

# Ekplexite $(\text{Nb},\text{Mo})\text{S}_2 \cdot (\text{Mg}_{1-x}\text{Al}_x)(\text{OH})_{2+x}$ , kaskasite $(\text{Mo},\text{Nb})\text{S}_2 \cdot (\text{Mg}_{1-x}\text{Al}_x)(\text{OH})_{2+x}$ and manganokaskasite $(\text{Mo},\text{Nb})\text{S}_2 \cdot (\text{Mn}_{1-x}\text{Al}_x)(\text{OH})_{2+x}$ , three new valleriite-group mineral species from the Khibiny alkaline complex, Kola peninsula, Russia

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## ABSTRACT

Three new valleriite-group minerals, ekplexite  $(\text{Nb},\text{Mo})\text{S}_2 \cdot (\text{Mg}_{1-x}\text{Al}_x)(\text{OH})_{2+x}$ , kaskasite  $(\text{Mo},\text{Nb})\text{S}_2 \cdot (\text{Mg}_{1-x}\text{Al}_x)(\text{OH})_{2+x}$  and manganokaskasite  $(\text{Mo},\text{Nb})\text{S}_2 \cdot (\text{Mn}_{1-x}\text{Al}_x)(\text{OH})_{2+x}$  are found at Mt Kaskasnyunchorr, Khibiny alkaline complex, Kola Peninsula, Russia. They occur in fenite consisting of orthoclase–anorthoclase and nepheline with fluorophlogopite, corundum, pyrrhotite, pyrite, rutile, monazite-(Ce), graphite, edgarite, molybdenite, tungstenite, alabandite, etc. Ekplexite forms lenticular nests up to 0.2 mm × 1 mm × 1 mm consisting of near-parallel, radiating or chaotic aggregates of flakes. Kaskasite and manganokaskasite mainly occur as flakes and their near-parallel ‘stacks’ (kaskasite: up to 0.03 mm × 1 mm × 1.5 mm; manganokaskasite: up to 0.02 mm × 0.5 mm × 1 mm) epitaxially overgrow Ti-bearing pyrrhotite partially replaced by Ti-bearing pyrite. All three new minerals are opaque, iron-black, with metallic lustre. Cleavage is {001} perfect and mica-like. Flakes are very soft, flexible and inelastic. Mohs hardness is ~1.  $D(\text{calc.}) = 3.63$  (ekplexite), 3.83 (kaskasite) and 4.09 (manganokaskasite) g cm<sup>-3</sup>. In reflected light all these minerals are grey, without internal reflections. Anisotropism and bireflectance are very strong and pleochroism is strong. The presence of OH groups and an absence of H<sub>2</sub>O molecules are confirmed by the Raman spectroscopy data. Chemical data (wt.%, electron probe) for ekplexite, kaskasite and manganokaskasite, respectively, are: Mg 6.25, 5.94, 0.06; Al 4.31, 3.67, 3.00; Ca 0.00, 0.04, 0.00; V 0.86, 0.16, 0.15; Mn 0.00, 0.23, 11.44; Fe 0.44, 1.44, 2.06; Nb 18.17, 13.39, 14.15; Mo 15.89, 23.18, 20.08; W 8.13, 7.59, 9.12; S 27.68, 27.09, 24.84; O 16.33, 15.66, 13.36; H (calc.) 1.03, 0.99, 0.89; total 99.09, 99.08, 99.15. The empirical formulae calculated on the basis of 2 S a.p.f.u. are: ekplexite:  $(\text{Nb}_{0.45}\text{Mo}_{0.38}\text{W}_{0.10}\text{V}_{0.04})_{\Sigma 0.97}\text{S}_2 \cdot (\text{Mg}_{0.60}\text{Al}_{0.37}\text{Fe}_{0.02})_{\Sigma 0.99}(\text{OH})_{2.36}$ ; kaskasite:  $(\text{Mo}_{0.57}\text{Nb}_{0.34}\text{W}_{0.10}\text{V}_{0.01})_{\Sigma 1.02}\text{S}_2 \cdot (\text{Mg}_{0.58}\text{Al}_{0.32}\text{Fe}_{0.06}\text{Mn}_{0.01})_{\Sigma 0.97}(\text{OH})_{2.32}$ ; manganokaskasite:  $(\text{Mo}_{0.54}\text{Nb}_{0.39}\text{W}_{0.13}\text{V}_{0.01})_{\Sigma 1.07}\text{S}_2 \cdot (\text{Mn}_{0.54}\text{Al}_{0.29}\text{Fe}_{0.10}\text{Mg}_{0.01})_{\Sigma 0.94}(\text{OH})_{2.28}$ . All three minerals are trigonal, space groups  $P3m1$ ,  $P3m1$  or  $P321$ , one-layer polytypes ( $Z = 1$ ). Their structures are non-commensurate and consist of the  $\text{MeS}_2$ -type ( $\text{Me} = \text{Nb}, \text{Mo}, \text{W}$ ) sulfide modules and the brucite-type hydroxide modules. Parameters of the sulfide (main) sub-lattices ( $a, c$  in Å,  $V$  in Å<sup>3</sup>) are: 3.262(2), 11.44(2), 105.4(4) (ekplexite); 3.220(2), 11.47(2), 102.8(4) (kaskasite); 3.243(3), 11.61(1), 105.8(3) (manganokaskasite). Parameters of the hydroxide sub-lattices ( $a, c$  in Å,  $V$  in Å<sup>3</sup>) are: 3.066(2), 11.52(2), 93.8(4) (ekplexite); 3.073(2), 11.50(2), 94.0(4) (kaskasite); 3.118(3), 11.62(1), 97.9(2) (manganokaskasite). Ekplexite was

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named from the Greek word  $\acute{\epsilon}\kappa\pi\lambda\eta\xi\eta$  meaning surprise, for its exotic combination of major chemical constituents, kaskasite after the discovery locality and manganokaskasite as a Mn analogue of kaskasite.

**KEYWORDS:** ekplexite, kaskasite, manganokaskasite, new mineral, valleriite group, hydroxide-sulfide, hybrid mineral, non-commensurate structure, niobium, molybdenum, fenite, alkaline rock, Khibiny, Kola peninsula.

## Introduction

HYDROXIDE-SULFIDE species belong to the family of hybrid minerals with modulated layered structures based on the alternation of sulfide and hydroxide modules (blocks). Valleriite, ferrovalleriite, haapalaite, yushkinite and three new minerals (ekplexite, kaskasite and manganokaskasite) described herein demonstrate trigonal or hexagonal symmetry with similar unit-cell dimensions. All of these minerals belong to the valleriite group (Tables 1a,b). Three other known hydroxide-sulfide minerals tochilinite, ferrotouchilinite and vyalosvite (Table 1c) are also related structurally to the valleriite group but differ in the structure of sulfide blocks and stacking of sulfide and hydroxide modules (Organova, 1989) which is reflected in their different symmetry and unit-cell parameters.

The general formula of all these minerals can be represented as  $mMeS_x \cdot nA(OH)_y$ . Prior to the current study only species with  $Me = Fe, Cu, Ni, V$  and  $A = Mg, Fe^{2+}, Al, Ca$  as essential constituents were known (Tables 1b,c). The discovery of three valleriite-group minerals with species-defining  $Me = Nb, Mo$  in the sulfide block was unexpected and due to that the first mineral was named ekplexite from the Greek word for surprise:  $\acute{\epsilon}\kappa\pi\lambda\eta\xi\eta$ . The combination of Nb, Mo, Mg, Al,  $S^{2-}$  and (OH) as major chemical constituents was previously unknown for natural and synthetic compounds. The second new mineral of the triad was named kaskasite after the discovery locality, Mount Kaskasnyunchorr in Khibiny. The name of this mountain means 'juniper mountain spur' (kaskas – juniper, nyun – spur, chorr – mountain range) in the Saami language of the Kola aboriginal people. Manganokaskasite is named as a manganese (with Mn instead of Mg) analogue of kaskasite. These names are spelled as  $\acute{\epsilon}\kappa\pi\lambda\epsilon\kappa\sigma\iota\tau$ ,  $\kappa\alpha\sigma\kappa\alpha\sigma\iota\tau$  and  $\mu\alpha\gamma\gamma\alpha\kappa\alpha\sigma\kappa\alpha\sigma\iota\tau$ , respectively, in Russian Cyrillic.

All three minerals and their names have been approved by the International Mineralogical Association (IMA) Commission on New Minerals, Nomenclature and Classification. The

type specimens are deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue numbers 93628 for ekplexite (IMA 2011-082), 94231 for kaskasite (IMA 2013-025) and 94232 for manganokaskasite (IMA 2013-026).

## Valleriite group: background information

Valleriite-group minerals are trigonal or hexagonal hybrid hydroxide-sulfides with non-commensurate (misfit) layered structures. Valleriite was the first and most studied mineral in the group. A history of its studies in the 'pre-structure' period was reported in detail by Evans *et al.* (1964) and by Evans and Allmann (1968). The crystal structure of valleriite is based on the alternation of sulfide and hydroxide modules with  $[(FeCu)_2S_2]$  and  $[(Mg_{1-x}Al_x)(OH)_{2+x}]$  compositions, respectively. Both modules are two-dimensional (2D). The hydroxide module can be considered as a derivative of the brucite structure, whereas the sulfide module demonstrates a nukundamite-like structure (Evans and Allmann, 1968; Organova, 1989; Makovicky, 2006; Pekov *et al.*, 2013b). The valleriite structure was described in terms of two separate trigonal sub-lattices. The sulfide module corresponds to  $R\bar{3}m$ ,  $a = 3.792$ ,  $c = 34.10$  Å, whereas the hydroxide module is also trigonal, but has  $P\bar{3}m1$ ,  $a = 3.07$ ,  $c = 11.37$  Å (Evans and Allmann, 1968). The 00l reflections correspond to both sub-lattices on the X-ray diffraction patterns of valleriite, while some of the other reflections are subdivided into two independent patterns that correspond to sulfide and hydroxide modules. The former is significantly more intense (there are more electrons in the sulfide module compared to the hydroxide one). These strong reflections are generally accepted to be 'major' and are species-characterizing for valleriite and related minerals (Tables 1a–c).

A valleriite modification with the one-layer sulfide module ( $a = 3.787$ ,  $c = 11.33$  Å) was first described by Organova (1989). Valleriite is known to form two polytype modifications in

## EKPLEXITE, KASKASITE AND MANGANOKASKASITE, THREE NEW MINERALS

TABLE 1a. Comparative data for natural, layered, hybrid hydroxide-sulfides: new valleriite-group members with Nb or Mo predominant in the sulfide module.

Mineral Formula	Ekplexite (Nb,Mo)S <sub>2</sub> · (Mg <sub>1-x</sub> Al <sub>x</sub> )(OH) <sub>2+x</sub>	Kaskasite (Mo,Nb)S <sub>2</sub> · (Mg <sub>1-x</sub> Al <sub>x</sub> )(OH) <sub>2+x</sub>	Manganokaskasite (Mo,Nb)S <sub>2</sub> · (Mn <sub>1-x</sub> Al <sub>x</sub> )(OH) <sub>2+x</sub>
Crystal system	Trigonal	Trigonal	Trigonal
Space group	<i>P</i> $\bar{3}$ <i>m</i> 1, <i>P</i> 3 <i>m</i> 1 or <i>P</i> 321	<i>P</i> $\bar{3}$ <i>m</i> 1, <i>P</i> 3 <i>m</i> 1 or <i>P</i> 321	<i>P</i> $\bar{3}$ <i>m</i> 1, <i>P</i> 3 <i>m</i> 1 or <i>P</i> 321
Unit-cell data			
sulfide sub-lattice			
<i>a</i> (Å)	3.262(2)	3.220(2)	3.243(3)
<i>c</i> (Å)	11.44(2)	11.47(2)	11.61(1)
<i>V</i> (Å <sup>3</sup> )	105.4(4)	102.8(4)	105.8(3)
<i>Z</i>	1	1	1
hydroxide sub-lattice			
<i>a</i> (Å)	3.066(2)	3.073(2)	3.118(2)
<i>c</i> (Å)	11.52(2)	11.50(2)	11.62(1)
<i>V</i> (Å <sup>3</sup> )	93.8(4)	94.0(4)	97.9(2)
<i>Z</i>	1	1	1
Strongest reflections of the X-ray powder pattern:	11.40, 100	11.46, 97	11.39, 85
<i>d</i> (Å), <i>I</i>	5.65, 56	5.72, 100	5.66, 100
	2.812, 21	2.786, 51	2.769, 43
	2.647, 9	2.627, 7	2.663, 25
	1.622, 11	2.219, 7	2.455, 18
		1.613, 33	1.608, 23
		1.557, 10	1.559, 13
<i>D</i> (calc.), g cm <sup>-3</sup>	3.63	3.83	4.09
Optical data			
( <i>R</i> <sub>max</sub> – <i>R</i> <sub>min</sub> , %)			
470 nm	18.9–8.7	21.5–8.6	25.6–10.4
546 nm	19.4–8.7	21.6–9.2	25.0–10.5
589 nm	19.0–8.8	21.5–9.2	24.7–10.6
650 nm	18.2–8.6	21.3–8.9	24.5–10.6
References	This work	This work	This work

nature, with the one-layer (*P* cell,  $c \approx 11.3$  Å) and the three-layer (*R* cell,  $c \approx 34$  Å) sulfide modules. They can be distinguished by the presence or absence of characteristic *h0l* reflections on the X-ray powder-diffraction patterns. The one-layer polytype is characterized by the presence of reflections with  $d_{101} \approx 3.15$ ,  $d_{103} \approx 2.5$  and  $d_{104} \approx 2.143$  Å. The X-ray powder pattern of the three-layer polytype contains reflections  $d_{104} \approx 3.05$ ,  $d_{105} \approx 2.95$  and  $d_{205} \approx 1.60$  Å (Organova, 1989; our studies). Ferrovaleriite, an analogue of valleriite with Fe<sup>2+</sup> instead of Mg and Al in the hydroxide module, is also represented in nature by both three-layer and one-layer polytypes (Pekov *et al.*, 2013*b*). The only three-layer modification

reported was for haapalaite (Huhma *et al.*, 1973). Another valleriite-related mineral with V in the sulfide module, yushkinite, belongs to the one-layer polytype (Makeev *et al.*, 1984).

Ekplexite, kaskasite and manganokaskasite are close to other valleriite-group minerals in terms of general stoichiometry, symmetry, X-ray diffraction patterns, morphology, physical properties and optical data.

### Occurrence

Ekplexite, kaskasite and manganokaskasite were found at Mount Kaskasnyunchorr in the central part of the Khibiny alkaline complex, Kola Peninsula, Russia. They occur in fenites formed

Table 1b. Comparative data for natural, layered, hybrid hydroxide-sulfides: valleriite-group members with Fe or V dominant in the sulfide part.

Mineral Formula	Valleriite 2(Fe,Cu)S· 1.5[(Mg <sub>1-x</sub> Al <sub>x</sub> )(OH) <sub>2+x</sub> ]	Ferrovalleriite* 2(Fe,Cu)S· 1.5Fe(OH) <sub>2</sub>	Haapaite 2(Fe,Ni)S· 1.5(Mg,Fe)(OH) <sub>2</sub>	Yushkinitite V <sub>1.0-1.2</sub> S <sub>2</sub> · 1.0-1.2[(Mg <sub>1-x</sub> Al <sub>x</sub> )(OH) <sub>2+x</sub> ]**
Crystal system	Trigonal	Trigonal	Hexagonal	Trigonal
Space group	<i>R</i> 3̄ <i>m</i>	<i>R</i> 3̄ <i>m</i> , <i>R</i> 3 <i>m</i> or <i>R</i> 32	<i>P</i> cell (?)	<i>P</i> 3̄ <i>m</i> 1 (?)
<i>a</i> (Å)***	3.7-3.8	3.79	3.64	3.21
<i>c</i> (Å)	34.1-34.4	34.06	34.02	11.3
<i>V</i> (Å <sup>3</sup> )	420-430	424	390	100
<i>Z</i>	3	3	3	1
<i>a</i> <sub>hydrox</sub> (Å)****	3.06-3.12	3.202	no data	3.06
Strongest reflections of the X-ray powder pattern:	11.4, 100	11.42, 18	11.3, 100	11.4, 30
<i>d</i> (Å), <i>I</i>	3.80, 50	5.69, 100	5.67, 90	5.68, 100
	3.27, 60	3.76, 60	3.18, 80	2.76, 80
	3.23, 50	3.27, 80	1.841, 70	1.596, 40
	2.846, 50	3.13, 40	1.821, 70	1.575, 60
	1.885, 50	2.84, 60		
	1.860, 50	1.894, 80		
		1.867, 70		
<i>D</i> (g cm <sup>-3</sup> )		3.1-3.2	3.57 (calc.)	2.94 (meas.)
References	Evans <i>et al.</i> (1964); Evans and Allmann (1968); Organova (1989)	Pekov <i>et al.</i> (2013b)	Huhma <i>et al.</i> (1973)	Makeev <i>et al.</i> (1984); Mošlò <i>et al.</i> (1999)

\* All data are given for the main polytype modification with space group *R*3̄*m*, *R*3*m* or *R*32, *a* = 3.792, *c* = 34.06 Å.

\*\* Formula calculated on the basis of 2 S a.p.f.u. for better comparison with other minerals in this Table as it was written originally as V<sub>1-x</sub>S<sub>2</sub>*n*[(Mg<sub>x</sub>Al)(OH)<sub>2</sub>]

(Makeev *et al.*, 1984).

\*\*\* For the major sub-lattice corresponding to the sulfide module.

\*\*\*\* The *a* parameter corresponding to the hydroxide module.

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Table 1c. Comparative data for natural layered hybrid hydroxide-sulfides: monoclinic and orthorhombic minerals related to the valleriite group.

Mineral Formula	Tochilinite 6FeS· 5(Mg,Fe)(OH) <sub>2</sub>	Ferrotchilinite 6FeS· 5Fe(OH) <sub>2</sub>	Vyalsovite FeS· Ca(OH) <sub>2</sub> ·Al(OH) <sub>3</sub>
Crystal system	Monoclinic*	Monoclinic	Orthorhombic
Space group	<i>P2/m</i> , <i>Pm</i> or <i>P2</i>	<i>C2/m</i> , <i>Cm</i> or <i>C2</i>	<i>C</i> -cell
<i>a</i> (Å)	5.2–5.4	5.463	14.20
<i>b</i> (Å)	15.3–15.9	15.865	20.98
<i>c</i> (Å)	10.7–10.9	10.825	5.496
β (°)	93.6–95.8	93.7	
<i>V</i> (Å <sup>3</sup> )	890–920	936	1637
<i>Z</i>	2	2	8
Strongest reflections of the X-ray powder pattern:	10.64, 30	10.83, 13	5.40, 100
<i>d</i> (Å), <i>I</i>	5.36, 100	5.39, 100	4.76, 40
	2.605, 30	2.696, 12	2.16, 50
	1.835, 50	2.524, 12	1.676, 40
	1.559, 40	1.834, 11	
<i>D</i> (g cm <sup>-3</sup> )	2.9–3.1	3.47 (calc.)	1.96 (calc.)
References	Organova <i>et al.</i> (1971, 1972); Jambor (1976); Or- ganova (1989)	Pekov <i>et al.</i> (2013a)	Evstigneeva <i>et al.</i> (1992)

\* In early studies (Organova *et al.*, 1971, 1972), tochilinite was considered as triclinic (pseudo-monoclinic) space group *C1*, *a* = 5.37, *b* = 15.65, *c* = 10.72 Å, α = 90°, β = 95°, γ = 90°, *V* = 897.5 Å<sup>3</sup>.

as a result of the influence of a peralkaline fluid (a source of Nb) on a large (~50 × 100 m) xenolith of alumina-rich metamorphic rocks (metapelites) located inside a huge intrusion of aegirite nepheline syenite (Men'shikov, 1978; Yakovleva *et al.*, 2010). Some authors consider that mafic material is involved in the fenitization (as an assumed source of Mg, Cr and V) and was located initially within the xenolith (Barkov *et al.*, 2006).

These mineralogically unusual fenites are massive grey rocks consisting of mainly alkali feldspars of the orthoclase–anorthoclase series (both homogeneous and exsolved, with micro-perthitic structure) and nepheline. Their relative amounts are variable as well as the size of grains: typically from 0.1 mm to 1 cm. A characteristic feature of these fenites is the presence of isolated prismatic or tabular crystals (up to 1.5 cm) of blue Ba-bearing (up to 4.1 wt.% BaO) and almost Fe- and Mn-free (<0.05 wt.% FeO + MnO) fluorophlogopite (1–3 vol.% of the rock). Other non-sulfide minerals are corundum (sometimes up to 5 vol.% of the rock) and accessory rutile, fluorite, zircon, muscovite, fluorapatite, monazite-(Ce), chrysoberyl and graphite.

The sulfide mineralization in these fenites is abundant and very unusual. The major sulfide mineral is pyrrhotite: sporadically its content reaches 15–20 vol.% of the rock. In some areas only fresh, unaltered pyrrhotite is observed whereas in other cases it is altered to pyrite or, less commonly, to marcasite. Both the disulfides form replacement rims or partial to complete pseudomorphs after pyrrhotite. The most interesting feature of these minerals is their high Ti content: up to 3 wt.% Ti and 2 wt.% V in pyrrhotite, up to 4 wt.% Ti and 0.7 wt.% V in pyrite and marcasite replacing such pyrrhotite. This is the first terrestrial occurrence of the Ti-enriched varieties of these sulfides (Barkov *et al.*, 1997; Yakovleva *et al.*, 2010). Ti-free pyrrhotite, pyrite and marcasite also occur here, as well as minor amounts of chalcopyrite and galena. The first natural Nb sulfide edgarite FeNb<sub>3</sub>S<sub>6</sub>, both W-free and W-rich molybdenite [(Mo,W)S<sub>2</sub> containing up to 23 wt.% W], Mo-free tungstenite WS<sub>2</sub> and Fe-enriched alabandite [(Mn,Fe)S with 6–10 wt.% Fe] were described from this locality (Barkov *et al.*, 2000a,b; Yakovleva *et al.*, 2010). Our recent studies

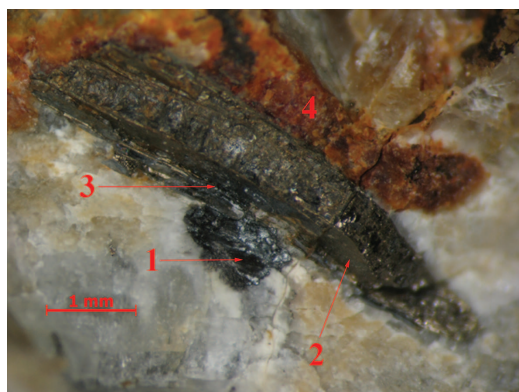


FIG. 1. Nest of ekplexite (1) in a nepheline-orthoclase fenite; (2) Ti-bearing pyrrhotite partially replaced by Ti-bearing pyrite, (3) iron-black flaky edgarite epitaxially overgrowing pyrrhotite; brown-orange area, (4) a micro-cavernous aggregate of the same rock-forming aluminosilicates coloured by 'limonite'. Photo: I.V. Pekov and A.V. Kasatkin.

revealed the presence of a Nb-rich variety of molybdenite  $(\text{Mo,Nb,W})\text{S}_2$  (first terrestrial occurrence; up to 17 wt.% Nb and up to 13 wt.% W: our unpublished data) and three new valleriite-group minerals with Nb, Mo and W in the sulfide portion: ekplexite, kaskasite and manganokaskasite described in this paper. Thus, five endemic Nb-rich sulfides ( $>10$  wt.% Nb) were discovered in this assemblage. Ekplexite, manganokaskasite and Nb-bearing molybdenite are rare, whereas edgarite and kaskasite are relatively common minerals at this locality.

This fenite locality is unique in terms of sulfide mineralization and formation conditions: high activity of  $\text{S}^{2-}$  and, unusually for terrestrial objects, extremely low oxygen fugacity (Barkov *et al.*, 1997; Drábek *et al.*, 2010; Yakovleva *et al.*, 2010). These conditions lead to some lithophile metals such as W, Nb and Ti demonstrating chalcophile behaviour resulting in the formation of sulfides.

Ekplexite, kaskasite and manganokaskasite (and probably edgarite) are hydrothermal minerals formed during the late stage of the evolution of the fenite rocks, with simultaneous hydrothermal alteration of pyrrhotite to pyrite and marcasite. All three new minerals occur in close association with significantly disulfidized pyrrhotite and edgarite (Figs 1–4). These valleriite-group minerals can be considered as indicators of the low-temperature hydrothermal alteration of a rock; tochilinites play the same indicator role in meteorites (Browning and Bourcier, 1996; Pekov *et al.*, 2013a).

Ekplexite, kaskasite, manganokaskasite and edgarite are relatively stable to the effects of weathering. Some observed samples have pyrrhotite, pyrite and marcasite partially altered to aggregates of 'limonite' ( $\pm$  native S) on the exposed surface, while the three new hydroxide-sulfide minerals associated closely with them remain fresh (Fig. 2).

### General appearance

Ekplexite was found initially as isolated, lenticular nests up to  $0.2 \text{ mm} \times 1 \text{ mm} \times 1 \text{ mm}$  in a nepheline-

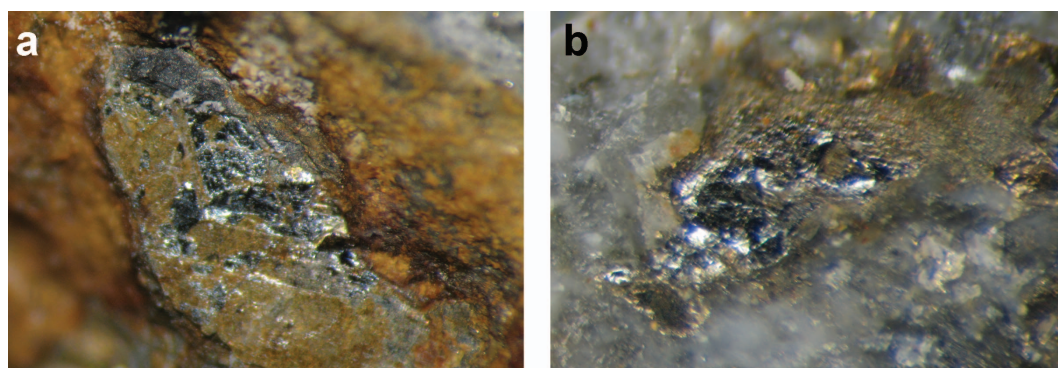


FIG. 2. Iron-black, lustrous flakes of kaskasite (a) and manganokaskasite (b) epitaxially overgrowing Ti-bearing pyrrhotite partially replaced by Ti-bearing pyrite. The host rock is a nepheline-orthoclase fenite with corundum; brown areas on (a) are 'limonite' crusts. Field of view: (a) 2.7 mm, (b) 1.5 mm. Photo: I.V. Pekov and A.V. Kasatkin.

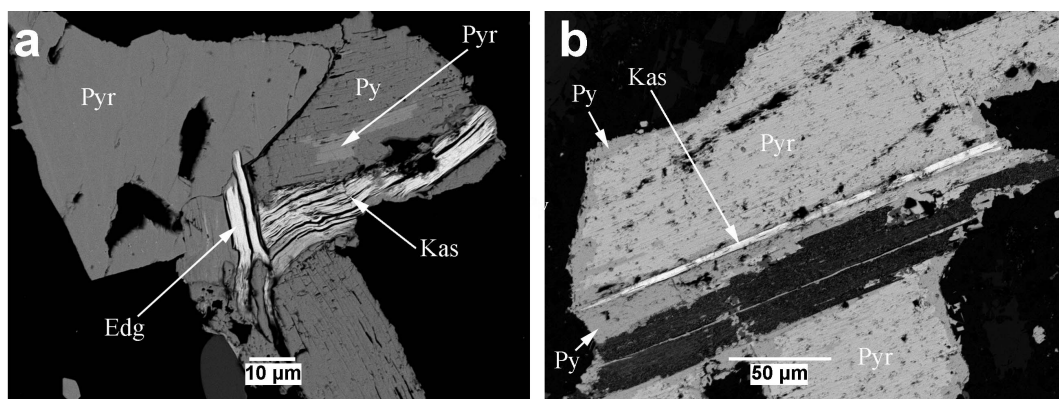


FIG. 3. Epitaxial intergrowths of kaskasite (Kas) lamellae (cross sections) with Ti-bearing pyrrhotite (Pyr) partially replaced by Ti-bearing pyrite (Py). Edg – edgarite; dark areas – host nepheline-feldspar fenite. Polished sections, scanning electron microscopy (SEM) backscatter (BSE) images.

feldspar fenite, in close association with edgarite and Ti-bearing varieties of pyrrhotite, pyrite and marcasite (Fig. 1). The nests consist of near-parallel, radiating or chaotic aggregates of mica-like, curved (corrugated) flakes of ekplexite, typically no more than 0.1 mm across and 0.01 mm thick. Later ekplexite was found as flakes up to 0.02 mm × 0.5 mm × 0.7 mm epitaxially overgrowing Ti-bearing pyrrhotite, as was kaskasite and manganokaskasite (see below).

Kaskasite commonly occurs as separate lamellar or flaky, mica-like crystals flattened on

[001] and with their parallel or near-parallel ‘stacks’ up to 1 mm × 1.5 mm in area and up to 0.03 mm thick epitaxially overgrowing Ti-bearing pyrrhotite that is usually partially replaced by Ti-bearing pyrite and marcasite (Fig. 2a). The {001} faces of kaskasite are coplanar to the {001} faces of pyrrhotite. Kaskasite occurs on the surface of pyrrhotite (Figs 2a and 3a) or in the (001) parting fractures inside pyrrhotite crystals (Fig. 3b). Both parallel and misoriented intergrowths of kaskasite with edgarite are common. Lamellae of kaskasite are usually irregularly shaped, but very rarely fragments of a crude hexagonal shape are observed. Striations on the {001} faces are typical; three systems of streaks cross at 60°. Rarely, kaskasite forms near-parallel, radiating or chaotic aggregates of flakes up to 0.1 mm × 0.15 mm inside pyrrhotite nests.

Manganokaskasite, like edgarite and kaskasite, forms lamellar to flaky crystals, typically overgrowing epitaxially Ti-bearing pyrrhotite (usually partially replaced by Ti-bearing pyrite and marcasite) (Fig. 2b). Its mica-like flakes and their near-parallel stacks are up to 0.5 mm × 1 mm in area and up to 0.02 mm thick. Manganokaskasite also forms clusters up to 0.05 × 0.15 mm on pyrrhotite (Fig. 4).

Curved or wavy and corrugated lamellae of kaskasite (Fig. 5) and manganokaskasite were observed in small open cracks. Numerous cleavage cracks (Figs 3a and 4) are typical for individual crystals of all three new minerals.

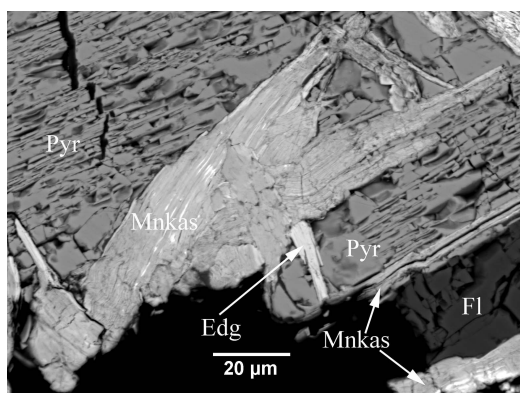


FIG. 4. Oriented (epitaxial) lamellae (cross sections) and misoriented clusters of manganokaskasite (Mnkas) in Ti-bearing pyrrhotite (Pyr) with edgarite (Edg) and fluorite (Fl); the black area is the host nepheline-feldspar fenite. Polished section, SEM (BSE) image.

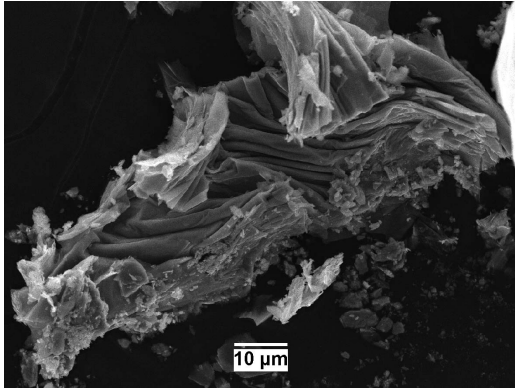


FIG. 5. SEM image of a wavy, corrugated, flaky aggregate of kaskasite.

### Physical properties

All three new minerals are opaque, iron-black, with metallic lustre and black streak. They show {001} perfect, mica-like cleavage. Fracture is laminated. The flakes are very flexible, easily bent and are inelastic. The minerals are very soft, like graphite: their Mohs hardness is  $\sim 1$ . The micro-indentation hardness values, measured by means of the PMT-3 instrument (LOMO, Russia) using a VHN load of 5 g, are  $64 \text{ kg mm}^{-2}$  (only one measurement was successful) for ekplexite and  $36 \text{ kg mm}^{-2}$  (range 34–38 for two measurements) for kaskasite.

Density could not be measured because aggregates of the minerals are small and contain numerous micro-cracks. The calculated density values are  $3.63$ ,  $3.83$  and  $4.09 \text{ g cm}^{-3}$  for ekplexite, kaskasite and manganokaskasite, respectively.

Ekplexite, kaskasite and manganokaskasite are visually indistinguishable from each other and from edgarite, tungstenite and graphite. They are also macroscopically similar to molybdenite but the latter has a lighter, lead-grey colour. All other known sulfide-hydroxide minerals (Tables 1*b* and 1*c*) are different in colour: yushkinite and vyalsovite are violet (bornite-like) whereas others show distinct bronze hue.

### Optical data

Under the microscope all three new minerals are similar but not identical. They have slightly different reflectance values and pleochroism colours. In reflected light all these minerals are

grey (light to dark grey, depending on section orientation), without internal reflections. Anisotropism is very strong. Bireflectance is also very strong, with  $\Delta R = 10.2$ ,  $12.4$  and  $14.1\%$  (589 nm) for ekplexite, kaskasite and manganokaskasite, respectively. Pleochroism is strong, from light grey to dark grey for ekplexite, from light grey with a yellowish hue to grey for kaskasite and from light yellowish to blue grey for manganokaskasite.

The reflectance values (Table 2) were measured by means of a MSF-21 microspectrophotometer (LOMO, Russia) in air using the SiC standard (Zeiss, No. 545). The configuration of spectral reflectance curves for all three minerals are close.

### Raman spectroscopy

Direct evidence for the presence of OH groups in the new minerals was obtained by Raman spectroscopy. The Raman spectrum of ekplexite was obtained using an InSpectr R532 spectrometer with a green laser (532 nm) at room temperature. The power of the laser beam on the sample was  $\sim 3 \text{ mW}$ . The spectrum was recorded using the EnSpectr expert mode program in the range  $100\text{--}4000 \text{ cm}^{-1}$  with the use of a holographic diffraction grating with 1200 lines/cm and a spectral resolution equal to  $5\text{--}8 \text{ cm}^{-1}$ . The diameter of the focal spot on the sample was  $\sim 15 \mu\text{m}$ . Some variously oriented flakes were observed in the focal spot. The backscattered Raman signal was collected with a  $\times 40$  objective; signal acquisition time for a single scan was 1 s and the signal was averaged over 30 scans.

The Raman spectrum of ekplexite (Fig. 6) demonstrates strong bands due to OH groups. Two distinct absorption bands with maxima at  $3530$  and  $3326 \text{ cm}^{-1}$  correspond to O–H stretching vibrations and the wide band at  $707 \text{ cm}^{-1}$ , which is probably two partially overlapped bands, to  $\text{Mg}\cdots\text{O}\text{--}\text{H}$  and  $\text{Al}\cdots\text{O}\text{--}\text{H}$  bending vibrations. Narrow bands at  $526$  and  $438 \text{ cm}^{-1}$  are due to  $\text{Al}\cdots\text{O}$  and  $\text{Mg}\cdots\text{O}$  stretching vibrations, respectively. The absence of absorption bands in the range  $1200\text{--}1700 \text{ cm}^{-1}$  indicates the absence of  $\text{H}_2\text{O}$  molecules, as well as other H-bearing groups in ekplexite and the absence of bands in the range  $750\text{--}1300 \text{ cm}^{-1}$  indicates the absence of S–O, Mo–O and Nb–O.

The Raman spectrum of brucite  $\text{Mg}(\text{OH})_2$  reveals three absorption bands with maxima at



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 TABLE 2. The reflectance data ( $R$ , %) of ekplexite, kaskasite and manganokaskasite.

$\lambda$ (nm)	— Ekplexite —		— Kaskasite —		Manganokaskasite	
	$R_{\max}$	$R_{\min}$	$R_{\max}$	$R_{\min}$	$R_{\max}$	$R_{\min}$
400	11.8	7.8	17.3	6.4	22.5	10.0
420	14.7	8.3	19.4	7.3	24.3	10.2
440	17.1	8.6	20.7	8.0	25.1	10.3
460	18.5	8.7	21.4	8.5	25.5	10.4
<b>470</b>	<b>18.9</b>	<b>8.7</b>	21.5	<b>8.6</b>	<b>25.6</b>	10.4
480	19.2	8.7	21.6	8.8	25.7	10.5
500	19.5	8.6	21.7	8.9	25.6	10.5
520	19.6	8.6	21.7	9.1	25.3	10.5
540	19.5	8.7	21.6	9.2	25.1	10.5
<b>546</b>	<b>19.4</b>	<b>8.7</b>	21.6	<b>9.2</b>	<b>25.0</b>	10.5
560	19.3	8.7	21.6	9.2	24.9	10.5
580	19.1	8.8	21.6	9.2	24.8	10.6
<b>589</b>	19.0	8.8	21.5	9.2	24.7	10.6
600	18.9	8.8	21.5	9.2	24.7	10.6
620	18.6	8.7	21.4	9.1	24.5	10.6
640	18.3	8.6	21.4	9.0	24.5	10.6
<b>650</b>	<b>18.2</b>	<b>8.6</b>	21.3	8.9	24.5	10.6
660	18.1	8.6	21.3	8.7	24.5	10.6
680	17.8	8.5	21.2	8.6	24.4	10.7
700	17.6	8.6	21.1	8.3	24.4	10.7

Note: The values for wavenumbers ( $\lambda$ ) recommended by the IMA Commission on Ore Microscopy (COM) are given in bold.

3652, 725 and 443  $\text{cm}^{-1}$  (Dawson *et al.*, 1973) corresponding to O–H stretching,  $\text{Mg}\cdots\text{O}-\text{H}$  bending and  $\text{Mg}\cdots\text{O}$  stretching vibrations, respectively. The Raman spectrum of gibbsite  $\text{Al}(\text{OH})_3$

is more complex. It contains two groups of bands corresponding to O–H stretching vibrations of OH groups (Wang and Johnston, 2000): (1) O–H vibrations in (001) plane (3623, 3526 and 3519

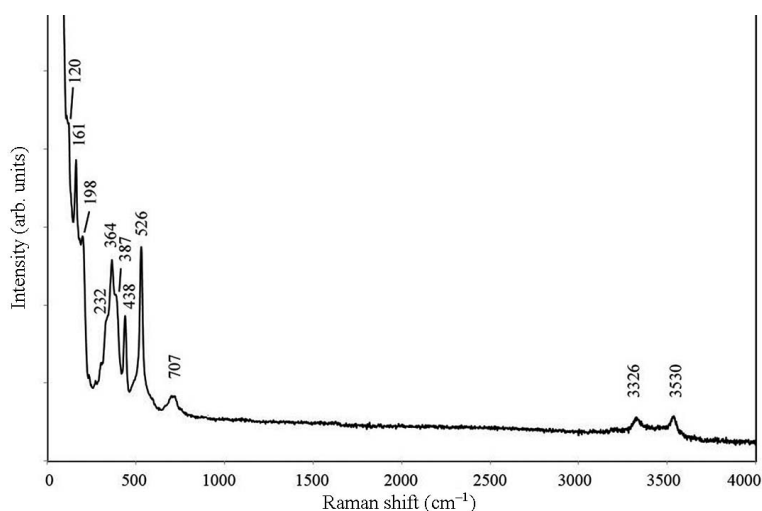


FIG. 6. Raman spectrum of ekplexite.

$\text{cm}^{-1}$ ); (2) O–H vibrations parallel to the *c* axis (3433, 3370 and 3363  $\text{cm}^{-1}$ ). The presence of two distinct bands corresponding to O–H stretching vibrations in ekplexite can be assumed tentatively to be due to the presence of both  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  cations in significant amounts in a brucite module.

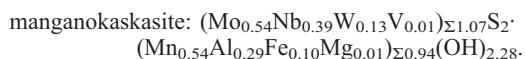
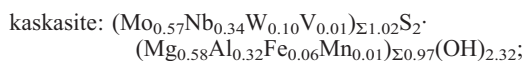
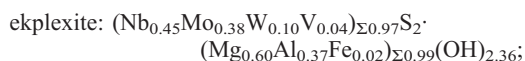
Hybrid sulfide-hydroxides have been studied previously using infrared (IR) spectroscopy. Their IR spectra are similar in general pattern to the Raman spectrum of ekplexite. The IR spectrum for ferrovalleriite  $2(\text{Fe,Cu})\text{S}\cdot 1.5\text{Fe}(\text{OH})_2$  contains absorption bands with maxima at 3537, 708, 580 and 481  $\text{cm}^{-1}$  (Pekov *et al.*, 2013b), tochilinite  $6\text{FeS}\cdot 5(\text{Mg,Fe})(\text{OH})_2$  at 3625, 3568, 732, 690, 562 and 420  $\text{cm}^{-1}$  and ferrotchilinite  $6\text{FeS}\cdot 5\text{Fe}(\text{OH})_2$  at 3515, 3457, 801, 615 and 477  $\text{cm}^{-1}$  (Pekov *et al.*, 2013a). The hydrous sulfides containing  $\text{H}_2\text{O}$  molecules instead of OH groups demonstrate rather different IR spectra. A good example is wilhelmsramsayite  $\text{Cu}_3\text{FeS}_3\cdot 2\text{H}_2\text{O}$  with the following absorption bands: 3240br (broad), 3177br, 3090br, 1578  $\text{cm}^{-1}$  (Pekov *et al.*, 2006). Strong bands in the range 3000–3300  $\text{cm}^{-1}$  correspond to O–H stretching vibrations. However these bands are characterized by significantly lower frequencies in comparison with corresponding bands in the IR spectra of hydroxide-sulfides, brucite and gibbsite. The presence of a narrow, relatively strong band at 1578  $\text{cm}^{-1}$  (bending vibrations of molecular  $\text{H}_2\text{O}$ ) and the absence of distinct bands in the range 350–1500  $\text{cm}^{-1}$  clearly demonstrate the presence of  $\text{H}_2\text{O}$  molecules and an absence of OH groups and  $\text{H}^+$  cations in wilhelmsramsayite. In particular, the absence of strong bands in the range 350–600  $\text{cm}^{-1}$  indicates the absence of  $\text{Me}\cdots\text{O}$  and  $\text{Me}\cdots\text{O}-\text{H}$  ( $\text{Me} = \text{Cu, Fe}$ ) bonds in wilhelmsramsayite. Unlike the latter, the spectra of valleriite-group members and other hydroxide-sulfides contain such bands.

## Chemical data

Chemical data for all three new minerals (Table 3) were obtained using a JEOL JSM-6480LV scanning electron microscope equipped with the INCA-Wave 500 wavelength-dispersive spectrometer (WDS). The operating voltage was 15 kV, beam current was 30 nA and the electron beam diameter was rastered on an area  $5 \times 5 \mu\text{m}$ . The following standards and lines were used: MgO (MgK $\alpha$ ),  $\text{Al}_2\text{O}_3$  (AlK $\alpha$ ), diopside (CaK $\alpha$ ), V (VK $\alpha$ ), Mn (MnK $\alpha$ ), FeS (FeK $\alpha$ , SK $\alpha$ ),  $\text{Cs}_2\text{Nb}_4\text{O}_{11}$  (NbL $\alpha$ ),  $\text{CaMoO}_4$  (MoL $\alpha$ , OK $\alpha$ ),

$\text{CaWO}_4$  (WM $\alpha$ ) and  $\text{SrSO}_4$  (OK $\alpha$ ). The analytical lines SK $\alpha$  and MoL $\alpha$  overlap partially, hence the Mo content was also measured using the MoK $\alpha$  line at 30 kV and 30 nA beam current and a very similar result was obtained. Hydrogen content was calculated by stoichiometry, based on the assumption that both O and H are present only as OH groups.

The empirical formulae were calculated on the basis of two S a.p.f.u., from the assumption that the sulfide blocks of the minerals are represented by  $\text{MeS}_2$  with  $\text{Me} = \text{Nb, Mo, W}$  (see below). The empirical formulae of the holotype samples after grouping the constituents in the sulfide and the hydroxide parts are as follows:



The amount of OH groups was calculated for each mineral on the basis of measured O content. The calculation of positive charge for all cations in the hydroxide modules (sums for Mg, Al,  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$ ; V was placed in the sulfide module, by analogy with yushkinite) gave +2.35, +2.26 and +2.17 for ekplexite, kaskasite and manganokaskasite, respectively. These obtained values are close to –2.36, –2.32 and –2.28 corresponding to the calculated amounts of OH groups on the basis of measured O contents for these minerals. This observation confirms the correctness of electron-microprobe analyses including O determination. The (Nb+Mo+W+V):S atomic ratio values are very close to 1:2 for all three new minerals and, together with a good charge balance in the hydroxide parts of the formulae, provide an indication of the  $\text{MeS}_2$  composition of the sulfide modules.

The simplified formulae are:  $(\text{Nb,Mo})\text{S}_2 \cdot (\text{Mg}_{1-x}\text{Al}_x)(\text{OH})_{2+x}$  for ekplexite,  $(\text{Mo,Nb})\text{S}_2 \cdot (\text{Mg}_{1-x}\text{Al}_x)(\text{OH})_{2+x}$  for kaskasite and  $(\text{Mo,Nb})\text{S}_2 \cdot (\text{Mn}_{1-x}\text{Al}_x)(\text{OH})_{2+x}$  for manganokaskasite.

The electron-probe data for >20 samples studied indicate the existence of a continuous solid-solution series between ekplexite and kaskasite, the magnesian minerals (Fig. 7). On the other hand, there are no data to suggest that the kaskasite–manganokaskasite solid-solution series exists: all analyses indicate that kaskasite is Mn-

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TABLE 3. Chemical compositions of ekplexite, kaskasite and manganokaskasite (the holotype samples; ranges are in parentheses).

Constituent	Ekplexite	Kaskasite	Manganokaskasite
Wt.%			
Mg	6.25 (5.91–6.82)	5.94 (5.76–6.10)	0.06 (0.00–0.14)
Al	4.31 (3.89–4.73)	3.67 (3.44–4.26)	3.00 (2.75–3.28)
Ca	0.00	0.04 (0.00–0.14)	0.00
V	0.86 (0.57–1.10)	0.16 (0.05–0.45)	0.15 (0.09–0.24)
Mn	0.00	0.23 (0.00–0.46)	11.44 (10.77–12.08)
Fe	0.44 (0.18–0.82)	1.44 (0.66–2.61)	2.06 (1.35–2.92)
Nb	18.17 (17.04–19.23)	13.39 (12.14–13.77)	14.15 (13.16–14.76)
Mo	15.89 (15.07–16.28)	23.18 (21.70–26.49)	20.08 (19.46–20.65)
W	8.13 (7.56–8.64)	7.59 (0.88–10.05)	9.12 (8.68–9.55)
S	27.68 (26.30–28.91)	27.09 (26.08–28.14)	24.84 (24.66–25.00)
O	16.33 (15.02–17.37)	15.66 (14.46–16.93)	13.36 (12.84–14.13)
H(calc.)	1.03	0.99	0.89
Total	99.09	99.08	99.15
Formula calculated on the basis of 2 S a.p.f.u.			
Mg	0.60	0.58	0.01
Al	0.37	0.32	0.29
V	0.04	0.01	0.01
Mn	-	0.01	0.54
Fe	0.02	0.06	0.10
Nb	0.45	0.34	0.39
Mo	0.38	0.57	0.54
W	0.10	0.10	0.13
S	2	2	2
OH	2.36	2.32	2.28
Number of analyses	5	5	3

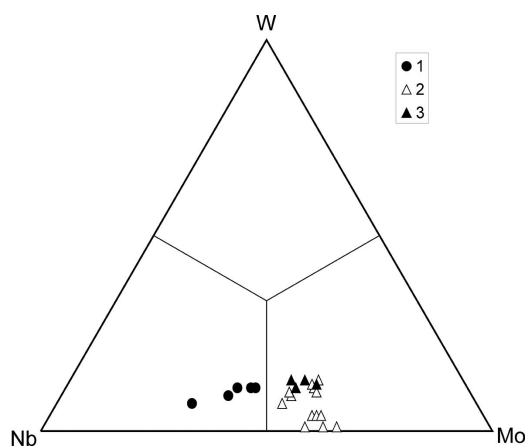


FIG. 7. Atomic ratios of major 'cations' in the sulfide modules of ekplexite (1), kaskasite (2) and manganokaskasite (3).

depleted and manganokaskasite is Mg-depleted (Fig. 8). The Mg:Al ratio in all of the samples of these three minerals studied is close to 2:1 (Fig. 8), i.e. in the simplified formulae  $x \approx 1/3$ .

Direct evidence for the presence of O in the hydroxide module (i.e. chemically bonded with Mg and Al but not with S or other constituents of the mineral) of the new minerals was found from the determination of the position of the  $OK\alpha$  X-ray line from the WDS data obtained during the electron-microprobe study of ekplexite and also, for comparison, in the study of synthetic compounds containing  $O^{2-}$  obviously bound with  $Mg^{2+}$ ,  $Al^{3+}$ ,  $Mo^{6+}$ ,  $W^{6+}$ ,  $Nb^{5+}$  and  $S^{6+}$ . Configuration of the  $OK\alpha$  X-ray line and the position of its maximum depend on the character (force characteristics, e.g. ionic potential) of cations forming chemical bonds with  $O^{2-}$  (chemical shift). The  $OK\alpha$  X-ray line was obtained and the position (wavelength) of its

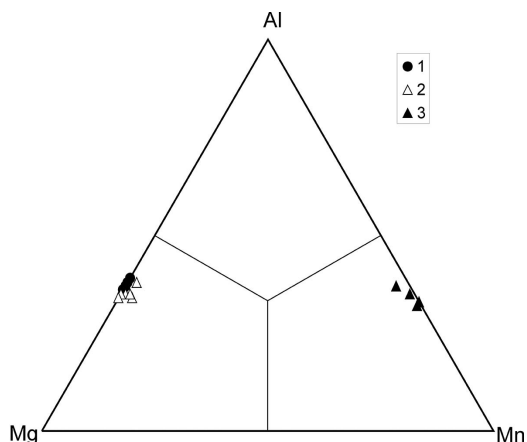


FIG. 8. Atomic ratios of major cations in the hydroxide modules of ekplexite (1), kaskasite (2) and manganokaskasite (3).

maximum in the WDS data was measured precisely for ekplexite and a series of reference samples. These standard samples contain the same chemical elements that are essential in the mineral studied (Mg, Al, Nb, Mo, W and S; Si was also involved for comparison) but obviously bound with  $O^{2-}$ . The O contents measured in all standard samples were in good agreement with values calculated from the idealized formulae. Control measurements showed the absence (i.e. content below the detection limit) of O in sulfide

minerals (pyrrhotite, pyrite and edgarite) in the polished samples with ekplexite studied.

Figure 9 and Table 4 clearly show that in each case the position of the  $OK\alpha$  X-ray line is individual (for Nb, three different compounds were examined and gave very close results) and depends on the ionic potential of the cation bound with  $O^{2-}$ . The position of the maximum of the  $OK\alpha$  X-ray line in ekplexite (23.610 Å) is between the values obtained for MgO (23.613 Å) and  $Al_2O_3$  (23.599 Å) but not in the range where compounds with  $Nb^{5+}-O$ ,  $Mo^{6+}-O$ ,  $W^{6+}-O$ ,  $Si^{4+}-O$  and  $S^{6+}-O$  bonds lie (23.595–23.57 Å). This clearly confirms that in ekplexite, O is bound to Mg and Al (and  $Mg > Al$  in agreement with the chemical composition) whereas sulfate, niobate, molybdate and tungstate groups are absent from the mineral. This conclusion corresponds to the Raman spectroscopy data very well.

### X-ray crystallography

All three new minerals form curved flaky crystals and are easily bent, which prevents their study by single-crystal X-ray diffraction (XRD). However, after numerous efforts, one attempt resulted in partial success using different single-crystal X-ray diffractometers. Crystals of kaskasite were examined using a Bruker Smart Apex II DUO diffractometer equipped with a microfocus X-ray tube (MoK $\alpha$  radiation) and CCD detector.

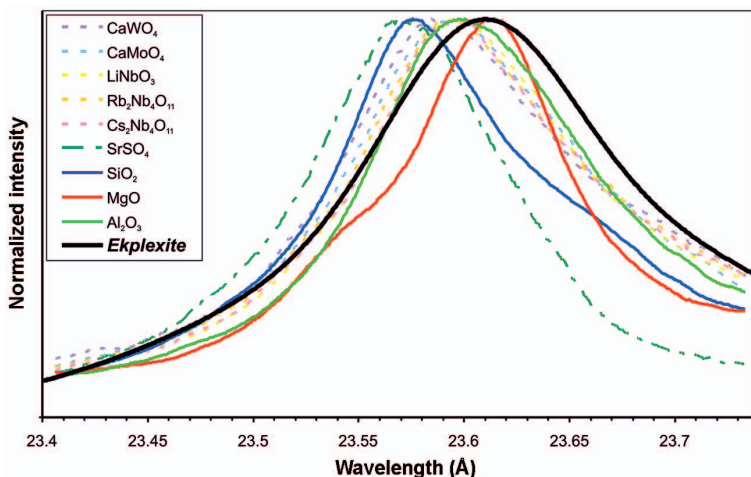


FIG. 9. Positions (wavelength, Å) and profiles of the  $OK\alpha$  X-ray line from the WDS of ekplexite and reference samples for synthetic compounds containing  $O^{2-}$  obviously bound with  $Mg^{2+}$ ,  $Al^{3+}$ ,  $Mo^{6+}$ ,  $W^{6+}$ ,  $Nb^{5+}$ ,  $Si^{4+}$  and  $S^{6+}$  (see also Table 4).

## EKPLEXITE, KASKASITE AND MANGANOKASKASITE, THREE NEW MINERALS

 TABLE 4. Position (wavelength, Å) of the maximum of the  $OK\alpha$  X-ray WDS line obtained during the electron-microprobe study of ekplexite and relevant synthetic compounds containing  $O^{2-}$  (see also Fig. 9).

Mineral/compound	Strongest chemical bonds formed by oxygen*	$OK\alpha$ X-ray line maximum (wavelength, Å)
MgO	$Mg^{2+}-O$	23.613
<b>Ekplexite</b>	$Mg^{2+}-O > Al^{3+}-O$	23.610
$Al_2O_3$	$Al^{3+}-O$	23.599
$LiNbO_3$	$Nb^{5+}-O$	23.595
$Cs_2Nb_4O_{11}$	$Nb^{5+}-O$	23.595
$Rb_2Nb_4O_{11}$	$Nb^{5+}-O$	23.594
$CaMoO_4$	$Mo^{6+}-O$	23.593
$CaWO_4$	$W^{6+}-O$	23.588
$SiO_2$	$Si^{4+}-O$	23.577
$SrSO_4$	$S^{6+}-O$	23.572

\* The influence of large cations ( $Cs^+$ ,  $Rb^+$ ,  $Sr^{2+}$ ,  $Ca^{2+}$  and even  $Li^+$ ) on the position of the  $OK\alpha$  X-ray line is assumed to be insignificant in the presence of highly charged ions such as  $S^{6+}$ ,  $W^{6+}$ ,  $Mo^{6+}$  or  $Nb^{5+}$  (in particular, this is confirmed by very close values for Cs, Rb and Li niobates).

Unfortunately, even the 'best' crystal available was imperfect (slightly curved and split on  $\{001\}$ )

and led to poor quality data being obtained. Kaskasite is trigonal,  $a = 3.27(3)$ ,  $c = 11.96(12)$  Å,

TABLE 5. X-ray powder-diffraction data of ekplexite.

$I_{obs}$	$d_{obs}$ (Å)	$d_{calc}$ (Å) S modulus*	$h k l$ S modulus	$d_{calc}$ (Å) OH modulus**	$h k l$ OH modulus
100	11.40	11.44	001	11.52	001
56	5.65	5.720	002	5.760	002
21	2.812	2.825	100		
9	2.647			2.655	100
2	2.553	2.533	102		
3	2.414			2.411	102
4	2.248	2.288, 2.267	005, 103	2.304	005
3	2.182			2.184	103
3	1.937	1.908	006	1.952, 1.920	104, 006
1	1.740	1.778	105	1.740	105
11	1.622	1.631, 1.615	110, 111		
4	1.573	1.569	112	1.556	106
3	1.518			1.520	111
1	1.505	1.500	113		
3	1.407	1.412, 1.402	200, 201		
2	1.397			1.399	107
2	1.263	1.267	204	1.266	108
3	1.242	1.239	116		
2	1.132	1.135	206		
2	1.062	1.068, 1.063, 1.060	120, 121, 1.0.10	1.057	1.0.10

\* Sulfide sub-lattice, space group  $P\bar{3}m1$ ,  $P3m1$  or  $P321$ ,  $a = 3.262(2)$ ,  $c = 11.44(2)$  Å,  $V = 105.4(4)$  Å<sup>3</sup>.

\*\* Hydroxide sub-lattice, space group  $P\bar{3}m1$ ,  $P3m1$  or  $P321$ ,  $a = 3.066(2)$ ,  $c = 11.52(2)$  Å,  $V = 93.8(4)$  Å<sup>3</sup>.

$V = 111.2(20) \text{ \AA}^3$ . These unit-cell dimensions of the sulfide sub-lattice confirm kaskasite as a one-layer polytype and are in agreement with powder XRD data. However, the  $a$  parameter obtained for kaskasite indicates the  $\text{MoS}_2/\text{NbS}_2$ -type sulfide module (see Discussion). These primary single-crystal data strongly support all the crystallographic interpretation (given below) based on powder XRD patterns.

Powder XRD data for ekplexite, kaskasite and manganokaskasite (Tables 5–7) were obtained using a STOE IPDS II single-crystal diffractometer equipped with an image plate detector (MoK $\alpha$  radiation; the distance between sample and detector = 200 mm) using the Gandolfi method. Unit-cell parameters calculated from the powder data for both the sulfide (main) and the hydroxide sub-lattices of these hybrid hydroxide-sulfides with non-commensurate layered structures are given in Table 1a and in the footnotes in Tables 5–7.

## Discussion

A combination of Nb and Mo occupying the same positions in the structure is very exotic for

minerals. Only Nb-bearing molybdenite was previously reported as micro-inclusions in a meteorite but with no analytical data given in the paper (El Goresy *et al.*, 1978). However, the continuous solid-solution system of synthetic layered  $\text{NbS}_2\text{--MoS}_2\text{--WS}_2$  disulfides crystallizing in the molybdenite structure type is well known. The synthetic  $(\text{Nb}_{0.6}\text{Mo}_{0.4})\text{S}_2$  adopts the structure type of molybdenite-3R,  $R3m$ ,  $a = 3.26$ ,  $c = 17.98 \text{ \AA}$  (Kalikhman and Golubnichaya, 1983). The synthetic  $\text{NbS}_2$  is a typical layered disulfide known to form in hexagonal and trigonal modifications including the molybdenite-2H structure type,  $P6_3/mmc$ ,  $a = 3.31$ ,  $c = 11.89 \text{ \AA}$ , while isostructural  $\text{MoS}_2\text{-}2H$  has  $a = 3.16$ ,  $c = 12.30 \text{ \AA}$  (Jelinek *et al.*, 1960; Kalikhman and Umansky, 1972) and  $\text{WS}_2\text{-}2H$  has  $a = 3.15$ ,  $c = 12.32 \text{ \AA}$  (Schutte *et al.*, 1987).

Values of the  $a$  parameter for the sulfide sub-lattice of ekplexite ( $a = 3.26 \text{ \AA}$ ), kaskasite ( $a = 3.22 \text{ \AA}$ ) and manganokaskasite ( $a = 3.24 \text{ \AA}$ ) are in the range for compounds belonging to the molybdenite-type  $\text{NbS}_2\text{--MoS}_2\text{--WS}_2$  solid-solution system (3.15–3.31  $\text{ \AA}$ ). Values of the  $c$  parameter for both sulfide (one-layer polytype)

TABLE 6. X-ray powder-diffraction data of kaskasite.

$l_{\text{obs}}$	$d_{\text{obs}} (\text{ \AA})$	$d_{\text{calc}} (\text{ \AA})$ S modulus*	$h k l$ S modulus	$d_{\text{calc}} (\text{ \AA})$ OH modulus**	$h k l$ OH modulus
97	11.46	11.47	001	11.50	001
100	5.72	5.735	002	5.750	002
51	2.786	2.789	100		
7	2.627			2.661, 2.593	100, 101
6	2.500	2.508	102		
4	2.415			2.415	102
7	2.219	2.253	103		
5	2.161			2.186	103
3	1.944	1.999, 1.912	104, 006	1.953, 1.917	104, 006
2	1.739	1.772	105	1.740	105
33	1.613	1.594	111		
10	1.557	1.577, 1.550	106, 112	1.555	106
4	1.524			1.523	111
3	1.497			1.484	112
6	1.396	1.404, 1.394	114, 200	1.398	107
2	1.349	1.355	202	1.355	114
3	1.244	1.254, 1.232	204, 116		
2	1.133	1.127	206		
3	1.057	1.062, 1.061, 1.054	207, 1.0.10, 120	1.056	1.0.10
2	1.049	1.050, 1.043	121, 0.0.11	1.050, 1.046	118, 0.0.11

\* Sulfide sub-lattice, space group  $P\bar{3}m1$ ,  $P3m1$  or  $P321$ ,  $a = 3.220(2)$ ,  $c = 11.47(2) \text{ \AA}$ ,  $V = 102.8(4) \text{ \AA}^3$ .

\*\* Hydroxide sub-lattice, space group  $P\bar{3}m1$ ,  $P3m1$  or  $P321$ ,  $a = 3.073(2)$ ,  $c = 11.50(2) \text{ \AA}$ ,  $V = 94.0(4) \text{ \AA}^3$ .

TABLE 7. X-ray powder-diffraction data of manganokaskasite.

$I_{\text{obs}}$	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å) S modulus*	$h k l$ S modulus	$d_{\text{calc}}$ (Å) OH modulus**	$h k l$ OH modulus
85	11.39	11.61	001	11.62	001
100	5.66	5.805	002	5.810	002
9	3.811	3.870	003	3.873	003
43	2.769	2.808, 2.730	100, 101		
25	2.663			2.700, 2.630	100, 101
18	2.455			2.449	102
12	2.324	2.322	005	2.324	005
10	2.231	2.273	103		
11	2.182			2.215	103
8	1.920	1.935	006	1.937	006
6	1.771			1.762	105
8	1.669	1.659	007	1.660	007
23	1.608	1.606	111		
13	1.559	1.562	112	1.559	110
6	1.508	1.496	113	1.506	112
7	1.395	1.404, 1.394	200, 201		
3	1.245	1.243	116		
2	1.144	1.137	206	1.137	117
3	1.058	1.061, 1.057, 1.056	120, 121, 0.0.11	1.063, 1.056	118, 0.0.11

\* Sulfide sub-lattice, space group  $P\bar{3}m1$ ,  $P3m1$  or  $P321$ ,  $a = 3.243(3)$ ,  $c = 11.61(1)$  Å,  $V = 105.8(3)$  Å<sup>3</sup>. \*\*Hydroxide sub-lattice, space group  $P\bar{3}m1$ ,  $P3m1$  or  $P321$ ,  $a = 3.118(2)$ ,  $c = 11.62(1)$  Å,  $V = 97.9(2)$  Å<sup>3</sup>.

and hydroxide sub-lattices of valleriite-group minerals are in the range 11–12 Å (Tables 1a and 1b), close to those of 2H polytypes of molybdenite-type disulfides of the NbS<sub>2</sub>–MoS<sub>2</sub>–WS<sub>2</sub> system. Thus, unit-cell dimensions, hexagonal or trigonal symmetry and a layered structure make these disulfides close to the nukundamite-like [nukundamite (Cu,Fe)<sub>4</sub>S<sub>4</sub>:  $P\bar{3}m1$ ,  $a = 3.783$ ,  $c = 11.195$  Å,  $V = 139$  Å<sup>3</sup> (Sugaki *et al.*, 1981)] sulfide module of valleriite-group minerals that favours the formation of hybrid hydroxide-sulfides with layered structures. Note that NbS<sub>2</sub> easily forms numerous non-commensurate layered compounds with Pb, Sn, Fe, Bi, REE, etc sulfides. These were studied extensively because of their superconductor properties (Wieggers *et al.*, 1990; Gressier *et al.*, 1997; Nader *et al.*, 1997; Lafond *et al.*, 1999).

Ekplexite, kaskasite and manganokaskasite are represented by one-layer modifications. Characteristic reflections for their hypothetical three-layer polytypes ( $c \approx 34.3$ – $34.9$  Å) are absent in their X-ray powder patterns. Reflections undoubtedly corresponding to the brucite-like hydroxide modules are observed in X-ray

powder patterns for all three new minerals (Tables 5–7). These reflections were used to calculate values for the  $a$  parameter of their hydroxide sub-lattices: 3.066(2), 3.073(2) and 3.118(2) Å for ekplexite, kaskasite and manganokaskasite, respectively. The  $a$  parameters of the hydroxide sub-lattice of ekplexite and kaskasite are very close to that of the hydroxide sub-lattice of valleriite without Fe in the hydroxide module, as well as that of yushkinite (3.06–3.07 Å), but are unlike ferrovalleriite, which contains only Fe<sup>2+</sup> instead of (Mg, Al) in the hydroxide module that increases the  $a$  value to 3.20 Å (Tables 1a and 1b). The latter observation confirms that the hydroxide module of ekplexite and kaskasite contains significantly more Mg<sup>2+</sup> and Al<sup>3+</sup> cations than larger cations. The  $a$  parameter of the hydroxide sub-lattice of manganokaskasite is 3.118 Å and corresponds to the cation composition of its hydroxide (Mn<sub>0.54</sub>Al<sub>0.29</sub>Fe<sub>0.10</sub>Mg<sub>0.01</sub>) module: the larger Mn<sup>2+</sup> cation is present instead of Mg<sup>2+</sup> (Table 1a). The substitution of Mg for Mn is also obviously accepted due to the higher reflectance values of manganokaskasite in comparison to kaskasite and ekplexite (Table 2).

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