0.5)	0.5 (0.4)
Na3	6.3 (12.2)	16.0 (21.7)	36.0 (35.2)	40.6 (29.5)	0.7 (1)	0.4 (0.4)
Na4	5.6 (10.8)	15.6 (21.2)	36.4 (36.4)	41.4 (30.5)	0.5 (0.6)	0.5 (0.5)

* wt.% (atom%)
Total Si, Ca, Fe, As, K and Mn are given normalized to 100%
n.d.: not detected

smaller Fe and As contents than those of yukonite from Venus Mine. Si contents up to 8.7 wt.% are greater than those previously reported for yukonite from any other locality. Relative numbers of atoms between Si and As show a strong negative correlation (Fig. 5). Consistently small As and large Si contents in yukonite from Nalychevskie hot springs suggest that Si substitutes for As.

The thermogravimetric (TG) curve of yukonite from Venus Mine gradually decreases to 82.3 wt.% by heating at 200ºC and to 78.2 wt.% by heating at 575ºC (Fig. 6*a*). The weight change is probably due to loss of both hydroxyl and molecular water, although two dehydration stages cannot be clearly discriminated. The TG curve of the deposit from Nalychevskie hot springs also shows a similar pattern, 13.6 wt.% loss by heating at 200ºC and 17.8 wt.% loss by heating at 400ºC (Fig. 6*b*). The final values are close to the estimated water contents of yukonite in previous studies (e.g. Dunn, 1982; ~18 wt.%).

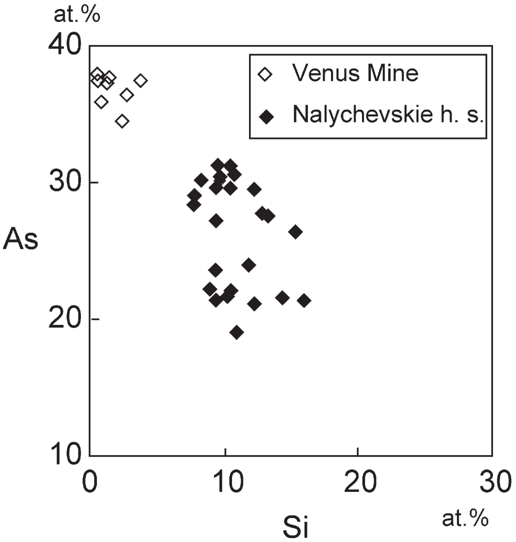

FIG. 5. Diagram showing the correlation between Si and As in yukonite.

It is reasonable to assume that As and Si exist as tetrahedral $(AsO_4)^{3-}$ and $(SiO_4)^{4-}$ ions in the yukonite crystal structure. Assuming 18 wt.% water contents, the composition of yukonite can be represented approximately as $Ca_2Fe_3(AsO_4)_3(OH)_4.4H_2O$ with up to 43% of the As replaced by Si, charge-balanced by change in the $OH:H_2O$ ratio.

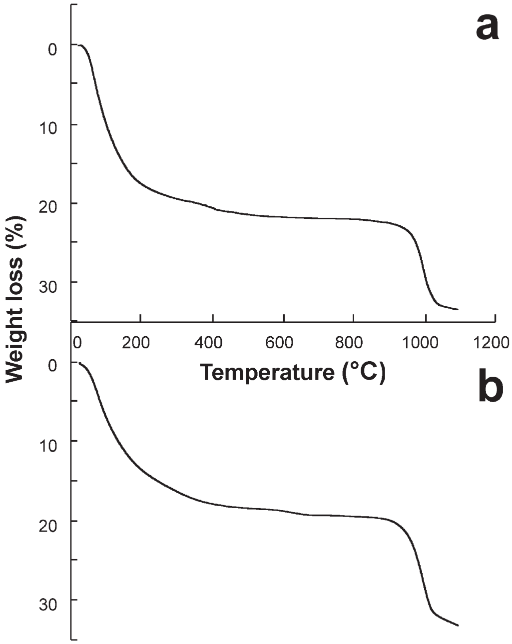

FIG. 6. TG curves of analysed samples: (*a*) Yukonite aggregates from Venus Mine; (*b*) Yukonite from Nalychevskie hot springs.

Conclusions

(1) Yukonite has been found in the deposit of Nalychevskie hot springs in Central Kamchatka, Russia. This is the first report of yukonite being found in eastern Eurasia and Siberia.

(2) Transmission electron microscopy revealed that yukonite is a crystalline material with extremely thin platy morphology, mostly ~5 nm thick. Electron diffraction patterns show orthorhombic symmetry for some crystals but hexagonal for others, although the orthorhombic and hexagonal unit meshes have the same dimensions.

(3) Yukonite from Nalychevskie hot springs contains anomalously high Si (up to 8.7 wt.%) with greater Ca and smaller Fe and As contents than those in yukonite from Venus Mine and those previously reported. The small As content implies that Si substitutes for As.

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