# New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. I. Yurmarinite, $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$

I. V. PEKOV<sup>1,\*</sup>, N. V. ZUBKOVA<sup>1</sup>, V. O. YAPASKURT<sup>1</sup>, D. I. BELAKOVSKIY<sup>2</sup>, I. S. LYKOVA<sup>1,2</sup>, M. F. VIGASINA<sup>1</sup>, E. G. SIDOROV<sup>3</sup> AND D. YU. PUSHCHAROVSKY<sup>1</sup>

<sup>1</sup> Faculty of Geology, Moscow State University, Vorobievy Gory, 119991 Moscow, Russia

<sup>2</sup> Fersman Mineralogical Museum of Russian Academy of Sciences, Leninsky Prospekt 18-2, 119071 Moscow, Russia
 <sup>3</sup> Institute of Volcanology and Seismology, Far Eastern Branch of the Russian Academy of Sciences, Piip Bulevard
 9, 683006 Petropavlovsk-Kamchatsky, Russia

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# ABSTRACT

A new mineral, yurmarinite, Na<sub>7</sub>(Fe<sup>3+</sup>,Mg,Cu)<sub>4</sub>(AsO<sub>4</sub>)<sub>6</sub>, occurs in sublimates of the Arsenatnaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. It is associated with hatertite, bradaczekite, johillerite, hematite, tenorite, tilasite and aphthitalite. Yurmarinite occurs as well-shaped, equant crystals up to 0.3 mm in size, their clusters up to 0.5 mm and thin, interrupted crystal crusts up to  $3 \text{ mm} \times 3 \text{ mm}$  on volcanic scoria. Crystal forms are  $\{101\}$ ,  $\{001\}$ ,  $\{100\}$ ,  $\{110\}$  and  $\{001\}$ . Yurmarinite is transparent, pale green or pale yellowish green to colourless. The lustre is vitreous and the mineral is brittle. The Mohs hardness is ~4½. One direction of imperfect cleavage was observed, the fracture is uneven.  $D_{\text{(calc.)}}$  is 4.00 g cm<sup>-3</sup>. Yurmarinite is optically uniaxial (-),  $\omega = 1.748(5)$ ,  $\varepsilon =$ 1.720(3). The Raman spectrum is given. The chemical composition (wt.%, electron microprobe data) is Na<sub>2</sub>O 16.85, K<sub>2</sub>O 0.97, CaO 1.28, MgO 2.33, MnO 0.05, CuO 3.17, ZnO 0.97, Al<sub>2</sub>O<sub>3</sub> 0.99, Fe<sub>2</sub>O<sub>3</sub> 16.44, TiO<sub>2</sub> 0.06, P<sub>2</sub>O<sub>5</sub> 0.12, V<sub>2</sub>O<sub>5</sub> 0.08, As<sub>2</sub>O<sub>5</sub> 56.68, total 99.89. The empirical formula, calculated on the basis of 24 O atoms per formula unit, is  $(Na_{6.55}Ca_{0.28}K_{0.22})_{\Sigma7.05}(Fe_{2.48}^{2.48}Mg_{0.70}Cu_{0.48}Al_{0.23}Zn_{0.14})$  $Ti_{0.01}Mn_{0.01}\Sigma_{4.05}(As_{5.94}P_{0.02}V_{0.01})\Sigma_{5.97}O_{24}$ . Yurmarinite is rhombohedral,  $R\bar{3}c$ , a = 13.7444(2), c = 13.744(2), c =18.3077(3) Å, V = 2995.13(8) Å<sup>3</sup>, Z = 6. The strongest reflections in the X-ray powder pattern [d, Å (I)(hkl)] are: 7.28(45)(012); 4.375(33)(211); 3.440(35)(220); 3.217(36)(131,214); 2.999(30)(223); 2.841(100)(125); 2.598(43)(410). The crystal structure was solved from single-crystal X-ray diffraction data to R = 0.0230. The structure is based on a 3D heteropolyhedral framework formed by  $M_4O_{18}$  clusters ( $M = Fe^{3+} > Mg,Cu$ ) linked with AsO<sub>4</sub> tetrahedra. Sodium atoms occupy two octahedrally coordinated sites in the voids of the framework. In terms of structure, yurmarinite is unique among minerals but isotypic with several synthetic compounds with the general formula  $(Na_{7-x} \Box_x)(M_{3+x}^{3+x}M_{1-x}^{2+})(T^{5+}O_4)_2$  in which T = As or P,  $M^{3+} = Fe$  or Al,  $M^{2+} = Fe$  and  $0 \le x \le 1$ . The mineral is named in honour of the Russian mineralogist, petrologist and specialist in studies of ore deposits, Professor Yuriy B. Marin (b. 1939). The paper also contains a description of the Arsenathaya fumarole and an overview of arsenate minerals formed in volcanic exhalations.

KEYWORDS: yurmarinite, new mineral, arsenate, crystal structure, fumarole sublimate, Tolbachik volcano, Kamchatka.

\* E-mail: igorpekov@mail.ru DOI: 10.1180/minmag.2014.078.4.10

# Introduction

NATURAL arsenates are numerous: ~340 valid mineral species belonging to this chemical class are known presently. The majority of arsenate minerals contain H2O molecules or/and OHgroups as species-defining constituents. The H-bearing arsenates form in the oxidation zone of ores with As-rich chalcogenides (arsenopyrite, fahlores, different arsenides, etc.) and in the lowtemperature hydrothermal formation. Only 47 natural arsenates are H free (in terms of idealized formula) including seven minerals with speciesdefining Cl and four with F. They are rare, except for mimetite, Pb<sub>5</sub>(AsO<sub>4</sub>)<sub>3</sub>Cl. The majority of H-free arsenates are known from relatively hightemperature formations characterized by oxidizing conditions; a well known example is the  $S^{2-}$ -deficient metamorphic and metasomatic rocks and ores of Långban-type deposits (Moore, 1970). Studies over the last three decades show that diverse H-free arsenates form in specific, highly-oxidized types of volcanic fumaroles; 19 of 47 minerals, including 15 species endemic to this kind of formation, have been found there since 1984. Hydrogen-bearing arsenates are unknown in fumarolic deposits.

The first publication on arsenates in volcanic exhalations was a description of the P-bearing variety of lammerite, Cu<sub>3</sub>[(As,P)O<sub>4</sub>]<sub>2</sub>, collected from a hot (440°C) fumarole chamber at the Tolbachik volcano, Kamchatka, Russia (Filatov et al., 1984). Two minerals were found in the deposits of palaeo-fumaroles related to extinct Cenozoic volcanoes: durangite, NaAl(AsO<sub>4</sub>)F, at Thomas Range, Utah, USA (Wilson, 1986) and a new alluaudite-group member nickenichite,  $Na(\Box,Cu)(\Box,Ca)(Mg,Fe^{3+})_3(AsO_4)_3$ , at Nickenicher Sattel, Eifel, Germany (Auernhammer et al., 1993). All later reported finds of fumarolic arsenates are at Tolbachik; seven new mineral species comprising alarsite, Al(AsO<sub>4</sub>) (Semenova et al., 1994), coparsite,  $Cu_4O_2[(As,V)O_4]Cl$  (Vergasova *et al.*, 1999), urusovite, CuAlO(AsO<sub>4</sub>) (Vergasova et al., 2000), bradaczekite, NaCu<sub>4</sub>(AsO<sub>4</sub>)<sub>3</sub> (Filatov et al., 2001), filatovite,  $K[(Al,Zn)_2(As,Si)_2O_8]$ (Vergasova *et al.*, 2004), lammerite- $\beta$ , Cu<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> (Starova et al., 2012) and hatertite, Na<sub>2</sub>(Ca,Na)(Fe<sup>3+</sup>,Cu)<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (Krivovichev et al., 2013), were discovered and the occurrences of johillerite, NaMg<sub>3</sub>Cu(AsO<sub>4</sub>)<sub>3</sub> (Glavatskikh and Bykova, 1998) and nickenichite (Rybin et al., 2012) were described from there. These nine

minerals, as well as lammerite, were found in small amounts in several active fumaroles located on the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption of 1975–76. However, the largest accumulation and the greatest diversity of fumarolic arsenates occurs in the Arsenatnaya fumarole, discovered by the authors in 2012 on the same scoria cone and named for this remarkable mineralogical and geochemical feature.

The Arsenatnaya fumarole is a unique mineralogical object due to its great mineral diversity and originality of the mineralization. Some 60 mineral species (Table 1) have been found here by the present authors to date. These include 15 arsenates of the 18 known at Tolbachik, excluding coparsite, filatovite and nickenichite. Nine new mineral species (six arsenates and three sulfates) discovered in the Arsenatnaya fumarole were approved by the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) in 2013–2014.

This article is the first of a series of papers on new arsenate minerals from the Arsenatnaya fumarole and their crystal chemistry. A description is presented of yurmarinite (Russian Cyrillic: юрмаринит), named in honour of the Russian mineralogist, petrologist and specialist in studies of ore deposits Yuriy Borisovich Marin (born 1939), Professor of Mineralogy and Petrology at Saint Petersburg Mining University, Vice-President of the Russian Mineralogical Society since 1992 and Editor-in-Chief of Zapiski Rossiiskogo Mineralogicheskogo Obshchestva, the oldest and major Russian mineralogical journal, since 1990. Both the new mineral and its name have been approved by the IMA CNMNC (IMA 2013-033, Pekov et al., 2013). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow; catalogue number 94134.

# The Arsenatnaya fumarole: description and general features of arsenate mineralization

The Arsenatnaya fumarole is located in the upper part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41'N 160°14'E, 1200 m asl). This cone, formed in 1975, is a monogenetic volcano ~300 m high and ~0.1 km<sup>3</sup> in volume (Fedotov and Markhinin,

#### YURMARINITE, A NEW MINERAL

Arsenates		Sulfates (secondary)	
Alarsite Al(AsO <sub>4</sub> )	XX	Antlerite Cu <sub>3</sub> (SO <sub>4</sub> )(OH) <sub>4</sub>	х
Bradaczekite NaCu <sub>4</sub> (AsO <sub>4</sub> ) <sub>3</sub>	XXX	Blödite Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	х
Dmisokolovite [2013-079] K <sub>3</sub> Cu <sub>5</sub> AlO <sub>2</sub> (AsO <sub>4</sub> ) <sub>4</sub>	х	Bonattite CuSO <sub>4</sub> ·3H <sub>2</sub> O	XX
Ericlaxmanite [2013-022] Cu <sub>4</sub> O(AsO <sub>4</sub> ) <sub>2</sub>	XXX	Chalcantite CuSO <sub>4</sub> ·7H <sub>2</sub> O	XXX
Hatertite Na <sub>2</sub> (Ca,Na)(Fe <sup>3+</sup> ,Cu) <sub>2</sub> (AsO <sub>4</sub> ) <sub>3</sub>	х	Epsomite MgSO <sub>4</sub> ·7H <sub>2</sub> O	х
Johillerite NaMg <sub>3</sub> Cu(AsO <sub>4</sub> ) <sub>3</sub>	XXX	Gypsum CaSO <sub>4</sub> ·2H <sub>2</sub> O	XXX
Kozyrevskite [2013-023] Cu <sub>4</sub> O(AsO <sub>4</sub> ) <sub>2</sub>	XX	Hexahydrite MgSO <sub>4</sub> ·6H <sub>2</sub> O	х
Lammerite Cu <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	XXX	Kaliochalcite [2013-037] KCu <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> [(OH)(H <sub>2</sub> O)]	XXX
Lammerite- $\beta$ Cu <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	XX	Picromerite K <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	XX
<b>Popovite</b> [2013-060] Cu <sub>5</sub> O <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub>	XX	Syngenite $K_2Ca(SO_4)_2 \cdot H_2O$	х
Shchurovskyite [2013-078] K <sub>2</sub> CaCu <sub>6</sub> O <sub>2</sub> (AsO <sub>4</sub> ) <sub>4</sub>	х	Uklonskovite NaMg(SO <sub>4</sub> )F·2H <sub>2</sub> O	х
Svabite Ca <sub>5</sub> (AsO <sub>4</sub> ) <sub>3</sub> F	XX		
Tilasite CaMg(AsO <sub>4</sub> )F	XX	Silicates	
Urusovite CuAlO(AsO <sub>4</sub> )	XXX	Fluorophlogopite KMg <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )F <sub>2</sub>	XXX
<b>Yurmarinite</b> [2013-033] $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$	х	Orthoclase (incl. As-rich variety) K[Al(Si,As,Al) <sub>3</sub> O <sub>8</sub> ]	XXX
Sulfates		Borates	
Alumoklyuchevskite K <sub>3</sub> Cu <sub>3</sub> (Al,Fe <sup>3+</sup> )O <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub>	XX	Fluoborite Mg <sub>3</sub> (BO <sub>3</sub> )F <sub>3</sub>	XX
Anglesite PbSO <sub>4</sub>	XX		
Anhydrite CaSO <sub>4</sub>	XXX	Oxides	
Aphthitalite K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub>	XXXX	Cassiterite SnO <sub>2</sub>	х
Arcanite K <sub>2</sub> SO <sub>4</sub>	XX	Corundum Al <sub>2</sub> O <sub>3</sub>	х
Calciolangbeinite K <sub>2</sub> (Ca,Mg) <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	XX	Gahnite (Cu-rich variety) (Zn,Cu)(Al,Fe <sup>3+</sup> ) <sub>2</sub> O <sub>4</sub>	
Chalcocyanite CuSO <sub>4</sub>	XXX	Hematite Fe <sub>2</sub> O <sub>3</sub>	
Dolerophanite Cu <sub>2</sub> O(SO <sub>4</sub> )	XXX	Pseudobrookite $Fe_{2}^{3+}TiO_{5}$	
Euchlorine KNaCu <sub>3</sub> O(SO <sub>4</sub> ) <sub>3</sub>	XXXX	x Tenorite CuO	
Fedotovite K <sub>2</sub> Cu <sub>3</sub> O(SO <sub>4</sub> ) <sub>3</sub>	XX	Zincite ZnO	х
Kononovite [2013-116] NaMg(SO <sub>4</sub> )F	х		
Krasheninnikovite KNa <sub>2</sub> CaMg(SO <sub>4</sub> ) <sub>3</sub> F	XXX	Oxides (secondary)	
Langbeinite K <sub>2</sub> Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	XXXX	Opal SiO <sub>2</sub> .nH <sub>2</sub> O	XXX
Palmierite $K_2Pb(SO_4)_2$	XX		
Piypite K <sub>8</sub> Cu <sub>9</sub> O <sub>4</sub> (SO <sub>4</sub> ) <sub>8</sub> Cl <sub>2</sub>	XX	Halides	
Steklite KAl(SO <sub>4</sub> ) <sub>2</sub>	XXX	Fluorite CaF <sub>2</sub>	х
Vanthoffite $Na_6Mg(SO_4)_4$	х	Halite NaCl	XXXX
Wulffite [2013-035] K <sub>3</sub> NaCu <sub>4</sub> O <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub>	XXX	Sylvite KCl	XXXX
		Halides (secondary)	
		Eriochalcite CuCl <sub>2</sub> .2H <sub>2</sub> O	xx
		Native elements	
		Gold Au	Х

TABLE 1. Minerals of the Arsenatnaya fu	umarole and their distribution.*
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\* Distribution in the Arsenatnaya fumarole: xxxx - abundant, xxx - common, xx - subordinate and x - rare mineral. The minerals first discovered in the Arsenatnaya fumarole are given in bold type with their IMA numbers in square brackets. The minerals marked as secondary were formed as a result of interactions between sublimate (primary) minerals and atmospheric agents, mainly water or water vapour, at temperatures, as shown by this current work, not greater than 100–150°C.

1983). Almost 40 y after the eruption, its fumarole fields are still active: numerous gas vents with temperatures up to 430°C were observed by the present authors in 2012–2013. Now the fumarolic gases at the Second scoria cone are compositionally close to atmospheric air, with the contents of

<1 vol.% water vapour and <0.1 vol.% acid species, mainly CO<sub>2</sub>, HF and HCl (Zelenski *et al.*, 2012) while in 1976–1977 these gases were significantly more enriched in H<sub>2</sub>O, SO<sub>2</sub>, CO<sub>2</sub>, HCl and, in some fumaroles, HF (Meniaylov *et al.*, 1980).

The Arsenatnaya fumarole was uncovered and first examined during fieldwork in July 2012. Hot gas vents and greenish efflorescences of Cu sulfates on the surface indicated the possible presence of a mineralized fumarole chamber inside. Indeed, the first chamber was found at a depth of 0.3 m, under a thick (20-30 cm) crust consisting of brecciated fragments of basalt scoria cemented by aggregates of sulfates (langbeinite, euchlorine, aphthitalite, etc.) with halite, sylvite, hematite, tenorite and opal (Fig. 1). Field observations in 2012-2013 showed that the Arsenatnaya fumarole is a system of numerous open pockets between blocks of basalt scoria and volcanic bombs, strongly mineralized and almost empty. The majority of pockets are cracks (typically not wider than 5-10 cm), usually sinuous and branched. The sublimate minerals form incrustations on the surface of scoria and bombs or fill thin cracks, small cavities and numerous bubbles in scoria. The mineralized zone considered as the Arsenatnava fumarole is ~5 m long and 1-1.5 m wide and runs along a large shrinkage fracture cross-cutting the top of the scoria cone in a near-meridional direction. Pockets with the richest and most diverse mineralization, including all arsenates known to be present there, were observed in the interval from 0.3 to 0.8 m under the present-day surface. Deeper, the sublimate mineralization becomes much poorer; near a depth of 1.0 m, hematite, tenorite, subordinate fluorophlogopite and intermediate members of the sylvite-halite series are observed whereas somewhat deeper only hematite occurs. At a depth of 1.2-1.4 m the sublimate minerals disappear.



FIG. 1. The uncovered chamber at the Arsenatnaya fumarole. Green spots in the upper part are areas enriched in Cu sulfates, mainly euchlorine. Photo: V.N. Kalachev, July 2012.

The temperature measured (July 2013; chromel-alumel thermocouple) in several pockets with rich arsenate mineralization immediately after their partial uncovering was  $360-380^{\circ}$ C. Deeper, in the tenorite-hematite and hematite zones the temperature was  $390-400^{\circ}$ C. Thus, all sublimate minerals are believed to have formed at temperatures  $\ge 360^{\circ}$ C.

All sublimate (primary) minerals and products of their supergene alteration (secondary mineralization) reliably identified by the present authors in the Arsenatnaya fumarole are listed, with their idealized formulae, in Table 1. The constituents of the host rocks are not included; nor are the >15 insufficiently studied mineral phases. The data on their distribution presented in Table 1 gives a general indication of the chemistry of sublimates in Arsenatnaya. The minerals were deposited under strongly oxidizing conditions (due to high fugacity of O in fumarolic gases chemically close to atmospheric air) that caused the high-valency states of S, As and Fe (S<sup>6+</sup>, As<sup>5+</sup>, Fe<sup>3+</sup>) in all the phases formed here.

The deposition of minerals in open space gives an opportunity to reconstruct their crystallization sequence. The major early constituents of these crusts are hematite, tenorite and fluorophlogopite. The next mineral assemblage includes all arsenates, typically together with As-bearing orthoclase, some sulfates, (mainly langbeinite and aphthitalite) and a second generation of tenorite. The majority of primary, H-free sulfates, including langbeinite and aphthitalite, crystallize somewhat later than arsenates. The post-sulfate arsenate minerals are minor and are represented mainly by second generations of lammerite- $\beta$  and kozyrevskite.

Arsenates are important constituents of polymineralic incrustations in Arsenatnava. The major arsenate minerals there are lammerite, johillerite, bradaczekite and, sporadically, urusovite and ericlaxmanite. They form rich crusts (usually interrupted, sometimes massive) up to  $20-30 \text{ cm}^2$ in area. Among the 15 arsenates known to be present there, 10 minerals contain speciesdefining Cu<sup>2+</sup>, including six oxyarsenates with additional, non-bonding  $As^{5+}$ ,  $O^{2-}$  anions. Significant amounts of As in the sublimates of this fumarole are concentrated in As-bearing orthoclase formed in cavities. This unusual chemical variety of K feldspar typically contains 1-12 wt.% and sometimes up to 28 wt.% As<sub>2</sub>O<sub>5</sub> in Arsenatnaya. The significant entry of As<sup>5+</sup> in the tetrahedral framework of orthoclase, up to the formation of its As-dominant analogue filatovite, was reported by Vergasova *et al.* (2004) as being typical for fumarole deposits of the Second scoria cone. In Arsenatnaya, as the present data show, the major scheme of substitutions in orthoclase is  $As^{5+} + Al^{3+} \rightarrow 2Si^{4+}$ .

In the upper part of the Arsenatnava fumarole. within a breccia-like crust cemented by sulfates (partially altered in the outer part of this crust to aggregates of secondary, hydrous phases, Table 1), chlorides and opal, but arsenates were not found. In general, no signs of supergene alteration of arsenates was detected in Arsenatnaya. All the arsenates observed and Asbearing orthoclase are considered to be deposited directly from the gaseous phase (assumed carrier of As) or were formed as a result of gas-rock interactions. The latter seems more probable for minerals containing Al, Mg and Ca, i.e. metals with very small quantities of volatilities in postvolcanic systems even at temperatures of 400-500°C (Symonds and Reed, 1993).

# Yurmarinite

#### Occurrence and general appearance

Yurmarinite is one of the rarest minerals at this locality. It was found in only one specimen collected in 2012. The new mineral is associated closely with three chemically different monoclinic arsenates of the alluaudite group: hatertite, bradaczekite (Figs 2 and 3) and johillerite; and hematite, tenorite, tilasite and aphthitalite.



FIG. 2. Crystal crusts of pale green yurmarinite (1) with yellowish-greenish hatertite (2) and blue bradaczekite (3) on volcanic scoria. Field of view: 5.4 mm. Photo: I.V. Pekov and A.V. Kasatkin.



FIG. 3. Close association of yurmarinite (1) with hatertite (2) and hematite (3). Polished section, Scanning electron microscopy (SEM) backscatter electron (BSE) image.

Yurmarinite occurs as crystals, equant or slightly elongated (short prismatic) or flattened (thick tabular) in different directions up to 0.3 mm in size (typically not larger than 0.1 mm), their clusters up to 0.5 mm across, with parallel intergrowths and thin, interrupted crusts up to 3 mm × 3 mm in area overgrowing basalt scoria (Figs 2 and 4). Crystals are well formed and complex. They belong to the symmetry class 3m and are shaped by the faces of rhombohedra {101} and {011}, hexagonal prisms {100} and {110} and the pinacoid {001} (Figs 5 and 6). Several subordinate, narrow, non-indexed faces were observed on some crystals.

#### Physical properties and optical data

Yurmarinite is transparent, pale green or pale yellowish green to colourless. The streak is white and the lustre vitreous. The mineral is non-fluorescent under ultraviolet irradiation or an electron beam. It is brittle and Mohs hardness is  $\sim$ 4½. One direction of imperfect cleavage, probably coplanar to one of rhombohedral faces, was observed under the microscope. Parting was not observed and the fracture is uneven. Density could not be measured because of the small grain size and the porous character of the material available (Figs 3 and 4). The calculated density is 4.001 g cm<sup>-3</sup> for the empirical formula.

Yurmarinite is optically uniaxial (-),  $\omega = 1.748(5)$ ,  $\varepsilon = 1.720(3)$  (589 nm). Under the microscope, the mineral is colourless and non-pleochroic.



FIG. 4. Crystal crusts of yurmarinite on volcanic scoria: (a) SEM secondary electron (SE) image; (b) polished section, SEM (BSE) image.

# Raman spectroscopy

The Raman spectrum of yurmarinite (Fig. 7) was obtained using an EnSpectr R532 Raman Analyser (Russia) with a green laser ( $\lambda = 532$  nm) at room temperature. The power of the laser beam at the sample surface was ~30 mW. The spectrum was processed using the EnSpectr expert mode program from 100 to 3800 cm<sup>-1</sup> with a holographic diffraction grating (1800 mm<sup>-1</sup>) and resolution ~4–6 cm<sup>-1</sup>. The diameter of the focal spot on the sample was ~10 µm. The backscattered Raman signal was collected with a 40× objective; signal acquisition time for a single scan was 1 s and the signal was averaged over five scans. The spectrum was obtained for a randomly oriented crystal.

Bands in the region  $700-950 \text{ cm}^{-1}$  correspond to As<sup>5+</sup>-O stretching vibrations of AsO<sub>4</sub><sup>3-</sup> groups. Bands with frequencies between 200 and 500 cm<sup>-1</sup> correspond to As<sup>5+</sup>–O bending vibrations and Fe<sup>3+</sup>–O stretching vibrations; a strong, narrow band at 409 cm<sup>-1</sup> is assigned to Fe<sup>3+</sup>–O (Sasaki *et al.*, 1998). Bands lower than 200 cm<sup>-1</sup> correspond to lattice modes. An absence of bands with frequencies >950 cm<sup>-1</sup> indicates the absence of groups with O–H, C–H, C–O, N–H, N–O and B–O bonds in yurmarinite.

### Chemical Composition

Chemical data were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength dispersive spectrometer (WDS) (Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University). The WDS mode was used, with an acceleration voltage of



FIG. 5. Yurmarinite crystals. SEM (SE) images.



FIG. 6. Idealized crystal forms of yurmarinite.

20 kV, a beam current of 20 nA and a 3  $\mu$ m beam diameter. The following standards were used: NaCl (Na), orthoclase (K), CaMoO<sub>4</sub> (Ca), diopside (Mg), Mn (Mn), CuFeS<sub>2</sub> (Cu), ZnS (Zn), Al<sub>2</sub>O<sub>3</sub> (Al), FeS (Fe), Ti (Ti), GaP (P), V (V) and FeAsS (As).

The average (five spot analyses) chemical composition of yurmarinite (wt.%, ranges in parentheses) is Na<sub>2</sub>O 16.85 (16.64–17.23), K<sub>2</sub>O 0.97 (0.79–1.11), CaO 1.28 (1.01–1.44), MgO 2.33 (1.95–2.72), MnO 0.05 (0.00–0.11), CuO 3.17 (2.85–3.59), ZnO 0.97 (0.87–1.07), Al<sub>2</sub>O<sub>3</sub> 0.99 (0.42–1.69), Fe<sub>2</sub>O<sub>3</sub> 16.44 (15.03–17.36),

TiO<sub>2</sub> 0.06 (0.00–0.17),  $P_2O_5$  0.12 (0.00–0.18), V<sub>2</sub>O<sub>5</sub> 0.08 (0.00–0.12), As<sub>2</sub>O<sub>5</sub> 56.68 (56.26–57.41), total 99.89. Contents of other elements with atomic numbers greater than that of C are below detection limits.

The empirical formula of yurmarinite, calculated on the basis of 24 O atoms per formula unit is:  $(Na_{6.55}Ca_{0.28}K_{0.22})_{\Sigma7.05}(Fe_{2.48}^{3+}Mg_{0.70}Cu_{0.48}$  $Al_{0.23}Zn_{0.14}Ti_{0.01}Mn_{0.01})_{\Sigma4.05}(As_{5.94}P_{0.02}V_{0.01})_{\Sigma5.97}$  $O_{24}$ . The simplified formula is  $Na_7(Fe^{3+},Mg,Cu)_4$  $(AsO_4)_6$ . The formula  $Na_7(Fe_3^{3+}Mg)(AsO_4)_6$ requires  $Na_2O$  18.29, MgO 3.40, Fe<sub>2</sub>O<sub>3</sub> 20.19,  $As_2O_5$  58.12, total 100.00 wt.%.

## X-ray crystallography and crystal structure

Single-crystal X-ray studies of yurmarinite were carried out using an Xcalibur S diffractometer equipped with a CCD detector. The mineral is rhombohedral, space group  $R_3^3c$ , a = 13.7444(2), c = 18.3077(3) Å, V = 2995.14(8) Å<sup>3</sup>, Z = 6.

X-ray powder diffraction data (Table 2) were collected using a STOE IPDS II diffractometer equipped with an image plate area detector (Gandolfi method; MoK $\alpha$ -radiation; detector-to-sample distance: 200 mm). Unit-cell parameters refined from the powder data are a = 13.751(2), c = 18.295(3) Å, V = 2996(1) Å<sup>3</sup>.

X-ray diffraction (XRD) measurements of yurmarinite were performed on a single crystal using an Xcalibur S CCD diffractometer. Crystal



FIG. 7. The Raman spectrum of yurmarinite.

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I <sub>obs</sub>	$d_{\rm obs}$	$I_{calc}*$	$d_{\rm calc}^{**}$	h k l
45	7.28	36	7.256	012
26	4.570	20	4.563	113
33	4.375	22	4.369	211
17	4.035	10	4.038	122
35	3.440	27	3.436	220
36	3.217	9, 25	3.249, 3.208	131, 214
7	3.109	3	3.106	312
30	2.999	23	2.994	223
100	2.841	100	2.840	125
29	2.696	18, 8	2.701, 2.677	321, 134
43	2.598	38	2.597	410
20	2.451	18	2.451	315
4	2.395	2	2.390	143
3	2.346	3	2.345	324
9	2.293	2, 5	2.304, 2.291	502, 330
4	2.236	3	2.233	241
3	2.182	2	2.189	235
3	2.151	1	2.147	333
3	2.119	1	2.112	054
4	2.086	2	2.082	152
3	2.045	1	2.050	137
19	1.984	16	1.984	600
17	1.938	11	1.937	514
14	1.809	5, 9, 1	1.814, 1.809, 1.806	048, 1.0.10, 161
6	1.748	6, 1	1.750, 1.750	229, 0.2.10
18	1.727	20	1.726	345
12	1.696	10, 2	1.696, 1.693	2.1.10, 351
11	1.653	3, 8	1.654, 1.650	443, 508
7	1.625	6	1.626	615
8	1.594	8	1.594	354
9	1.559	3, 8	1.562, 1.559	158, 4.0.10
5	1.522	2, 2	1.526, 1.521	173, 3.2.10
12	1.504	9, 4	1.505, 1.503	265, 452
11	1.451	9, 4	1.451, 1.450	0.5.10, 271
2	1.421	1	1.421	2.3.11
3	1.413	1	1.415	084
12	1.390	3, 9, 4, 2	1.391, 1.391, 1.389, 1.386	529, 5.1.10, 811, 274
12	1.376	1, 12	1.377, 1.374	182, 550
7	1.352	7	1.352	725
7	1.341	3	1.344	2.1.13
8	1.336	1, 3, 2, 5	1.338, 1.337, 1.336, 1.333	4.2.11, 4.3.10, 731, 814
3	1.314	2, 3	1.315, 1.313	4.1.12, 449

# TABLE 2. X-ray powder diffraction data for yurmarinite.

\* Only reflections with intensities  $\ge 1$  are given.

\*\* Calculated from the single-crystal structure model.

data, data-collection information and structurerefinement details are given in Table 3. Systematic absences and intensity statistics (mean  $|E^2 - 1| = 0.951$ ) indicated the centrosymmetric space group  $R\bar{3}c$ . The structure model was obtained by direct methods and refined with the *SHELX-97* software package (Sheldrick, 2008) on the basis of 1015 independent reflections with  $I > 2\sigma(I)$  to R = 0.0230. Atom coordinates and displacement parameters are given in Table 4 and selected interatomic distances in Table 5.

Formula weight* Temperature (K) Radiation and wavelength (Å) Crystal system, space group; Z Unit-cell dimensions (Å) V (Å <sup>3</sup> ) Absorption coefficient $\mu$ (mm <sup>-1</sup> )* $F_{000}$ * Crystal size (mm) Diffractometer $\theta$ range for data collection (°) Index ranges Reflections collected Independent reflections Independent reflections with $I > 2\sigma(I)$ Structure solution Refinement method Number of refined parameters Final <i>R</i> indices $[I > 2\sigma(I)]$	1173.92 293(2) MoK $\alpha$ ; 0.71073 Trigonal, $R\bar{3}c$ ; 6 a = 13.7444(2) c = 18.3077(3) 2995.14(8) 12.389 3304 0.09 × 0.12 × 0.18 Xcalibur S CCD 2.81-30.49 -19 $\leq h \leq 19, -19 \leq k \leq 19, -26 \leq l \leq 26$ 20,993 1024 ( $R_{int} = 0.0431$ ) 1015 Direct methods Full-matrix least-squares on $F^2$ 68 R1 = 0.0230, wR2 = 0.0447
Number of refined parameters	
Final R indices $[I > 2\sigma(I)]$ R indices (all data)	R1 = 0.0230, WR2 = 0.0447 R1 = 0.0236, WR2 = 0.0449
Gof	1.384
Largest diff. peak and hole, $e(\dot{A}^{-3})$	0.46  and  -0.43

TABLE 3. Crystal data, data-collection information and structure-refinement details for yurmarinite.

\* Calculated on the basis of e<sub>ref</sub> for Fe(1), Fe(2), Na(1) and Na(2) positions.

The crystal structure of yurmarinite (Fig. 8*a*) is based on a 3D heteropolyhedral framework formed by  $M_4O_{18}$  clusters ( $M = Fe^{3+} > Mg$ , Cu, Al, Zn) linked with AsO<sub>4</sub> tetrahedra. In each cluster, a regular Fe(1)O<sub>6</sub> octahedron shares three edges with three slightly distorted Fe(2)O<sub>6</sub> octahedra. Each AsO<sub>4</sub> tetrahedron shares two O vertices with one  $M_4O_{18}$  cluster (Fig. 8*b*) and one

O vertex with an adjacent cluster. In the Fe(1) site, admixed Mg and Al are significantly concentrated ( $e_{ref} = 17.21$ ; Table 4) while the Fe(2) site contains other admixed cations, Cu, Zn and residual Mg ( $e_{ref} = 21.35$ ; Table 4). Cationic site composition was assumed taking into account both the electron microprobe analysis and structural data.

TABLE 4. Final coordinates, equivalent displacement parameters  $(U_{eq}, \text{ in } \text{\AA}^2)$  and site multiplicities (Q) for yurmarinite.

Atom	x/a	y/b	z/c	$U_{ m eq}$	Q
As	0.18108(2)	-0.01128(2)	0.145958(14)	0.00890(8)	36
Fe(1)*	0.0	0.0	0.25	0.0080(4)	6
Fe(2)*	0.77801(4)	0.0	0.25	0.00892(19)	18
Na(1)*	0.0	0.0	0.0	0.0077(6)	6
Na(2)*	0.78711(12)	0.01548(12)	0.05276(7)	0.0263(4)	36
O(1)	0.52485(16)	0.06215(16)	0.15330(11)	0.0164(4)	36
O(2)	0.71532(16)	0.06116(16)	0.17686(11)	0.0158(4)	36
O(3)	0.59857(15)	0.19631(15)	0.02568(10)	0.0122(3)	36
O(4)	0.01471(19)	0.15464(18)	0.06052(10)	0.0206(4)	36

\* The e<sub>ref</sub> values are: Fe(1) 17.21, Fe(2) 21.35, Na(1) 13.05 and Na(2) 11.00.

As - O(4) = 1.656(2)	$Na(1) - O(4) 2.314(2) \times 6$
-O(2) 1.6801(19)	<na(1)–o> 2.314</na(1)–o>
-O(1) 1.6847(19)	
-O(3) 1.7142(18)	Na(2)-O(4) 2.306(2)
<as-o> 1.684</as-o>	-O(1) 2.561(2)
	-O(2) 2.576(2)
$Fe(1) - O(3) \ 1.9429(18) \ \times 6$	-O(4) 2.633(3)
<fe(1)-o> 1.943</fe(1)-o>	-O(2) 2.674(2)
	-O(4) 2.735(3)
Fe(2)-O(2) 1.991(2) × 2	-O(1) 2.905(2)
$-O(1) 2.0142(19) \times 2$	-O(1) 2.953(2)
$-O(3) 2.1170(19) \times 2$	$-O(3) \ 3.093(2)$
<fe(2)-o> 2.041</fe(2)-o>	<na(2)–o> 2.715</na(2)–o>

TABLE 5. Selected interatomic distances (Å) in the structure of yurmarinite.

Italics indicates elongated distances - see text.

Two crystallographically independent positions Na(1) and Na(2) are located in the voids of the heteropolyhedral framework. The Na(1)O<sub>6</sub> polyhedron is a symmetrical octahedron (Table 5); the Na(1) site contains minor Ca and K ( $e_{ref} = 13.05$ ; Table 4). The Na(2) cation is surrounded by six O atoms with distances in the range 2.306(2)-2.735(3) Å, forming a significantly distorted octahedron occupied by only Na ( $e_{ref} = 11.00$ ; Table 4). Moreover, three elongated Na(2)-O distances 2.905(2), 2.953(2) and 3.093(2) Å (given in italics in Table 5) could be added by analogy with synthetic Na<sub>7</sub>(Fe<sub>3</sub><sup>3+</sup>Fe<sup>2+</sup>)(AsO<sub>4</sub>)<sub>6</sub> (Masquelier *et al.*, 1995), which is structurally identical to yurmarinite.

#### Discussion

No minerals related to yurmarinite are known. The two natural anhydrous arsenates with speciesdefining Na and Fe, hatertite, Na<sub>2</sub>(Ca,Na)(Fe<sup>3+</sup>,Cu)<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (Krivovichev *et al.*, 2013) and maxwellite, NaFe<sup>3+</sup>(AsO<sub>4</sub>)F (Foord *et al.*, 1991), are quite different, not only chemically but also in terms of structure.

However, yurmarinite is a representative of a structure type well known for synthetic arsenates and phosphates that were synthesized and studied because of their ion-conductor properties. These compounds are trigonal, space group  $R\bar{3}c$ , with a = 13.35 - 13.8, c = 18.3 - 18.6 Å for arsenates and a = 13.4, c = 17.85 - 17.9 Å for phosphates. Their generalized formula is  $(Na, \Box)_7 M_4(T^{5+}O_4)_6$ , with T = As or P. The prevailing M cations are trivalent

(Fe<sup>3+</sup> or Al) in all cases; if the *M* sites are occupied completely by trivalent cations then Na sites are forced to be vacant by 1/7, i.e. the formula is  $(Na_6 \square_1)_{\Sigma 7} M_4^{3+} (T^{5+}O_4)_6$ , or  $Na_3 M_2^{3+} (T^{5+}O_4)_3$ . Examples are synthetic II-Na<sub>3</sub>Fe<sub>2</sub><sup>3+</sup>(AsO<sub>4</sub>)<sub>3</sub> (d'Yvoire et al., 1988), Na<sub>3</sub>(Al<sub>1.89</sub>Y<sub>0.11</sub>)(AsO<sub>4</sub>)<sub>3</sub> (Belam et al., 2000) and  $Na_3Fe_2^{3+}(PO_4)_3$ (Belokoneva et al., 2002). A topologically close structure characterized by monoclinic distortion (space group C2, a = 14.576, b = 13.409, c =9.728 Å,  $\beta = 96.95^{\circ}$ ) was reported for  $\alpha$ -Na<sub>3</sub>Al<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub>, while the high-temperature  $(>44^{\circ}C)$   $\beta$ -Na<sub>3</sub>Al<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> phase is rhombohedral and isotypic with II-Na<sub>3</sub>Fe<sub>2</sub><sup>3+</sup>(AsO<sub>4</sub>)<sub>3</sub> (Masquelier et al., 1995). All these compounds containing vacancies in Na sites are Na ion conductors. Full occupancy of the Na sites is possible only if trivalent cations in the M sites are partially substituted by bivalent cations. This substitution was found in  $Na_7(Fe_3^{3+}Fe^{2+})(AsO_4)_6$  (Masquelier et al., 1995) and Na<sub>7</sub>(Fe<sub>3</sub><sup>3+</sup>Fe<sup>2+</sup>)(PO<sub>4</sub>)<sub>6</sub> (Lii, 1996). Thus, the general formula of the above-mentioned synthetic compounds can be written as  $(Na_{7-x}\Box_x)(M_{3+x}^{3+}M_{1-x}^{2+})(T^{5+}O_4)_2$  with T = As or P,  $M^{3+}$  = Fe or Al (±Y),  $M^{2+}$  = Fe and  $0 \le x \le 1$ .

Yurmarinite can be considered as a natural analogue of the compound  $Na_7(Fe_3^{3+}Fe^{2+})(AsO_4)_6$  ( $R\bar{3}c$ , a = 13.794, c = 18.360 Å, V = 3025 Å<sup>3</sup>: Masquelier *et al.*, 1995) with (Mg,Cu) instead of Fe<sup>2+</sup>. Their X-ray powder diffraction patterns are almost identical.

Note that the above-mentioned synthetic compounds have polymorphous modifications with quite different structures. In particular, YURMARINITE, A NEW MINERAL



FIG. 8. (a) The crystal structure of yurmarinite with unit cell outlined; and (b) its main building unit, the  $M_4O_{18}$  octahedral cluster ( $M = Fe^{3+} > Mg$ , Cu) with connected AsO<sub>4</sub> tetrahedra.

 $\gamma$ -Na<sub>3</sub>Fe<sub>2</sub><sup>3+</sup>(PO<sub>4</sub>)<sub>3</sub>, space group  $R\bar{3}c$ , adopts the Nasicon structure (Masquelier *et al.*, 2000) and Na<sub>3</sub>Fe<sub>2</sub><sup>3+</sup>(AsO<sub>4</sub>)<sub>3</sub> with the garnet structure (*Ia3d*) is known to exist (Ouerfelli *et al.*, 2008). The existence of their natural analogues is not excluded.

The trivalent state of Fe in yurmarinite, like all known synthetic compounds with the same structure, is confirmed by the structure data including M–O [Fe(1)–O and Fe(2)O] distances (Table 5) and by charge balance. This is in good agreement with the strongly oxidizing conditions of mineral deposition in the Arsenatnaya fumarole.

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