Gasparite-(La), La(AsO₄), a new mineral from Mn ores of the Ushkatyn-III deposit, Central Kazakhstan, and metamorphic rocks of the Wanni glacier, Switzerland

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ABSTRACT

Gasparite-(La), La(AsO₄), is a new mineral (IMA 2018-079) from Mn ores of the Ushkatyn-III deposit, Central Kazakhstan (type locality) and from alpine fissures in metamorphic rocks of the Wanni glacier, Binn Valley, Switzerland (co-type locality). Gasparite-(La) is named for its dominant lanthanide, according to current nomenclature of rare-earth minerals. The occurrences and parageneses in both localities are distinct: minute isometric grains up to 15 µm in size, associated with friedelite, jacobsite, pennantite, manganhumite series minerals (alleghanyite, sonolite), sarkinite, tilasite, and retzian-(La) are typically embedded into calcite-rhodochrosite veinlets (Ushkatyn-III deposit) vs. elongated crystals up to 2 mm in size in classical alpine fissures in two-mica gneiss without indicative associated minerals (Wanni glacier). Their chemical compositions have been studied by EDX and WDX; crystal-chemical formulas of gasparite-(La) from the Ushkatyn-III deposit (holotype specimen) and Wanni glacier (co-type specimen) are $(La_{0.65}Ce_{0.17}Nd_{0.07}Ca_{0.06}Mn_{0.05}Pr_{0.02})_{1.02}[(As_{0.70}V_{0.28}P_{0.02})_{1.00}O_4]$ and $(La_{0.59}Ce_{0.37}Nd_{0.02}Ca_{0.02}Th_{0.01})_{1.01}[(As_{0.81}P_{0.16}Si_{0.02}S_{0.02})_{1.01}O_4]$, respectively. In polished sections, crystals are yellow and translucent with bright submetallic luster. Selected reflectance values R_1/R_2 (λ , nm) for the holotype specimen in air are: 11.19/9.05 (400), 11.45/9.44 (500), 10.85/8.81 (600), 11.23/9.08 (700). The structural characteristics of gasparite-(La) were studied by means of EBSD (holotype specimen), XRD, and SREF (co-type specimen). Gasparite-(La) has a monoclinic structure with the space group $P2_1/n$. Our studies revealed that gasparite-(La) from the Ushkatyn-III deposit and Wanni glacier have different origins. La/Ce and As/P/V ratios in gasparite-(La) may be used as an indicator of formation conditions.

Keywords: Gasparite-(La), new mineral, arsenate, REE, Mn ores, monazite-type structure, Ushkatyn-III, Kazakhstan, Wanni glacier, Binn Valley, Switzerland

INTRODUCTION

In the course of this study, we described a new rare-earth element (REE) arsenate mineral gasparite-(La) [La(AsO₄), IMA 2018-079] from the Ushkatyn-III deposit, Central Kazakhstan, and the Wanni glacier, Binn Valley, Switzerland. Gasparite-(La) is named for the dominant lanthanide according to current nomenclature of REE minerals (Bayliss and Levinson 1988).

The type locality of gasparite-(La) is the Ushkatyn-III deposit, Central Kazakhstan. Minute isometric grains of gasparite-(La) up to 15 μ m in size were discovered in samples from the Ushkatyn-III deposit collected during field work in 2017. The holotype specimen of gasparite-(La) was deposited at the Mineralogical Museum of St. Petersburg State University, St.

Petersburg, Russia, catalog number 19692.

The co-type locality of gasparite-(La) is the Wanni glacier, Binn Valley, Valais, Switzerland. Elongated crystals of gasparite-(La) up to 2 mm in size were discovered in autumn 2005 and visually classified as "monazite." Because of their unusual appearance, the material was subjected to further analyses, and recognized as likely identical to the gasparite-(La) later discovered in the Ushkatyn-III deposit. The co-type specimen from Wanni glacier is preserved in Musée Cantonal de Géologie in Lausanne under catalog number MGL 093518.

The use of crystals from different localities allowed us to describe the whole range of physical and chemical properties of gasparite-(La), investigate its crystal chemistry and identify some features characteristic of different genetic types of deposits.

REE-arsenates are among rare minerals: CNMNC IMA has approved only 14 mineral species to date. Most of them

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are representative of Ce-dominant species, and only three Ladominant minerals have been discovered (Modresky 1983; Dunn et al. 1984; Mills et al. 2010).

Despite the limited number of approved mineral species, REE-arsenates are widely distributed in distinct mineral assemblages at numerous localities. Mineralogical information about arsenates (both discovered and crystal-chemically characterized) provides a key to understanding the occurrence and subsequent evolution of many localities (e.g., Campbell and Nordstrom 2014; Majzlan et al. 2014; Wu et al. 2018; Yang et al. 2018).

REE-arsenates have been reported from several postmagmatic and metasedimentary rocks, whose mineral compositions were strongly influenced by late hydrothermal fluids (metasomatic replacement). In the Slovak rhyolites (Ondrejka et al. 2007), primary monazite-(Ce) and xenotime-(Y) were transformed into secondary gasparite-(Ce) and chernovite-(Y), respectively. In case of the granite cupola at Zinnwald (Germany) or Cínovec (Czech Republic), As-rich hydrothermal fluids dissolved and severely altered primary magmatic REE-Y-Th-U-Zr mineralization and gave rise to the formation of REEarsenates: arsenoflorencite-(Ce), chernovite-(Y), and hydrous xenotime-(Y)-chernovite-(Y) solid solutions (Förster et al. 2011). In the Hora Svaté Kateøiny granite (Czech Republic), reaction with oxidizing As-bearing fluids caused the decomposition of xenotime-(Y), and led to the precipitation of chernovite-(Y) and the incorporation of As into altered zircon and thorite (Breiter et al. 2009). Migrating As-bearing solutions are also believed to have formed the remarkable, classical assemblage of numerous arsenates and arsenites in the Wanni glacier/Mt. Cervandone area at the frontier between the Binn Valley (Switzerland) and Alpe Devero (Italy) (Graeser and Roggiani 1976; Hofmann and Knill 1996; Guastoni et al. 2006). Besides indirect evidence of the presence of multiple REE-arsenates in close association, several minerals show direct evidence of originating from such fluids: gasparite-(Ce) was found as a reaction rim around synchysite-(Ce) (Graeser and Schwander 1987), deveroite-(Ce) was found as a dissolution product of cervandonite-(Ce) (Guastoni et al. 2013), agardite-(Y) (Gatta et al. 2018), and rhabdophane-(Ce) on synchysite-(Ce) (Cuchet et al. 2019), and uranyl arsenates on cafarsite (Appiani et al. 2017).

Manganese rocks of different geneses are often enriched in arsenic, reaching concentrations several times higher than the mean values for both sedimentary rocks and for the upper part of the continental crust as a whole (Li and Schoonmaker 2003; Maynard 2003). More than half of all discovered Mn-arsenates were found in the famous Mn deposits in Franklin/Sterling Hill, U.S.A.; Långban, Sweden, and Moss Mine, Sweden.

Both Långban, Sweden, and Franklin/Sterling Hill, New Jersey, are represented by strongly metamorphosed Precambrian rocks of sedimentary origin (Frondel and Baum 1974; Holtstam and Langhof 1999; Lundström 1999). According to Frondel and Baum (1974), the only primary As-bearing ore minerals in Franklin/Sterling Hill are löllingite, arsenopyrite, and the calcium arsenate svabite. In both cases (Långban and Franklin/Sterling Hill), the greatest mineralogical diversity is found among the minerals in veins and fissures.

A limited number of small Fe–Mn–(Ba,V,As,Sb,Be,W,REE) deposits, containing arsenates including REE-arsenates, have

been found in the Swiss, Italian, and Austrian Alps (Abrecht 1990; Brugger and Giere 1999; Cabella et al. 1999; Brugger and Meisser 2006). These occurrences are thought to represent syngenetic exhalative Fe-Mn accumulations (Majzlan et al. 2014) metamorphosed during the Alpine orogeny (Abrecht 1990; Brugger and Meisser 2006). Brugger and Meisser (2006) argued that the chemical composition of the rocks reflects the pre-metamorphic state. Cabella et al. (1999) reported that the abundance of arsenates reduces sharply as a function of proximity to the Fe-Mn ores. The same genetic conclusion was made for Mn-rich metamorphic rocks in the Hoskins manganese mine, New South Wales, Australia (Ashley 1989).

Gasparite-(Ce) is, although generally rare, the most widely distributed REE-arsenate. The type locality for gasparite-(Ce), and several other REE-arsenates and arsenites, is Mt. Cervandone, a summit on the frontier of Italy (Cervandone, Val Devero) and Switzerland (Wanni glacier, Binntal), where it occurs in metasedimentary rocks (Graeser and Schwander 1987). Besides that, gasparite-(Ce) was found as an accessory mineral in the Black Range Tin District, New Mexico, U.S.A. (Foord et al. 1991, 1999); Tisovec-Rejkovo, Slovakia (Ondrejka et al. 2007); Beryllium Virgin Claim, New Mexico, U.S.A. (Anthony et al. 2000); Chudnoe and Nesterovskoe occurrences, Maldynyrd Range, Prepolar Ural, Russia (Moralev et al. 2005); Kesebol deposit, Sweden (Kolitsch and Holtstam 2004; Kolitsch et al. 2004); Grubependity Lake cirque, Maldynyrd Range, Prepolar Ural, Russia (Mills et al. 2010); Artana, Carrara, Apuane Alps, Italy (Mancini 2000); Tanatz Alp, Switzerland (Roth and Meisser 2013), and Ponte dei Gonazzi, the Maritime Alps, Italy (Cabella et al. 1999).

In most cases, lanthanum is present in gasparite in subordinate amounts (<15 wt% La₂O₃). However, La-dominant grains of gasparite were found in Mn-enriched metamorphosed rocks from the Ponte dei Gonazzi, the Maritime Alps, Italy (up to 45 wt% La₂O₃; Cabella et al. 1999) and in A-type rhyolite from Western Carpathians, Slovakia (up to 26 wt% La₂O₃; Ondrejka et al. 2007). The particle size was insufficient to allow for the investigation of the properties of La-dominant gasparite, and therefore these studies did not describe their findings as a new mineral phase.

OCCURRENCE

Ushkatyn-III deposit, Central Kazakhstan

The Ushkatyn-III deposit (48°16′06″N, 70°10′43″E) is located in Central Kazakhstan 300 km southwest of the city of Karaganda and 20 km to the northeast of the village Zhayrem. The deposit was discovered in 1962. Manganese ore mining started in 1982 and has continued to date. Beginning in 2015, barite-lead ores started to be mined. As of 2015, manganese ore reserves amounted to 102 million tons, with an average Mn content of 24 wt% and Fe 3.5 wt%, and barite-lead ore reserves of 42 million tons, with an average Pb = 2.6 wt% and BaSO₄ = 19 wt% [Annual report for the year 2015, Publishing house JSC ZHGOK, 103 p (in Russian).].

The geological structure of the deposit was considered in the works of Kayupova (1974), Buzmakov et al. (1975), Mitryaeva (1979), Rozhnov (1982), and Skripchenko (1980, 1989). The Ushkatyn-III deposit is located in the western part of the Zhailinsky graben-syncline. This large riftogenic structure originated in the Late Devonian during the destruction of the epi-Caledonian Central-Kazakhstan continental block. The claysiliceous-carbonate rocks of the Famennian stage of the Upper Devonian are ore-bearing. In the eastern part of the deposit, they are represented by reefogenic limestones containing stratiform barite-lead mineralization. In the western part of the deposit, these rocks are replaced by detrital and nodular-layered siliceous limestones containing layers of manganese ores. Altogether, there are fourteen ore layers, each of which has a well-marked, rhythmically stratified structure with alternating layers of manganese ore and limestones. The thickness of individual rhythms range from 15 cm up to 1 m, and the total thickness of ore layers varies from 5 to 25 m. A series of adjacent layers are grouped into a large pack, traced over a strike of more than 1.5 km, a drop of 760 m, and a thickness of 50-150 m. Volcanic rocks are present on the deposit but in volumetric inferior amount (no more than 10% of the whole volume of the ore-bearing strata).

Manganese ores are fine-grained rocks (average size of mineral grains 10-30 µm) with layered and lenticular-banded textures. Altogether, more than 60 minerals have been identified in manganese ores of the Ushkatyn-III deposit by optical, electron microscopy, powder X-ray diffraction, and electron microprobe analysis (Kayupova 1974; Brusnitsyn et al. 2017, 2018). The main minerals are braunite, hausmannite, quartz, calcite, rhodochrosite, tephroite, friedelite, and minerals of manganhumite series (sonolite, alleghanyite). The most characteristic secondary minerals are hematite, jacobsite, rhodonite, caryopilite, pennantite, manganese clinochlore, albite, and barite. Among the most interesting accessory minerals are cinnabar, pyrobelonite, cerianite-(Ce), fluorite, and several REE and arsenate minerals: sarkinite, svabite, tilasite, and retzian group minerals.

Manganese ores can be divided into two types: (1) braunite: braunite + calcite + quartz \pm albite, and (2) hausmannite: hausmannite + calcite + rhodochrosite \pm tephroite (sonolite, alleghanyite) \pm friedelite (caryopilite). These types of ores can form separate layers and can be combined within a single layer. In the latter case, the mineral composition of ores changes as a result of the substitution of braunite for hausmannite/associated silicates/rhodochrosite.

The first arsenates in the Ushkatyn-III deposit were discovered in the early 1970s (Kayupova 1974). However, due to the lack of appropriate analytical instruments, only relatively big grains of minerals (sarkinite, tilasite, and brandtite) were identified.

Gasparite-(La) was found in hausmannite ores, associated with other arsenates. The mineral was found in microveins cutting layers of hausmannite, calcite, and rhodochrosite. Gasparite-(La) is associated with friedelite, jacobsite, pennantite, manganhumite series minerals (alleghanyite, sonolite), sarkinite, tilasite, and retzian-(La). The microveins containing gasparite-(La) range in size from micrometers to 1-5 mm in thickness and to 1-3 cm in length. Gasparite-(La) forms grains of 2-25 µm in size, as well as aggregates with other arsenates of irregular shape up to 50 µm and was found in association with retzian-(La) and alleghanyite (Fig. 1a).

Wanni glacier, Binn Valley, Valais, Switzerland

The Wanni glacier, located in the Binn Valley, Valais (Wallis), Switzerland, represents the Swiss side of the Scherbadung or Pizzo Cervandone of which the Italian side is located in Alpe Devero, Piemonte, Italy. Its mineral assemblage extends to both sides of this mountain and is the type locality of seven REE-arsenates and REE-arsenites (Graeser 1966; Graeser and Schwander 1987; Armbruster et al. 1988; Demartin et al. 1994; Graeser et al. 1994; Guastoni et al. 2006, 2013) and its geology has been summarized in Streckeisen et al. (1974), Steck (1987), Klemm et al. (2004), Hettman et al. (2014), and Bergomi et al. (2017). The REE-As mineralization is hosted in two-mica gneisses of the Monte Leone nappe and extends multiple kilometers westward to the Gischi glacier (Graeser and Roggiani 1976), Chummibort (Cuchet et al. 2005), and Mättital (Krzemnicki 1992, 1997) and eastward to the Lercheltini area. According to Krzemnicki and Reusser (1998), several Pre-alpine ore concentrations within this nappe were locally re-mobilized during Alpine metamorphism, thus generating some unique hydrothermal mineralization.

The sample containing gasparite-(La) was found in rocks



grains and aggregates in calcite veins from the Ushkatyn-III deposit (BSE image), (b) 2 mm sized, elongated crystal (yellow) with albite crystals (white) from the Wanni glacier (optical microscopy). Note: gasparite-(La) = Gas; jacobsite = Jac; retzian-(La) = Ret; alleghanyite = All; calcite = Cal. (Color online.)



of the Monte Leone nappe (46°19'20,N, 8°12'48E). The Monte Leone nappe includes fine-grained banded orthogneisses and minor coarse-grained augen gneiss interlayered with paragneisses, hornblende gneisses, and amphibolites (Klemm et al. 2004; Hettmann et al. 2014) and shows a penetrative amphibolite-facies metamorphic overprint of Alpine age (Maxelon and Mancktelow 2005; Bergomi et al. 2017).

The specimen containing gasparite-(La) was extracted from a small, classical Alpine fissure. The stratum containing the fissure with gasparite-(La) is a fine-layered, two-mica gneiss and is located outside the main Cu-As-F-mineralization that has cafarsite as the dominating As-containing mineral. Based on our observation, the As-enrichment is not very dense in this sublayer. While the occurrence of REE-arsenates [chernovite-(Y), gasparite-(Ce)] is increased, arsenites (cafarsite and asbecasite) are a diminished.

The specimen containing gasparite-(La) (containing three elongated crystals) was located on one side of the cavity; the remainder was empty, apart from minerals that belong to the classical fissure parageneses: minor titanite, quartz, feldspar, and albite. Crystals of gasparite-(La) are prismatic of a size up to 2 mm (Fig. 1b). An interesting feature of the studied crystals is that their prism appears non-translucent (as if fractured) and yellow, whereas the summit faces are perfectly, gemmy translucent and more orange.

ELEMENTAL COMPOSITION

Elemental compositions of rock-forming minerals were studied on the carbon-coated polished sections using a Hitachi S-3400N scanning electron microscope equipped with an Oxford X-Max 20 energy-dispersive X-ray spectrometer (EDX). EDX spectra were obtained under the following conditions: 20 kV accelerating voltage and 2 nA beam current with an acquisition time of 30 s per spectrum.

Elemental analyses for gasparite-(La) were obtained using an Inca Wave 500 wavelength-dispersive X-ray (WDX) spectrometer also equipped on the microscope mentioned above. WDX spectra collection conditions were: 20 kV, 10 nA, beam diameter 5 μ m, 30 s peak, and 30 s background collection per element, XPP matrix correction. Fe metal, Mn metal, V metal, InP, InAs, wollastonite, Th-, Y-, La-, Ce-, Nd-, and Sm-bearing glass standard samples (MAC-standards) were used for spectrometer calibration.

Preliminary EDX analyses showed that gasparite-(La) from the Ushkatyn-III deposit has almost no chemical zoning or consistent element ratios; all analyzed grains showed La > Ce > Nd and As > V > P. In the case of gasparite from the Ushkatyn-III deposit, Central Kazakhstan, five analyses (WDX) from three different grains were performed on one carbon-coated polished section (Table 1). The empirical formula of gasparite-(La) from the Ushkatyn-III deposit, based on four oxygen atoms, is (La_{0.65}Ce_{0.17} Nd_{0.07}Ca_{0.06}Mn_{0.05}Pr_{0.02})_{1.02}[(As_{0.70}V_{0.28}P_{0.02})_{1.00}O₄].

One elongated crystal of gasparite from Wanni glacier was studied by EDX and WDX analyses. EDX analysis showed that the crystal has chemical zoning: its La/Ce/Nd ratio varies significantly, whereas As/P ratio is approximately constant (Fig. 2). The optically more translucent summit of the crystal is La-dominant, while the prismatic part of the crystal is Ce-dominant; and thus, it

TABLE 1. Chemical composition of gasparite-(La)

Constituent	Ushkat	yn-III deposit	Wan	Wanni glacier		
constituent	wt%	Range	wt%	Range		
Fe ₂ O ₃	0.05	0.00-0.16	0.00	0.00		
MnO	1.30	0.91-1.96	0.00	0.00		
CaO	1.33	0.97-1.54	0.34	0.24-0.48		
ThO₂	0.00	0.00	0.58	0.37-0.72		
Y_2O_3	0.01	0.00-0.05	0.01	0.00-0.03		
La ₂ O ₃	40.21	37.83-41.17	35.59	34.57-36.74		
Ce ₂ O ₃	10.69	9.76-11.61	22.55	21.26-23.67		
Pr ₂ O ₃	1.46	0.00-1.99	0.29	0.00-0.88		
Nd ₂ O ₃	4.24	3.53-4.69	1.04	0.50-1.30		
Sm ₂ O ₃	0.09	0.00-0.33	0.07	0.00-0.35		
V ₂ O ₅	9.77	8.58-11.21	0.00	0.00		
P_2O_5	0.64	0.22-0.99	4.29	4.18-4.45		
As ₂ O ₅	30.32	29.46-31.41	34.48	33.27-35.22		
Total	100.11		99.24			

represents gasparite-(Ce). We performed five WDX analyses from the summit of the crystal and the overall empirical formula of gasparite-(La) from the Wanni glacier, based on four oxygen atoms, is $(La_{0.59}Ce_{0.37}Nd_{0.02}Ca_{0.02}Th_{0.01})_{1.01}[(As_{0.81}P_{0.16}Si_{0.02}S_{0.02})_{1.01}O_4]$. The simplified formula of gasparite-(La) from both the Ushkatyn-III deposit and the Wanni glacier is La(AsO₄).

Gasparite-(La) belongs to the monazite group, which contain seven monoclinic phosphate and arsenate minerals (Table 2). It is a La-dominant analog of gasparite-(Ce) (Graeser and Schwander 1987) and an arsenate-dominant analog of monazite-(La). According to the Nickel-Strunz Classification, gasparite-(La) belongs to 8.AD (8 = phosphates, arsenates, vanadates; A = phosphates, etc. without additional anions, without H_2O ; D = with only large cations).

PHYSICAL PROPERTIES AND OPTICAL DATA

Gasparite-(La) crystals are yellow and translucent with bright submetallic luster. The Vickers Hardness Number (VHN) measured on gasparite-(La) from the Wanni glacier was 325 with a range 308–340 kg mm⁻² (load 20 g) by means of HMV-2T (Shimadzu). This data are in a good agreement with the data on



FIGURE 2. Chemical zoning of a gasparite crystal from the Wanni glacier. (Color online.)

Mineral	Gasparite-(La)	Gasparite-(Ce)	Rooseveltite	Monazite-(La)	Monazite-(Ce)	Monazite-(Nd)	Monazite-(Sm)	Cheralite
Chemical formula	La(AsO ₄)	Ce(AsO ₄)	Bi(AsO ₄)	La(PO ₄)	Ce(PO ₄)	Nd(PO ₄)	Sm(PO₄)	CaTh(PO ₄) ₂
Crystal system				Monoclinic				
Space group				P2 ₁ /n				
a (Å)	6.9576(4)	6.929(3)	6.879(1)	6.8313(10)	6.7880(10)	6.7352(10)	6.6818(12)	6.7085(8)
b (Å)	7.1668(4)	7.129(3)	7.159(1)	7.0705(9)	7.0163(9)	6.9500(9)	6.8877(9)	6.4152(6)
c (Å)	6.7155(4)	6.697(3)	6.732(1)	6.5034(9)	6.4650(7)	6.4049(8)	6.3653(9)	6.4152(6)
β (°)	104.414(1)	104.46(3)	104.84(1)	103.27(1)	103.43(1)	103.68(1)	103.86(1)	103.71(1)
Ζ				4				
Reference	а	b	c	d	d	d	d	e
Notes: For comparis	on u c n given as a	a>c ª This study W	anni glacier ^b Koli	itschiet al. 2004. ° F	Redlivy and Mereit	er 1982 ^d Nietal	1995 ^e Raison et al	2008

TABLE 2. Comparative crystallographic data for monazite group minerals

gasparite-(Ce) (VHN = 327 kg mm⁻²; Graeser and Schwander 1987). Mohs hardness could not be determined because of the tiny sizes of the crystals. The Mohs hardness calculated from the VHN value was approximately $4\frac{1}{2}$.

As gasparite-(La) from the Ushkatyn-III deposit had no chemical zoning, one of its grains was chosen for optical study. In polished sections, gasparite-(La) from the Ushkatyn-III deposit looked dark gray under reflected light. The mineral was slightly anisotropic with $\Delta R_{ss9} = 2.04\%$. The reflectivity of gasparite-(La) in the air (Supplemental¹ Table S1) was measured against a SiC standard (reflection standard = 474251, no. 545) using MSF-21 spectrophotometer with a monochromator slit of 0.4 mm and a 100 µm zone diameter. The measurement parameters were as follows: lens magnification $21\times$, aperture 0.4, and $\Delta\lambda = 10$ nm, SiC. The reflectivity spectrum is shown in Figure 3.

Raman spectra

Gasparite-(La) crystals from both localities were used for Raman studies. Raman spectra (Fig. 4) were recorded with a Horiba Jobin-Yvon LabRAM HR800 spectrometer equipped with an Olympus microscope having $50 \times$ and $100 \times$ objectives. Raman spectra were excited by an Ar ion laser at a wavelength of 514 nm and a maximum power of 50 mW. The spectra were obtained in the range of 100– 4000 cm^{-1} at a resolution of 2 cm⁻¹ at room temperature. To improve the signal-to-noise ratio, the number of acquisitions was set to 20. The spectra were processed using licensed Labspec and Origin software. Band fitting was done using a Lorentz function with the minimum number of component bands used for the fitting process (Table 3).



FIGURE 3. Reflectance spectra in the air for gasparite-(La) from the Ushkatyn-III deposit.

Raman spectra of gasparite-(La) from both the Ushkatyn-III deposit and the Wanni glacier were very close to that of synthetic La(AsO₄) (Fig. 4, Table 3). Bands in the region from 4000 to 1100 cm⁻¹ were not registered, which means that gasparite-(La) contained no (OH)- groups. Bands assigned to stretching vibrations v_1 and v_3 of arsenate ion are observed in the region 900-800 cm⁻¹. There were bending vibrations v_2 and v_4 of arsenate ion in the region of 500-350 cm⁻¹. The lattice vibrations were located below 320 cm⁻¹. The main differences of Raman spectra of the minerals in comparison with the pure synthetic phase were associated with impurities of (VO₄)³⁻ (Ushkatyn-III) and $(PO_4)^{3-}$ (Wanni glacier). Vibrations $v_1(PO_4)$ was about 960 cm⁻¹, $v_1(VO_4)$ near 840 cm⁻¹ (Solecka et al. 2018; Song et al. 2018). In the region of the v_4 band, the main differences are associated with the overlapping of bands related to $(AsO_4)^{3-}$, $(PO_4)^{3-}$, and $(VO_4)^{3-}$. Raman spectra reveal the predominance of La+Ce in the mineral composition of $v_1(AsO_4)$ of 861–863 cm⁻¹. The Raman spectrum of Ho(AsO₄) v_1 (AsO₄) was about 895 cm⁻¹ (Barros et al. 2009). Impurity tetrahedral cations (P,V) did not influence the $v_1(AsO_4)$ band shift.

Crystallography

Because gasparite-(La) from the Ushkatyn-III deposit occurs as microscopic grains up to 15 µm in size (Fig. 2) it was not pos-



FIGURE 4. Raman spectra in the air for gasparite-(La) from the Ushkatyn-III deposit, gasparite-(La) from the Wanni glacier and synthetic La(AsO₄) (Botto and Baran 1982). (Color online.)

Raman shift, cm ⁻¹ /Relative Intensity		Assignment	Rama	an shift (cm ⁻¹)/Re	Assignment	
Wanni glacier	Botto and Baran 1982		Ushkatyn-III	Wanni glacier	Botto and Baran 1982	
94/vw			364/vw	367/w	350/vw 367/w	v ₄ (AsO ₄)
107/w						
125/w			379/st	395/st	392/m	$v_2(AsO_4)$
139/vw						
155/w			422/w	421/m	418/w	$v_4(AsO_4)$
190/w						
203/vw						
			452/w	462/w	440/sh	
					461/w	
		Lattice				
		vibrations				
267 vw			822/m	812/sh	798/vw	$v_3(AsO_4)$
	322/w					
337/w	336/w					
			843/sh	826/sh	827/m	
				848/sh	845/st	
					872/sh	
			860/vs	864/vs	861/vs	v ₁ (AsO ₄)
				951/w		<i>v</i> ₁ (PO ₄)
	n shift, cm ⁻¹ /Rela Wanni glacier 94/vw 107/w 125/w 139/vw 135/w 190/w 203/vw 267 vw 337/w	n shift, cm ⁻¹ /Relative Intensity Wanni glacier Botto and Baran 1982 94/vw 107/w 125/w 139/vw 155/w 190/w 203/vw 267 vw 322/w 337/w 336/w	n shift, cm ⁻¹ /Relative Intensity Assignment Wanni glacier Botto and Baran 1982 94/vw 107/w 125/w 139/vw 155/w 190/w 203/vw Lattice vibrations 267 vw 322/w 337/w 336/w	n shift, cm ⁻¹ /Relative Intensity Assignment Rama Wanni glacier Botto and Baran 1982 Ushkatyn-Ill 94/vw 107/w 125/w 139/vw 155/w 203/vw 267 vw 322/w 337/w 322/w 336/w 822/m 822/m 843/sh 860/vs	n shift, cm ⁻¹ /Relative Intensity Assignment Raman shift (cm ⁻¹)/Re Wanni glacier Botto and Baran 1982 Ushkatyn-III Wanni glacier 94/vw 367/w 364/vw 367/w 107/w 379/st 395/st 139/vw 422/w 421/m 190/w 203/vw 452/w 462/w Lattice vibrations 822/m 812/sh 337/w 336/w 843/sh 826/sh 843/sh 826/sh 848/sh	n shift, cm ⁻¹ /Relative Intensity Assignment Raman shift (cm ⁻¹)/Relative Intensity Wanni glacier Botto and Baran 1982 Botto and Baran 1982 94/vw 364/vw 367/w 350/vw 367/w 94/vw 364/vw 367/w 350/vw 367/w 107/w 379/st 395/st 392/m 139/vw 422/w 421/m 418/w 190/w 452/w 462/w 440/sh 190/w 452/w 462/w 440/sh 100/w 203/vw 822/m 812/sh 798/vw 267 vw 322/w 336/w 822/m 812/sh 798/vw 337/w 336/w 826/sh 827/m 843/sh 848/sh 845/st 860/vs 864/vs 864/vs 861/vs 951/w 951/w 951/w

TABLE 3. Raman spectral signatures of gasparite-(La)

sible to determine its crystal structure with single-crystal X-ray diffraction. All diffraction data were obtained by electron back-scatter diffraction (EBSD) (Fig. 5). In the case of gasparite-(La) from the Wanni glacier, we managed to isolate the La-enriched zone of the elongated crystal and refine its crystal structure using single-crystal X-ray diffraction. The same crystal fragment was used for powder X-ray diffraction studies.

Powder X-ray diffraction (XRD)

The powder XRD pattern for gasparite-(La) from the Wanni glacier was recorded in Debye–Scherrer geometry using a Rigaku R-AXIS Rapid II diffractometer equipped with a curved (cylindrical) imaging plate detector (r = 127.4 mm). CoKa radiation ($\lambda = 1.79021$ Å) was generated by a rotating anode (40 kV, 15 μ A) with microfocus tube optics; exposure time was set to 15 min. The data were processed using the osc2xrd program (Britvin et al. 2017) and Stoe WinXPOW software XRD data for gasparite-(La) from the Wanni glacier is presented in Supplemental¹ Table S2 and is similar to that of synthetic La(AsO₄) (Le Berre et al. 2007; JCPDS file 15-0756). Calculated data were obtained using Rietveld analysis of the powder pattern [c = 6.7087(3), b = 7.1499(2), a = 6.9429(2) Å, $\beta = 104.442(2)^{\circ}$].

Single-crystal X-ray diffraction and refinement (SREF)

REE arsenates, chromates, phosphates, and vanadates of Ln(XO₄) type can crystallize in monoclinic (monazite structure) or tetragonal (zircon-type structure) symmetry (Schwarz 1963; Botto and Baran 1982; Clavier et al. 2011). In the REE arsenate and phosphate series, the La, Ce, Pr, and Nd end-members possess the monazite structure (Clavier et al. 2011). REE vanadates have more complex behavior: the majority of REE vanadates (Ce–Lu, Sc) have the zircon-type structure, whereas La(VO₄) crystallizes in both the zircon-type and monazite-type structures (Witzke et al. 2008).

The monazite-type structure was first reported by Mooney (1948) and then refined by several researchers for various REE-phosphates (Feigelson 1964; Ghouse 1968; Beall et al. 1981; Pepin and Vance 1981; Mullica et al. 1984; Mullica et al. 1985; Ni et al. 1995). The structural arrangement in the monazite-type structure



FIGURE 5. (a) EBSD pattern of the gasparite-(La) crystal (30 kV accelerating voltage, 0.3 nA beam current, 5 s exposure per frame, averaging of 20 frames, 1344×1024 pixels image size), and (b) the pattern indexed with the $P2_1/n$ structure (MAD 0.15, 80 bands are represented on the image). (Color online.)

American Mineralogist, vol. 104, 2019

is based on ninefold coordination of the metallic cation and can be described as an equatorial pentagon interpenetrated by a tetrahedron (Clavier et al. 2011). The tetrahedron located out of the equatorial plane can then be described as a link between the REE O₉ polyhedra, leading to the formation of infinite chains along the c axis.

According to the published data, both synthetic $La(AsO_4)$ (Schmidt et al. 2005) and natural gasparite-(Ce) (Kolitsch et al. 2004) have a monoclinic structure with the space group $P2_1/n$. The crystal structure of gasparite-(La) from the Wanni glacier (co-type specimen) was solved by direct methods and refined to $R_1 = 0.014$ using a SHELX-2015 set of programs (Scheldrick 2015) via Olex2 ver.1.2.8 graphical user interface (Dolomanov et al. 2009) (Tables 4 and 5; Supplemental¹ Table S3). Data collection and structure refinement details are given in Tables 4 and 5 and in the CIF¹ file. The La site is coordinated by nine O atoms, with (La-O) distances of 2.586 (Table 6). The As site was found to be almost fully occupied by As (As_{0.84}P_{0.16}), in agreement with the chemical data. The unit-cell parameters of gasparite-(La) are larger than the values for gasparite-(Ce) (Kolitsch et al. 2004), smaller than those for synthetic La(AsO₄) (Schmidt et al. 2005) and in good agreement with the values derived from powder XRD data of the same crystal.

Electron backscatter diffraction (EBSD)

EBSD measurements were performed on an Oxford HKLNordlys Nano EBSD detector equipped on a Hitachi

TABLE 4. Crystal data, XRD data collection and structure refinement details for gasparite-(La) from the Wanni glacier

31	5
Crysta	l data
Chemical formula	(La _{0.6} Ce _{0.40})[(As _{0.84} P _{0.16})O ₄]
M _r	271.39
Crystal system, space group	Monoclinic, P2 ₁ /n
a, b, c (Å)	6.7155(4), 7.1668(4), 6.9576(4)
β (°)	104.414(1)
V (Å ³)	324.32(3)
Ζ	4
D_x (g/cm ³)	5.558
Crystal size (mm)	$0.04 \times 0.04 \times 0.03$
Data col	lection
Diffractometer	Bruker APEX-II CCD
Radiation type	MoKα (0.71073 Å)
μ (mm ⁻¹)	21.95
Absorption correction	Multi-scan
No. of measured, independent	3839, 944, 869
and observed [<i>l</i> > 2s(<i>l</i>)] reflections	
20 range for data collection (°)	7.55 to 60.00
Index ranges	–9 ≤ h ≤9, –9 ≤ k ≤10, –9 ≤ l ≤9
Structure re	efinement
R _{int} , R _s	0.0207, 0.0175
$R_1 [F^2 > 2\sigma(F^2)], wR_2(F^2), S$	0.014, 0.029, 1.12
No. of reflections	944
No. of parameters	57
$\Delta \rho_{max} \Delta \rho_{min} (e/Å^3)$	0.76, -0.55

TABLE 5.	Fractional atomic coordinates and isotropic displacemen
	parameters (II. $Å^2$) for as parite-(I a) from the Wanni alacie

	Ferraria (eliso) :							
Site	x	у	Z	$U_{\rm iso}$	Occupancy (<1)			
M (4e)	0.40018(2)	0.34494(2)	0.21899(2)	0.00827(6)	(La _{0.6} Ce _{0.4}) ^a			
X (4e)	0.38653(4)	0.16300(4)	0.69644(4)	0.00626(11)	(As _{0.84} P _{0.16})			
O1 (4e)	0.2803(3)	0.2142(3)	0.8797(3)	0.0131(4)				
O2 (4e)	0.5664(3)	-0.0012(3)	0.7481(3)	0.0133(4)				
O3 (4e)	0.5031(3)	0.3390(3)	0.6113(3)	0.0122(4)				
O4 (4e)	0.1793(3)	0.1075(3)	0.5181(3)	0.0130(4)				
^a The occupancy of <i>M</i> site was fixed according to electron microprobe data.								

S-3400N scanning electron microscope. Operating conditions are listed in Supplemental¹ Table S4. Both acquisition and analysis of Kikuchi-patterns were made using Oxford AZtecHKL software. Synthetic La(AsO₄) structural data (ICSD) were used as inputs (Schwartz et al. 2009). The sample was polished with progressively smaller polycrystalline diamond suspensions with the ending step of Ar ion etching for 10 min at the final stage (Oxford IonFab 300) to remove amorphized layers for EBSD analysis. The sample was pre-tilted 70° along the normal to the EBSD detector. The fit factor [mean angular deviation (MAD)], which describes the angular deviation between the calculated and measured Kikuchi lines (good fit for deviations <1.0°), is less than 0.3° for synthetic La(AsO₄) and Ce(AsO₄) (Brahim et al. 2002; Kang and Schleid 2005).

Eighteen electron backscatter patterns from three different gasparite-(La) grains were collected (Fig. 6). Good matches were obtained for all patterns using monoclinic La(AsO₄) structure with the space group $P2_1/n$ (Schmidt et al. 2005).

DISCUSSION

Crystal chemistry and substitution mechanisms

The REE ratio in gasparite-(La) from the Ushkatyn-III deposit shows no significant variations and in all analyzed grains, La > Ce. The REE ratio in crystals of gasparite-(La) from the Wanni glacier varies significantly from Ce-dominant to La-dominant species in the same crystal (Fig. 2).

Our data revealed a very limited P-for-As substitution (P up to 0.02 apfu) but a large extent of V-for-As substitution (V up to 0.28 apfu) in gasparite-(La) from the Ushkatyn-III deposit (Fig. 7). On the other hand, gasparite-(La) from the Wanni glacier contains no V and exhibits extensive P-for-As substitution (P up to 0.16 apfu).

The impurity of tetrahedral cations (P,V) does not appear to influence the (AsO₄) band shift as isolated tetrahedra [(AsO₄), (PO₄), and (VO₄)] in the gasparite structure surrounded by polyhedral [(LaO₉), (CeO₉), and (NdO₉)]. As a result, cations in the polyhedra have a major impact on the positions of the bands related to As-O vibrations in (AsO₄)³⁻. Both P-for-As and V-for-As are reflected in the appearance of additional bands or broadening of the main bands. The band around 390 cm⁻¹ in the case of P-for-As (Wanni glacier), shifts upward, and in the case of V-for-As (Ushkatyn-III deposit), shifts downward (Fig. 4).

No natural vanadates of monazite structure-type have been reported yet. Only wakefieldite group minerals with the zircon structure were reported (Deliens and Piret 1986; Witzke et al. 2008). No experimental evidence for the existence of AsO_4 – PO_4 substitution was reported. Cabella et al. (1999) described gasparite-(Ce) enriched with P and V and reported a wide range of V-for-As substitutions (V up to 0.30 apfu) and P-for-As substitutions (P up to 0.15 apfu). Kolitsch et al. (2004) reported that 10% of the As atoms are substituted by P (P up to 0.12 apfu) in gasparite-(Ce).

The crystal chemistry of the MXO_4 monazite-type compounds in general (M = La, Ce; X = As, P, V) have been studied intensively (e.g., Clavier et al. 2011; Kolitsch et al. 2004). Kolitsch et al. (2004) assumed that the substitution of P for As leads to the substantial decrease of the *c*-parameter, which can be explained by the stacked arrangement along the [001] direction of the XO_4



FIGURE 6. Chemical composition variations in gasparite group minerals: (a) La-Ce-Nd ratio and (b) As-V-P ratio. (Color online.)

groups in the structure.

Our data confirmed that both cell parameters *a* and *c* are influenced mainly by the size of XO_4 tetrahedra (r = 0.99, r = 0.92, respectively; Fig. 8a), whereas the *b* parameter is mainly influenced by the size of the MO_9 polyhedra (r = 0.92; Fig. 8b).

Comparison of LaXO₄ monazite-type compounds shows that the (La-O) distance in MXO_4 monazite-type compounds varies significantly: 2.579 [La(PO₄); Ni et al. 1995] to 2.599 Å [La(AsO₄); Schmidt et al. 2005]. This may explain the distortion of LaO₉ polyhedra, which is well correlated to (X-O) distance (r = 0.99; Table 6) and could be the reason for the *b* vs. (*M*-O) correlation.

Origin of gasparite-(La)

As stated above, gasparite-(La) was found in occurrence with distinct geological situations. Gasparite-(La) from the Wanni glacier, Binn Valley was found in an alpine fissure with evidence of hydrothermal alteration (well-shaped crystals in an almost empty cavity), whereas gasparite-(La) from the Ushkatyn-III deposit was found in primary Mn ores (irregular-shaped grains in calcite-rhodochrosite-friedelite veins).



We believe that in the case of gasparite-(La) from the Wanni

FIGURE 7. As vs. V+P+S substitution. (Color online.)

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glacier, the source of arsenic was an As-rich hydrothermal fluid, as in the case of gasparite-(Ce) (Graeser and Schwander 1987) from the same area. More challenging to explain is the source of lanthanum. The host mineral could be the main source of REE, as was shown in the case of synchysite-(Ce) (Graeser and Schwander 1987), monazite-(Ce) (Ondrejka et al. 2007), and cervandonite-(Ce) (Guastoni et al. 2013). High P content in gasparite-(La) from the Wanni glacier indicates that monazite could be the host mineral. However, additional process of REE redistribution was needed, as (1) crystal of gasparite-(La) had La/Ce zoning and (2) (Ce)- and (Y)-dominant species were the rule in this region, supported by Ce/Y >> La in whole-rock samples (Hofmann and Knill 1996). Another possible explanation to La-enrichment is the partial oxidation of Ce3+ to insoluble Ce4+ during fluid transportation and subsequent LREE (La, Nd, Sm) enrichment. This mechanism is well recorded in uranyl minerals (e.g., Meisser et al. 2010).

Thus, gasparite-(La) from the Wanni glacier was formed as a metasomatic mineral in the process of alteration of primary REE minerals by As-rich hydrothermal fluid and the ensuing La/Ce separation.

The Ushkatyn-III deposit is considered as an object of hydrothermal-sedimentary genesis, transformed by processes of low-grade regional metamorphism (Mitryaeva 1979; Skripchenko 1980; Rozhnov 1982; Brusnitsyn et al. 2018).

Gasparite-(La) from the Ushkatyn-III deposit was found in microveins in hausmannite ores. It was found in association with friedelite, jacobsite, pennantite, manganhumite series minerals, sarkinite, tilasite, and retzian-(La) and embedded into calcite-rhodochrosite veinlets. Similar veinlets in other rocks have a different composition. Calcite and quartz were found in microveins in the enclosing limestone. Calcite, kutnohorite, rhodonite, axinite-(Mn), friedelite, hematite, jacobsite, and barite were found in microveins in braunite ores. A regular change in the composition indicates the segregation mechanism of the genesis of such microveins. They were formed by local redeposition of a substance from the rocks in which they developed into thin cracks. These processes probably occurred during the period of



6.60 6.55 7.10 b а 6.50 $r^2 = 0.98$ $r^2 = 0.86$ 6.45 7.05 2.585 2.605 1.500 1.550 1.600 1.650 1.700 1.750 2.575 2.580 2.590 2.595 2 600 (M-O), Â (X-O),

FIGURE 8. Unit-cell parameters of $M(XO_4)$ compounds (M = La, Ce; X = As, P, V): (a) c vs. (X-O) and (b) b vs. (M-O). (Color online.)

tectonic deformation of the region during Late Paleozoic time.

6.85

6.80

6.75

6.70

⊲ ^{6.65}

ບ່

Brahim et al. 2002

• Ni et al. 1995

We believe that As and REE were accumulated syngenetically with manganese sediments in the Ushkatyn-III deposit. Most likely, the initial manganese oxides absorbed these elements, as it happens in modern oceans, where the absorption of REE to manganese oxides occurs much more intensively than many other precipitation minerals (Dubinin 2006).

The occurrence of As-minerals in the Ushkatyn-III deposit is connected to the manganese ores only and has not been found in the host rocks or tectonic deformation zones. Manganese rocks of different genesis are often enriched in arsenic, and more than half of all discovered Mn-arsenates were found in the famous Mn deposits (Frondel and Baum 1974; Abrecht 1990; Brugger and Giere 1999; Cabella et al. 1999; Holtstam and Langhof 1999; Lundström 1999; Brugger and Meisser 2006). Therefore, As and REE infiltration into ore layers from any external source is unlikely in this case.

Apparently, REE and As accumulated in the initial orebearing sediments as a component of Mn minerals. In the process of metamorphism and tectonic deformation, these elements were mobilized by pore solutions and re-deposited into secant

TABLE 6. Selected bond lengths (Å) and the distortion of *M*-polyhedra for gasparite-(La) from the Wanni glacier and structurally related $M(XO_4)$ compounds (M = La, Ce; X = As, P, V)

Bond			Len	ath		
bond	Gasparite- (La)	Gasparite- (Ce)	La(AsO ₄)	Ce(AsO ₄)	La(VO ₄)	La(PO ₄)
<i>M</i> –01 ⁱⁱⁱ	2.554 (2)	2.486(5)	2.571(3)	2.939(8)	2.521(4)	2.479(3)
<i>M</i> –01 ^{iv}	2.481 (2)	2.527(5)	2.489(3)	2.636(9)	2.497(3)	2.554(3)
<i>M</i> –02 ^v	2.479 (2)	2.902(5)	2.498(4)	2.460(7)	2.656(3)	2.783(3)
<i>M</i> –O2 ⁱⁱ	2.559 (2)	2.544(4)	2.560(4)	2.619(8)	2.568(3)	2.589(3)
<i>M</i> –O3 ⁱⁱ	2.901 (2)	2.632(5)	2.655(3)	2.472(8)	2.528(4)	2.615(3)
<i>M</i> –03 ^{vi}	2.562 (2)	2.620(6)	2.577(3)	2.551(7)	2.677(4)	2.503(3)
<i>M</i> –O3	2.6440 (19)	2.457(5)	2.912(4)	2.562(7)	2.887(4)	2.672(3)
<i>M</i> –04 ⁱⁱⁱ	2.624 (2)	2.488(5)	2.644(4)	2.476(7)	2.533(4)	2.466(3)
<i>M</i> -04 ^{vii}	2.472 (2)	2.555(4)	2.486(3)	2.543(7)	2.502(4)	2.548(3)
(<i>M</i> -O)	2.586	2.579	2.599	2.584	2.597	2.579
ΔM	0.035	0.036	0.035	0.038	0.037	0.030
<i>X</i> –01	1.650 (2)	1.647(5)	1.670(4)	1.682(8)	1.724(4)	1.523(3)
<i>X</i> –O2	1.660 (2)	1.664(5)	1.680(4)	1.699(7)	1.720(4)	1.553(3)
<i>X</i> –O3	1.669 (2)	1.659(5)	1.695(4)	1.692(7)	1.699(4)	1.541(3)
<i>X</i> –O4	1.6656 (19)	1.615(5)	1.691(3)	1.686(8)	1.693(4)	1.537(3)
(X-O)	1.661	1.646	1.684	1.690	1.709	1.538
Referen	ce This	Kolitsch	Schmidt	Brahim et	Rice and	Ni et al.
	study	et al. 2004	et al. 2005	al. 2002	Robinson 1976	1995

ore veins. A similar mechanism for the genesis of REE-bearing arsenates is also assumed for metamorphosed Fe-Mn deposits in other regions (Cabella et al. 1999; Kolitsch et al. 2004).

Gasparite-(La) from the Ushkatyn-III deposit is characterized by relatively small amount of other REE (Ce+Nd+Pr < 0.3 apfu) compared to other gasparite-(Ce) (Fig. 6), and has a nearly constant La/Ce ratio. Its occurrence with retzian-(La) (Fig. 2) may indicate specific conditions of mineral formation in which rocks were depleted by cerium.

Lanthanum and cerium have very close chemical properties, but the average content of lanthanum in the Earth's crust is almost two times lower than cerium: 30 and 58 ppm, respectively (Li and Schoonmaker 2003). Gasparite-(La) and retzian-(La) formation require separating lanthanum from cerium. This could be done in two stages: (1) during the accumulation of manganese sediment or (2) later during lithification.

In favor of the first option is the fact that accumulations of manganese oxides of hydrothermal genesis are characterized by cerium deficiency relative to the remaining REE. In the REE spectra of such rocks, a negative cerium anomaly is usually well expressed (Dubinin 2006; Bau et al. 2014). In other words, La/Ce is higher in them than in "normal" marine sediments, which determines the possibility of the formation of lanthanum minerals. If this assumption is correct, then lanthanum minerals, including gasparite-(La) and retzian-(La), should be considered as indicators of the hydrothermal-sedimentary genesis of manganese ores. However, this issue requires further study.

According to the second option, the separation of lanthanum and cerium occurred at the post-sedimentation stage of the development of the deposit. The very low Ce content of both gasparite-(La) and retzian-(La) (less than 12 and 9 wt%, respectively) could be explained by formation from a strongly Ce-depleted source due to oxidation of Ce³⁺ and subsequent formation of insoluble cerianite-(Ce) as shown in the case of wakefieldite-(La) (Witzke et al. 2008). Cerianite-(Ce) was observed in several cases in the same samples from the Ushkatyn-III deposit where La arsenates were found. According to experimental data (Ohta and Kawabe 2001), the oxidation of cerium with manganese oxides proceeds according to the reaction:

$$2Ce^{3+} + MnO_2 + 2H_2O = 2CeO_2 + Mn^{2+} + 4H^+$$

The reaction will shift to the right by a weak alkaline mineral formation medium, typical for carbonate associations. As a result, cerianite-(Ce) can coexist with Mn²⁺ minerals (rhodochrosite, tephroite, friedelite, etc.). However, it is possible only in the absence of organic matter. Otherwise, there will be a dissolution of cerianite-(Ce) with the restoration of cerium by the reaction (Dubinin 2006):

$$CH_2O + 5H_2O + 11CO_2 + 4CeO_2 \rightarrow 4Ce^{3+} + 12HCO_3^{-}.$$

Accordingly, the formation of cerianite-(Ce) and, as a consequence, the formation of La-rich (Ce-depleted) minerals are controlled by the local distribution of Mn, REE, and organic matter.

Both scenarios considered (cerium deficiency in initial sediments and cerium concentration in cerianite-(Ce) at post-sedimentary stages) do not contradict each other. Most likely, each of them contributed to the formation of gasparite-(La) and other La-rich minerals in manganese ores of the Ushkatyn-III deposit.

Thus, gasparite-(La) from the Ushkatyn-III deposit was formed in primary ores and was not influenced by metasomatic processes. We believe that it is precisely the features of the chemical composition of the initial Mn-Fe ores that predetermined the possibility of the formation of lanthanum minerals in the Ushkatyn-III deposit.

IMPLICATIONS

Gasparite-(La) from Mn ores of the Ushkatyn-III deposit and metamorphic rocks of the Wanni glacier have different geological settings and different formation conditions. Thus, an occurrence of gasparite-(La) in rocks and its chemical composition could be used as a tool for geological reconstruction of their host rock formation.

In the case of gasparite-(La) from the Ushkatyn-III deposit, both REE and As were sourced from the host Mn ores. In all analyzed grains, the As/V/P and La/Ce ratios are nearly constant, while As > V > P and La > Ce. Constant lanthanum predominance in analyzed gasparite grains indicates specific conditions of Mn ore formation: Ce depletion or La enrichment and no metasomatic process. Besides that, gasparite from Mn ores is characterized by low P and high V content (our data; Cabella et al. 1999). Modern metalliferous sediment is mainly composed of Fe- and Mn-oxy/hydroxides and smectite minerals (e.g., Vereshchagin et al. 2019), which are carriers of V and REE (Gurvich 2006). Ferromanganese ores are sources of several REE-dominant vanadates (Moriyama et al. 2011; Witzke et al. 2008). Thus, the content of V originated from primary Fe-,Mn-sediments could be used as an indicator of gasparite origin.

Gasparite-(La) from the Wanni glacier has different chemical features. Although its As/V/P ratio is also nearly constant, in its As > P > V. High P content is a typical feature of gasparite from metasomatic rocks (Graeser and Schwander 1987; Ondrejka et al. 2007). In addition, it has variable La/Ce ratios, which is typical for gasparite from metasomatic rocks, probably due to La/Ce separation during recrystallization.

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Endnote:

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