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GAJARDOITE-(NH₄), (NH₄)As³⁺₄O₆Cl₂[(Ca_{0.5}□_{0.5})(H₂O)₅], A NEW MINERAL FROM THE KHOVU-AKSY DEPOSIT, EASTERN SIBERIA, RUSSIA

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Abstract. The new mineral gajardoite-(NH₄), ideally (NH₄)As³⁺₄O₆Cl₂[(Ca_{0.5}□_{0.5})(H₂O)₅], is found at the Khovu-Aksy Ni-Co deposit, Republic of Tyva, Russia. Gajardoite-(NH₄) occurs as tiny lamellar coarsely hexagonal or irregular curved and divergent crystals up to 0.01 mm in size. The crystals are combined in groups, rosette-like clusters or spherulitic aggregates up to 0.2 mm, which are intimately intergrown with annabergite, arsenolite, and pharmacolite on a matrix of skutterudite, safflorite, and other minerals. The new mineral is colorless, white in aggregates, transparent with a white streak and a vitreous lustre. It is brittle, with a perfect cleavage on {001}. The Mohs hardness is ~1½. The calculated density (*D*_{calc}) is 2.583 g/cm³. Gajardoite-(NH₄) is optically non-pleochroic, uniaxial (–), ω = 1.745(10), ε = 1.558(5) (589 nm). The chemical composition determined by electron microprobe (wt. %, H₂O content calculated by stoichiometry) is as follows: (NH₄)₂O 3.17, Na₂O 0.40, K₂O 1.07, CaO 5.28, As₂O₃ 67.25, Cl 12.21, H₂O 15.30, O=Cl–2.76, total 101.92. The empirical formula based on four As and 11 O atoms per formula unit is [(NH₄)_{0.72}K_{0.13}Na_{0.08}]_{Σ0.93}Ca_{0.55}As³⁺₄O₆Cl_{2.03}(H₂O)₅. Gajardoite-(NH₄) is hexagonal, space group *P6/mmm*; the unit-cell parameters are as follows: *a* = 5.263(3), *c* = 16.078(5) Å, *V* = 385.8(5) Å³, *Z* = 1. The strongest lines of the powder X-ray diffraction pattern [*d*, Å (*I*, %) (*hkl*)] include 16.08 (34) (001), 5.36 (34) (003), 4.565 (41) (100), 3.466 (23) (103), 2.637 (100) (110), 2.360 (25) (113). Gajardoite-(NH₄) is an ammonium analog of gajardoite KCa_{0.5}As³⁺₄O₆Cl₂ · 5H₂O. Their structural identity is confirmed by powder X-ray diffraction and infrared and Raman spectroscopy.

Keywords: gajardoite-(NH₄), new mineral, chemical composition, powder X-ray diffraction, IR spectrum, Raman spectrum, gajardoite, Khovu-Aksy deposit, Eastern Siberia.

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Conflict of interest. The authors declare that they have no conflicts of interest.

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INTRODUCTION

Several rare secondary As minerals, both arsenates and arsenites, were found as a result of study of an old mineral collection from the Khovu-Aksy Ni-Co deposit in the Republic of Tyva, Russia. Some of the minerals were found for the first time at the territory of Russian Federation, e.g., weilite and haidingerite (Kasatkin, 2021), as well as babánekite, cobaltkoritnigite, cuatrocapaite-(K), cuatrocapaite-(NH₄), and guérinite. One unknown phase contained a significant amount of N, Ca, As, Cl and O and its powder X-ray diffraction (PXRD) pattern was similar to gajardoite KCa_{0.5}As³⁺₄O₆Cl₂ · 5H₂O described from the Torrecillas Mine in Chile (Kampf et al., 2016). Further studies showed that this phase is an ammonium analog of gajardoite, thus, it was named gajardoite-(NH₄). It was submitted as a new mineral species and later approved along with its name and symbol (Gaj-NH₄) by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) (IMA2023–070, Kasatkin et al., 2024). The holotype specimen is deposited in a systematic collection of the Fersman Mineralogical Museum, Russian Academy of Sciences (Moscow, Russia) with catalog number 98430.

The Khovu-Aksy deposit is currently a type locality of five mineral species: argentopentlandite (Rudashevskiy et al., 1977), lazarenkoite (Yakhontova, Plusnina, 1981), shubnikovite (Nefedov, 1953), smolyaninovite (Yakhontova, 1956), and vladimirite (Nefedov, 1953; Yakhontova, Stolyarova, 1970). Gajardoite-(NH₄) is the sixth new mineral discovered at the deposit.

BRIEF CHARACTERISTIC OF THE DEPOSIT

The Khovu-Aksy Ni-Co deposit (51°9'35" N, 93°41'9" E) in the Chedi-Khol district of the Republic of Tyva was discovered in 1947 and has been mined for Co, Ni and Co till 1991, when a processing plant was closed because of unprofitability. The Khovu-Aksy deposit is well studied. The details of its geological structure and mineralogy are described by (Shishkin, Mikhailova, 1969; Bogomol, 1970; Krutov, 1978; Borishanskaya et al., 1981; Borisenko, Lebedev, 1982;

Lebedev, 1998, 2021; Lebedev, Borisenko, 1984; Gusev, 2019). The deposit includes the lower, middle and upper structural units. The ore field is mainly composed of rocks of the middle structural unit with Lower Devonian, Silurian and Cambrian volcanic and sedimentary rocks and widespread volcanic dikes (Fig. 1). The Lower Devonian volcanosedimentary series includes tuffs, tuffaceous conglomerates, tuffites, and sandstones intercalated with quartz and trachyte porphyry. Tuffs and tuffaceous conglomerates of the lower horizons are intensely altered with the formation of skarn mineralization. The Silurian rocks comprise limestones, sandstones and siltstones. The Lower Cambrian rocks include volcanic rocks and miarolitic granophyric granites. A significant part of the ore field is occupied by thick Tertiary and Quaternary rocks.

The ore bodies of the deposit are typically fractured carbonate veins, which are associated with a fault system and mainly consist of calcite, dolomite and ankerite with abundant Co, Ni, and Fe arsenides (skutterudite, safflorite, nickelskutterudite, nickeline, rammelsbergite, löllingite, etc.). The near-vein metasomatites contain quartz, chlorite, talc, kaolinite, muscovite, and carbonates. The oxidation zone is widely developed in the surface outcrops of ore veins. The fully oxidized and semi-oxidized ores contain 0–5 % and 25–30 % of primary ore minerals, respectively. The most common minerals of the oxidation zone include Co and Ni arsenates of the vivianite group: erythrite and annabergite (Bogomol, 1970; Krutov, 1978; Gusev, 2019).

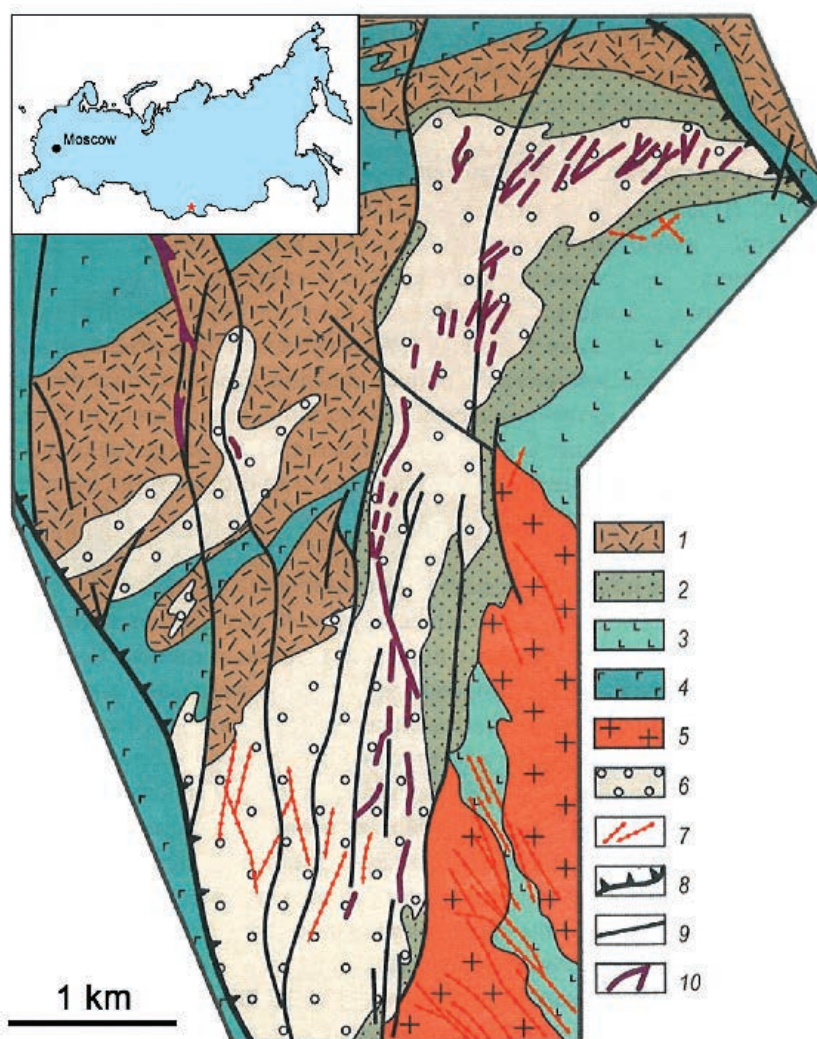
It was suggested that the NH₄⁺ cations for the formation of gajardoite-(NH₄) were sourced from organic matter of sedimentary rocks. This is supported by the analysis of water extracts from fluid inclusions in calcite that showed the presence of NH₄⁺ in ore-forming fluids (Lebedev et al., 2019).

MODE OF OCCURRENCE, PHYSICAL PROPERTIES AND OPTICAL DATA

Gajardoite-(NH₄) is supergene mineral and occurs in semi-oxidized ores. It forms crusts on various ore and gangue minerals. The primary ore minerals include major skutterudite and safflorite with subordinate chalcopyrite, löllingite, molybdenite, and tennantite-(Cu). The gangue minerals include major calcite and subordinate montmorillonite, muscovite,

Fig. 1. Geographic location (inset) and geological map of the Khovu-Aksy deposit, simplified after (Gusev, 2019).

1 – Lower Devonian sedimentary-volcanic rocks; 2 – Silurian and Cambrian sedimentary rocks; 3 – Lower Cambrian volcanic rocks; 4 – gabbrodiabases; 5 – Lower Cambrian miarolitic granophyric granites; 6 – calcareous skarns and metasomatites after skarns; 7 – mafic dikes; 8 – thrusts; 9 – major faults; 10 – ore bodies (carbonate-arsenide veins).



and quartz. Supergene minerals associated with gajardoite-(NH₄) include annabergite, arsenolite, erythrite, and pharmacolite.

Gajardoite-(NH₄) occurs as tiny lamellar coarse-hexagonal or irregular curved and divergent crystals up to 0.01 mm. The crystals are combined in groups, rosette-like clusters or spherulitic aggregates up to 0.2 mm across (Fig. 2). These aggregates form crusts lining the cavities in the matrix. Gajardoite-(NH₄) is intimately intergrown with annabergite, arsenolite, and pharmacolite (Fig. 3).

The new mineral is colorless, white in aggregates, transparent with a white streak and a vitreous lustre. It is brittle and has a laminated fracture and a perfect cleavage on {001}. No parting is observed. Gajardoite-(NH₄) does not fluoresce under an ultraviolet light. The Mohs hardness based on scratch tests is ~1½. The density of the mineral could not be measured because

of the tiny size of its individuals and their intimate intergrowths with other minerals. A density value calculated using the empirical formula and the unit-cell parameters refined from PXRD data is 2.583 g/cm³.

In transmitted plane-polarized light, gajardoite-(NH₄) is colorless non-pleochroic. Optically, it is uniaxial (–), ω = 1.745(10), ε = 1.558(5) (589 nm).

CHEMICAL DATA

The chemical composition of gajardoite-(NH₄) (five spots) was analyzed on a Cameca SX-100 electron microprobe (WDS mode, 15 kV accelerating voltage, 8 nA beam current, 8-μm beam size). The following standards and analytical lines were used: BN, NKα; Amelia albite, NaKα; orthoclase, KKα; fluorapatite, CaKα; lammerite, AsLα; PbCl₂, ClKα. Nitrogen was measured in an integration mode using a 2d = 60-Å



Fig. 2. White aggregates mainly composed of gajardoite-(NH₄) on the skutterudite-safflorite matrix.

Holotype sample. Field of view of 2 × 2 mm. Photo by Maria D. Milshina.

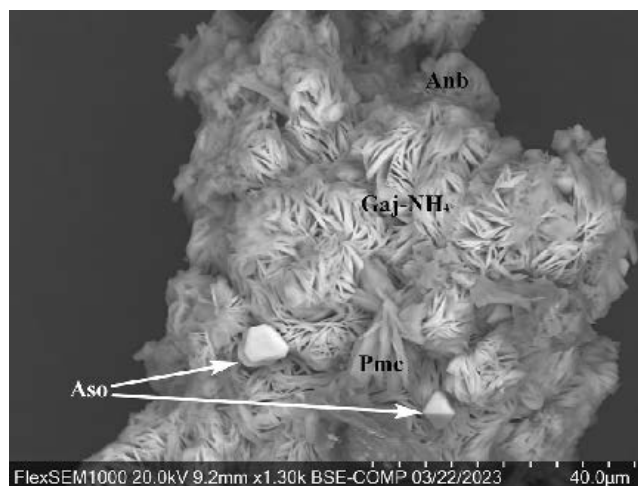


Fig. 3. Multiple rosettes of gajardoite-(NH₄) (Gaj-NH₄) intimately intergrown with pharmacolite (Pmc), annabergite (Anb), and arsenolite (Aso) crystals. BSE image.

monochromator. The amount of H₂O was not determined directly due to the scarcity of pure material and was calculated by stoichiometry on the basis of As = 4 and O = 11 atoms per formula unit (*apfu*) by analogy with gajardoite (Kampf et al., 2016). The infrared (IR) and Raman spectra confirm the presence of NH₄-groups and H₂O and the absence of B–O and C–O bonds in the new mineral (see below). The electron microprobe analytical data are given in Table 1. The content of other elements with atomic numbers higher than that of carbon are below detection limits.

The empirical formula of gajardoite-(NH₄) calculated on the basis of 4 As and 11 O *apfu* is [(NH₄)_{0.72}K_{0.13}Na_{0.08}]_{Σ0.93}Ca_{0.55}As³⁺₄O₆Cl_{2.03}(H₂O)₅. The ideal formula (NH₄)As³⁺₄O₆Cl₂[(Ca_{0.5}□_{0.5})(H₂O)₅] requires (wt. %) (NH₄)₂O 4.38, CaO 4.71, As₂O₃ 66.53, Cl 11.92, H₂O 15.15, O=Cl –2.69, total 100 wt. %. This type of writing of the ideal formula was suggested by voting members of the CNMNC of the IMA and accepted as the final one.

The Gladstone-Dale compatibility index (1 – *K_p*/*K_c*) calculated for gajardoite-(NH₄) using its empirical formula and the unit-cell parameters determined from the powder XRD data is 0.011 rated as superior (Mandarino, 1981). Gajardoite-(NH₄) very slowly dissolves in water and diluted HCl and HNO₃ at room temperature.

INFRARED SPECTROSCOPY

No published IR absorption spectra of gajardoite are available in literature for the comparison with that of gajardoite-(NH₄), therefore, we collected the IR spectra of both minerals (Fig. 4). A sample of gajardoite from the Torrecillas Mine (Chile) was obtained from Maurizio Dini, one of the authors of gajardoite, as a part of the original material used for the description of the species. Its identity as gajardoite was additionally confirmed by PXRD (a Rigaku R-AXIS Rapid II single-crystal diffractometer) and SEM-EDS (a Hitachi FlexSEM 1000 SEM equipped with an Xplore Contact 30 EDS detector) methods. Its empirical formula is [K_{0.78}(NH₄)_{0.22}]Ca_{0.51}As_{4.00}Cl_{1.99}O_{6.01}(H₂O)₅.

The IR spectra of both minerals were acquired from powdered samples mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) in the range of 360–3800 cm⁻¹, at a resolution of 4 cm⁻¹. A total of 16 scans was collected for each sample. The IR spectrum of an analogous pellet of pure KBr was used as a reference. The comparison of spectra shows many similarities between gajardoite and gajardoite-(NH₄), as well as between spectra of the related minerals cuatrocapaite-(K) K₃(NaMg□)(As₂O₃)₆Cl₆ · 16H₂O and cuatrocapaite-(NH₄) (NH₄)₃(NaMg□)(As₂O₃)₆Cl₆ · 16H₂O (Kampf et al., 2019). In particular, the bands in the range of 1600–1650 cm⁻¹ correspond to locally nonequivalent H₂O molecules and a strong band at 595 cm⁻¹ is due

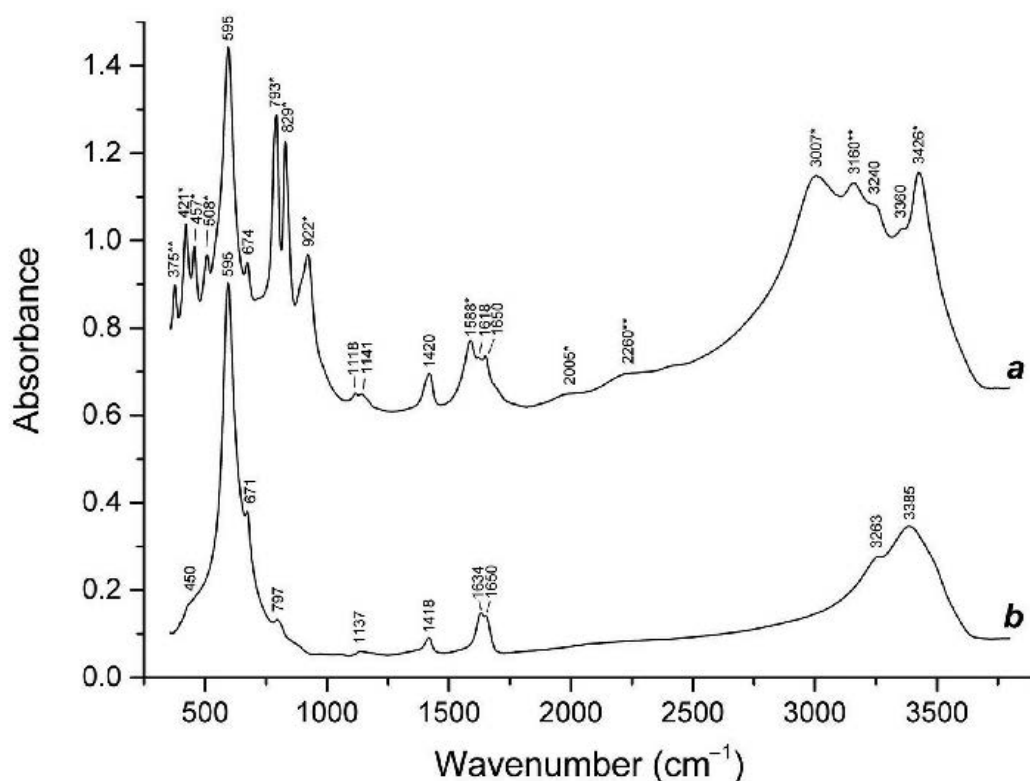


Fig. 4. IR spectra of (a) gajardoite-(NH₄) with admixture of annabergite (*) and pharmacolite (**) and (b) gajardoite from the type locality (Torrecillas Mine, Chile).

Table 1

Chemical composition (wt. %) of gajardoite-(NH₄)

Analysis no.	(NH ₄) ₂ O	Na ₂ O	K ₂ O	CaO	As ₂ O ₃	Cl	H ₂ O*	O=Cl	Total	Empirical formula
1	3.10	0.40	1.10	5.23	67.17	12.25	15.28	-2.77	101.76	[(NH ₄) _{0.70} K _{0.14} Na _{0.08}] _{0.92} Ca _{0.55} As ³⁺ ₄ O ₆ Cl _{2.04} (H ₂ O) ₅
2	3.15	0.37	1.07	5.35	67.35	12.36	15.32	-2.79	102.18	[(NH ₄) _{0.71} K _{0.13} Na _{0.07}] _{0.91} Ca _{0.56} As ³⁺ ₄ O ₆ Cl _{2.05} (H ₂ O) ₅
3	3.22	0.41	1.09	5.18	67.23	12.30	15.32	-2.78	101.97	[(NH ₄) _{0.73} K _{0.14} Na _{0.08}] _{0.95} Ca _{0.54} As ³⁺ ₄ O ₆ Cl _{2.04} (H ₂ O) ₅
4	3.24	0.38	1.05	5.43	67.25	12.05	15.31	-2.72	101.99	[(NH ₄) _{0.73} K _{0.13} Na _{0.07}] _{0.93} Ca _{0.57} As ³⁺ ₄ O ₆ Cl _{2.00} (H ₂ O) ₅
5	3.16	0.42	1.03	5.19	67.23	12.11	15.32	-2.74	101.72	[(NH ₄) _{0.71} K _{0.13} Na _{0.08}] _{0.92} Ca _{0.54} As ³⁺ ₄ O ₆ Cl _{2.01} (H ₂ O) ₅
Mean	3.17	0.40	1.07	5.28	67.25	12.21	15.30	-2.76	101.92	[(NH ₄) _{0.72} K _{0.13} Na _{0.08}] _{0.92} Ca _{0.55} As ³⁺ ₄ O ₆ Cl _{2.03} (H ₂ O) ₅
Standard deviation	0.06	0.02	0.03	0.11	0.07	0.13				

Note. * – By stoichiometry.

to As³⁺–O stretching vibrations. A band at 1418–1420 cm⁻¹ corresponds to bending vibrations of (NH₄)⁺ cation groups. This band is weak in the IR spectra of gajardoite and cuatrocapaite-(K) and is significantly stronger in the IR spectra of gajardoite-(NH₄) and cuatrocapaite-(NH₄). No splitting of the band of bending vibrations of (NH₄)⁺ in the IR spectra of these minerals is observed in contrast to, e.g., ammoniojarosite

(Basciano, Peterson, 2007) and tschermigite (Zhitova et al., 2019), where ammonium cation occurs in different local environments due to structure disordering (different orientations of (NH₄)⁺ and disordering of (SO₄)₂⁻, respectively). The IR bands of gajardoite-(NH₄) in the O–H stretching region (3200–3400 cm⁻¹) are overlapped with bands of H₂O molecules of the associated annabergite and pharmacolite.

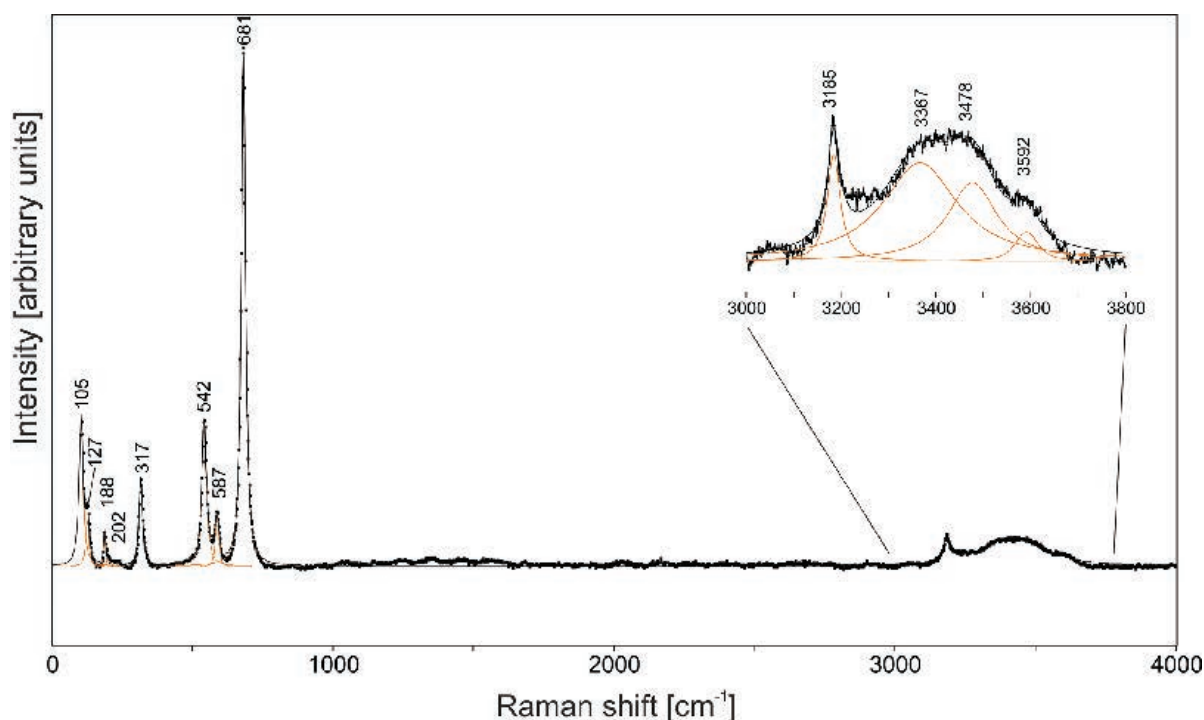


Fig. 5. Raman spectrum of gajardoite-(NH₄) in the 100–4000 cm⁻¹ region and inset (upper right corner) in the 3000–3800 cm⁻¹ region with better resolution.

The measured spectrum is shown by dots. The curve matching the dots is a result of spectral fitting as a sum of individual Voigt peaks shown below the curve.

RAMAN SPECTROSCOPY

A Raman spectrum of gajardoite-(NH₄) (Fig. 5) was registered on a Horiba Labram HR Evolution spectrometer. This dispersive edge-filter-based system is equipped with an Olympus BX 41 optical microscope, a diffraction grating with 600 groove/mm, and a Peltier-cooled Si-based charge-coupled device (CCD) detector. The Raman signal was excited by a 532-nm laser. A nominal laser beam energy of 50 mW was attenuated to 5 % using a neutral density filter to avoid the thermal damage of the analytical area. The Raman signal was collected in a range of 100–4000 cm⁻¹ with a 100' objective. The system was operated in a confocal mode, at a beam diameter of ~2.6 mm, an axial resolution of ~5 mm, a time acquisition of 120 s per spectral frame, and 10 accumulations. The wavenumbers were calibrated using the Rayleigh line and low-pressure Ne-lamp emissions. A wavenumber accuracy was ~0.5 cm⁻¹ and a spectral resolution was ~2 cm⁻¹. Band fitting was applied after appropriate background correction assuming combined Lorentzian-Gaussian band shapes using a Voigt function (*PeakFit*; Jandel Scientific Software).

The group of peaks of gajardoite-(NH₄) in the range of 540–700 cm⁻¹ corresponds to different As³⁺-O stretching modes (Bahfenne, 2011). Similar bands are observed in a Raman spectrum of gajardoite (Kampf et al., 2020). The specific features of the Raman spectrum of gajardoite-(NH₄) in contrast to gajardoite are the bands at 3185, 317 and 105 cm⁻¹. Taking into account that no similar bands are observed in the Raman spectrum of gajardoite or they are very weak, they can tentatively be assigned to stretching, librational and translational modes of NH₄⁺ cations, respectively. The overlapping Raman bands of gajardoite-(NH₄) in the range 3300–3600 cm⁻¹ correspond to stretching vibrations of locally non-equivalent H₂O molecules forming hydrogen bonds of different strengths.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

Because the gajardoite-(NH₄) crystals are too thin and typically divergent and occur as intimate intergrowths with annabergite, arsenolite, and pharmacolite, it was impossible to perform single crystal XRD study. The PXRD data were thus collected using a Rigaku R-Axis Rapid II single-crystal

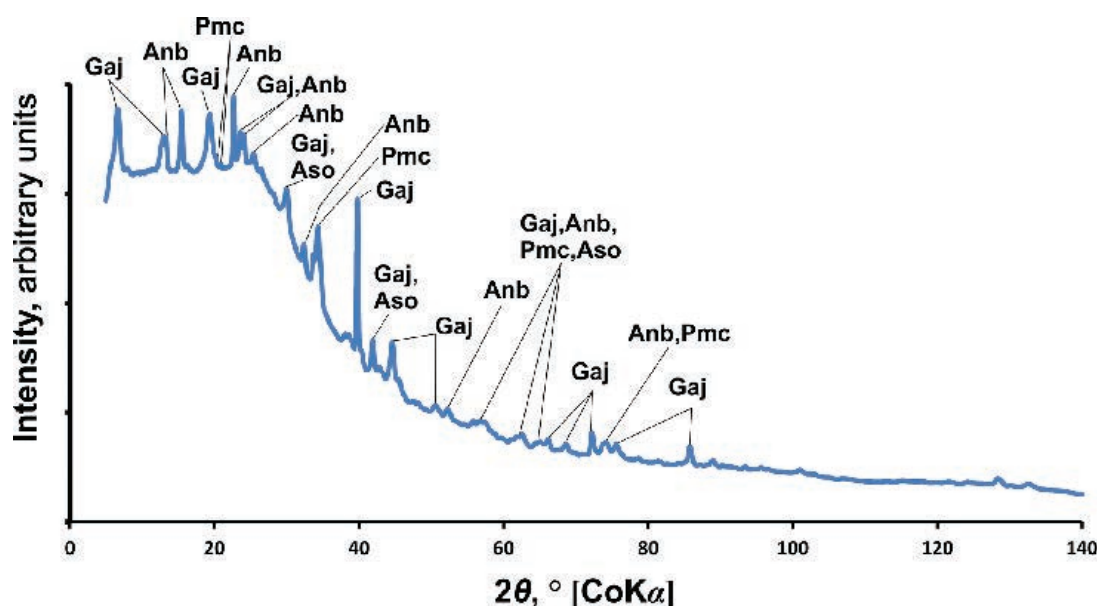


Fig. 6. Powder X-ray diffraction pattern of the gajardoite-(NH₄)-bearing sample.

Gaj – gajardoite-(NH₄); Anb – annabergite; Aso – arsenolite; Pmc – pharmacolite. The phase distribution is given only for the intense peaks for clarity.

diffractometer equipped with a cylindrical image plate detector (a radius of 127.4 mm) using Debye-Scherrer geometry, CoK α radiation (a rotating anode with VariMAX microfoc optics), an acceleration voltage of 40 kV, a current intensity of 15 mA, and an exposure time of 10 min (Fig. 6). The angular resolution of the detector was 0.045 2θ (a pixel size of 0.1 mm). The data were integrated using the Osc2Tab software package (Britvin et al., 2017). The PXRD data of gajardoite-(NH₄) are in good agreement with those published for gajardoite (Kampf et al., 2016). Both are given in Table 2.

The unit-cell parameters of gajardoite-(NH₄) were calculated from the observed d spacing data using UnitCell software (Holland, Redfern, 1997). The new mineral is hexagonal, space group $P6/mmm$, $a = 5.263(3)$, $c = 16.078(5)$ Å, $V = 385.8(5)$ Å³, and $Z = 1$. These parameters are in good agreement with those given for gajardoite: $a = 5.2558(8)$ Å, $c = 15.9666(18)$ Å, $V = 381.96(13)$ Å³ (Kampf et al., 2016).

We suggest that gajardoite-(NH₄) is isotypical with gajardoite, $\text{KCa}_{0.5}\text{As}^{3+}_4\text{O}_6\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ (Kampf et al., 2016), with NH₄⁺ cations substituting K⁺ cations. The crystal structure of gajardoite contains seven non-equivalent atomic sites. Among them, the fully occupied sites of As, Cl and O atoms belong to As-centered trigonal pyramids, whereas another site of O atom belongs to H₂O molecule from a coordination sphere of Ca cations. The other three sites are partially

occupied by K and Ca cations and O atom of the isolated H₂O molecule. The presence of two locally non-equivalent sites occupied by H₂O molecules is confirmed by results of IR and Raman spectroscopic studies.

The crystal structure of gajardoite is based on two types of layers (Figure 7). The first type contains two electroneutral As₂O₃ layers, between which the K cations are arranged. The As₂O₃ layers are formed by vertex-shared AsO₃ pyramids through common O atoms. All O atoms of the layers are oriented toward each other and participate in the formation of K–O bonds to build hexagonal prisms as coordination polyhedra for K/NH₄⁺ atoms. The As atoms are arranged in the apical vertices of AsO₃ pyramids forming an outer surface of As–O–K–O–As layers, which are in addition decorated by Cl anions. The ideal formula for this layer is thus [KAs³⁺₄O₆Cl₂][−]. The second type of the layers includes a sheet formed by edge-sharing Ca(H₂O)₆ trigonal prisms in a kagome-like manner with isolated H₂O molecules arranged in the centers of hexagonal cavities within the sheet. The (NH₄)–K substitution is followed by an increase in the unit-cell parameters and the volume of gajardoite-(NH₄) comparing to gajardoite due to a higher ionic radius of N compared to that of K (Gagné, Hawthorne, 2015; García-Rodríguez et al., 2000): 5.263(3) vs. 5.2558(8) Å, 16.078(5) vs. 15.9666(18) Å, and 385.8(5) vs. 381.96(13) Å³ for gajardoite-(NH₄) and gajardoite (Kampf et al., 2016), respectively. Note

Table 2

Powder X-ray diffraction data of gajardoite-(NH₄) and gajardoite (Kampf et al., 2016)

Gajardoite-(NH ₄)				Gajardoite (Kampf et al., 2016)			
<i>d</i> _{obs} , Å	<i>I</i> _{obs} , %	<i>d</i> _{calc} , Å	<i>hkl</i>	<i>d</i> _{obs} , Å	<i>I</i> _{obs} , %	<i>d</i> _{calc} , Å	<i>I</i> _{calc} , %
16.08	34	16.078	0 0 1	16.00	100	15.9666	100
8.04	17	8.039	0 0 2	7.94	8	7.9833	7
5.36	34	5.3593	0 0 3	5.31	48	5.3222	29
4.565	41	4.5585	1 0 0	4.550	11	4.5517	5
4.386	19	4.3857	1 0 1	4.393	8	4.3773	5
4.025	8	4.0195	0 0 4	3.978	7	3.9917	4
			1 0 2			3.9541	1
3.466	23	3.4723	1 0 3	3.466	31	3.4592	21
3.020	42	3.0149	1 0 4	3.013	44	3.0011	23
			0 0 6			2.6611	2
2.637	100	2.6319	1 1 0	2.624	51	2.6279	22
2.598	9	2.5973	1 1 1			2.5930	5
2.498	7	2.5012	1 1 2	2.498	11	2.4961	5
2.360	25	2.3624	1 1 3	2.353	36	2.3563	19
2.298	2	2.3101	1 0 6			2.2973	4
			0 0 7	2.288	3	2.2809	1
			2 0 0			2.2758	1
2.191	2	2.1928	2 0 2			2.1886	1
2.096	5	2.0975	2 0 3	2.0929	6	2.0925	4
2.042	6	2.0367	1 1 5	2.0231	4	2.0291	2
			2 0 4			1.9771	1
1.868	5	1.8777	1 1 6	1.8647	21	1.8698	11
			2 0 5			1.8533	1
			1 0 8			1.8278	2
1.776	2	1.7865	0 0 9	1.7893	3	1.7741	1
1.727	5	1.7362	2 0 6			1.7296	5
			1 1 7	1.7267	14	1.7226	3
			2 1 0			1.7204	1
			2 1 1			1.7105	1
1.654	6	1.6633	1 0 9			1.6530	2
			2 1 3	1.6391	9	1.6370	5
1.587	5	1.5836	2 1 4	1.5820	6	1.5799	5
1.521	15	1.5195	3 0 0			1.5172	4
			3 0 1	1.5132	13	1.5104	1
			2 0 8			1.5005	2
1.496	9	1.4931	3 0 2			1.4905	1
			1 1 9			1.4704	5
1.459	7	1.4619	3 0 3	1.4605	17	1.4591	4
			2 1 6			1.4447	2
			2 0 9			1.3992	2
1.372	2	1.3738	3 0 5			1.3704	1
			1 1 10			1.3645	2
1.332	1	1.3398	0 0 12			1.3306	1
1.316	12	1.3218	3 0 6	1.3133	15	1.3180	3
			2 2 0			1.3140	4
			2 2 1			1.3095	1
			2 0 10			1.3071	1

Note. The strongest reflections are typed in bold.

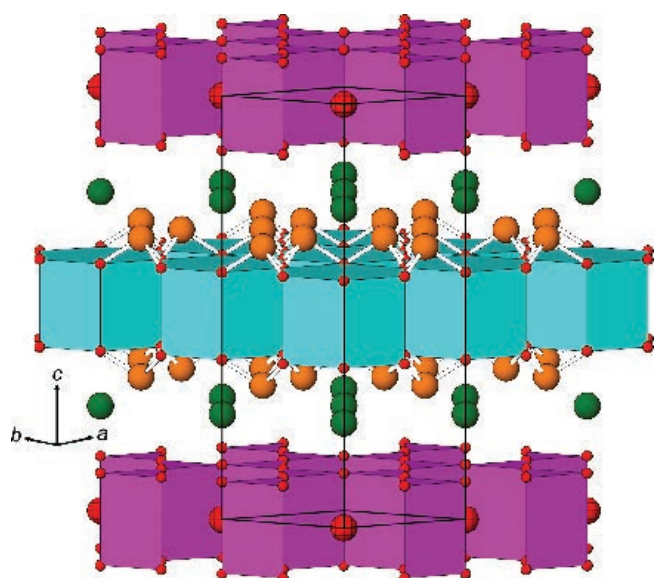


Fig. 7. Crystal structure of gajardoite/gajardoite-(NH₄).

Lilac – Ca polyhedra; cyan – K/(NH₄) polyhedra; orange – As atoms; red – O atoms; green – Cl atoms; red hatched sphere – isolated H₂O molecule.

that the (NH₄)⁺ ions with their tetrahedral geometry can ideally be fitted within a hexagonal prism (Fig. 7) to form a required H-bonding system.

DISCUSSION AND CONCLUSIONS

Gajardoite-(NH₄) is a NH₄-analogue of gajardoite (Kampf et al., 2016). Both minerals possess similar physical and optical properties, unit-cell parameters, PXRD patterns, and IR and Raman spectra. Their detailed comparison is provided in Table 3. Their structures are related to those of cuatrocapaite-(NH₄), cuatrocapaite-(K) (Kampf et al., 2019), and lucabindiite (K,NH₄)As₄O₆(Cl,Br) (Garavelli et al., 2013). All these structures contain neutral As₂O₃ (arsenite) layers, between which the layers containing various combinations of cations, anions, and H₂O molecules are arranged. The arsenite layers in all these minerals are planar and have hexagonal symmetry.

Table 3

Comparative data for gajardoite-(NH₄) and gajardoite

Mineral	Gajardoite-(NH ₄)	Gajardoite
Ideal formula	(NH ₄)As ³⁺ ₄ O ₆ Cl ₂ [(Ca _{0.5} □ _{0.5})(H ₂ O) ₅]	KCa _{0.5} As ³⁺ ₄ O ₆ Cl ₂ · 5H ₂ O
Crystal system	Hexagonal	Hexagonal
Space group	<i>P6/mmm</i>	<i>P6/mmm</i>
<i>a</i> , Å	5.263(3)	5.2558(8)
<i>c</i> , Å	16.078(5)	15.9666(18)
<i>V</i> , Å ³	385.8(5)	381.96(13)
<i>Z</i>	1	1
Colour	Colorless; white in aggregates	Colorless
Streak	White	White
Lustre	Vitreous, transparent	Vitreous, transparent
Tenacity	Brittle	Brittle
Fracture	Laminated	Irregular
Density, g cm ⁻³		
Measured	–	2.64(2)
Calculated	2.583	2.676
Hardness	~1½	~1½
Optical sign	Uniaxial (–)	Uniaxial (–)
ω	1.745(10)	1.780(3)
ε	1.558(5)	1.570(5)
Pleochroism	Nonpleochroic	Nonpleochroic
Main bands in Raman spectra	3592w, 3478, 3367, 3185 , 681s, 587, 542s, 317s , 202w, 188, 127, 105s	3370, 3185w , 680s, 545s, 313w , 187, 125
Source	This paper	Kampf et al., 2016, 2020

Note. Main bands in Raman spectra: s – strong band, w – weak band; the characteristic bands of NH₄⁺ are typed in bold.

The main difference between gajardoite-(NH₄) and gajardoite lies in their chemistry: first is NH₄-dominant while second is K-dominant. It is interesting that the empirical formula of gajardoite was reported as (K_{0.77}Ca_{0.71}Na_{0.05}Mg_{0.05})_{Σ1.58}As₄O₁₁Cl_{1.96}H_{9.62} (Kampf et al., 2016), whereas our analyses of the original material from Chile showed the presence of some (NH₄)₂O content and a lower Ca content resulting in the formula [K_{0.78}(NH₄)_{0.22}]Ca_{0.51}As_{4.00}Cl_{1.99}O_{6.01}(H₂O)₅. We suggest that the low NH₄ content could probably be missed in the original description (Kampf et al., 2016), which was recently admitted (Kampf et al., 2020). The Raman spectrum of gajardoite indicates the presence of a low amount of NH₄, which is most likely partly, replaced K in the structure of the mineral (Kampf et al., 2020). We also believe that a real Ca content of the type material should be close to that detected by us and the ideal formula of gajardoite. Our assumption is confirmed by a significantly better Gladstone-Dale compatibility index calculated using our empirical formula and, at the same time, the unit-cell parameters and refractive indices from (Kampf et al., 2016): -0.029 (excellent) vs. -0.044 (good), respectively. In the absence of the single-crystal XRD data, the influence of Ca atoms on stability of the crystal structure of gajardoite is speculative. It is likely that the increase in the (NH₄)₂O content decreases the crystal quality of gajardoite-(NH₄), as well the amount of alkalies, if we consider a close Ca content of gajardoite and gajardoite-(NH₄). It is evident from the analysis of crystallographic sites occupied by Ca (2c) and Cl (2e), however, that the distance between the latter ions within the layer is significantly larger than between the Ca atoms (5.26 vs. 3.04 Å), which indirectly indicates that the incomplete occupancy of Ca sites allows the strong connection of As–O–K–O–As and Ca–H₂O layers.

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