

Chemical composition of a metamict (Mn,Fe)-Y-(Sb,As)-(Nb,Ti) oxide mineral from the Tennvatn amazonite pegmatite, Sørfold, Nordland, north Norway

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Introduction

The mineralogy of the amazonite pegmatite at Tennvatn was briefly described by Ellingsen et al. (1995, 2000). One of the unidentified phases, designated UK-2 (Ellingsen et al. 2000), is a metamict mineral occurring as well-formed crystals (Fig. 1). It has an unusual chemical composition. The purpose of the present publication is to present and discuss the electron-microprobe analytical data of the mineral.

Description of the mineral

The metamict mineral forms both euhedral crystals to almost 1 cm in cavities, as well as anhedral to subhedral inclusions in other minerals, mainly quartz, albite and fluorite. On fresh surfaces, the mineral is dark brown with high lustre and conchoidal fracture. No cleavage, parting or macroscopical twinning have been observed. Crystal faces are less reflective and often encrusted by other phases. The prismatic crystals have rhombus-like cross sections and are terminated by several crystal forms, indicating low symmetry, possibly triclinic.

Associations

The mineral is not uncommon in the pegmatite and has been found in several different associations:

- The best developed crystals occurred in a cavernous area in quartz and microcline in the central part of the pegmatite body, associated with chernovite-(Y), fluorapatite, hingganite-(Y), löllingite, magnetite, pharmacosiderite, pyrophanite, stibiocolumbite, svabite, xenotime-(Y), a chlorite group mineral and a mica group mineral. The metamict mineral is partly enclosed in quartz and seems to be one of the oldest minerals in this association.
- Aggregates of anhedral to subhedral individuals to 3 cm have been found in two limited areas close to the margins of the pegmatite. The aggregates are embedded in a porous matrix of schorl and albite. This material is partly altered: the colour varies from dark brown in the cores to pale yellowish brown towards the grain margins. When grown in cavities, the surface of the metamict mineral is encrusted by an unidentified pale brown, globular mineral. Both the encrustations and the paler outer zones of the metamict mineral are often cracked, probably due to expansion during alteration. SEM-EDS of the metamict mineral from this association indicates a certain U content.
- The mineral is also common in association with cm-sized masses of fluorite, where it forms thin layers between the fluorite and the surrounding minerals. Associated minerals are hingganite-(Y) and chernovite-(Y). Fluorite in contact with the metamict mineral is usually purple, possibly due to radiation from U.
- Small (<1 mm) pale brown crystals of the metamict mineral occur with partly altered asbecasite in connection with cavities in albite and microcline. From the few available samples it seems that schorl is the oldest mineral, followed by the metamict mineral and albite, then asbecasite and finally titanite, chernovite-(Y) and an unidentified green, radiating K-Fe-Al-silicate.

X-ray powder diffraction

X-ray powder diffraction (9 cm Debye-Scherrer camera, Mineralogical-Geological Museum, Oslo) was attempted on an untreated fragment of the mineral; the film was without visible lines, indicating the mineral being in a metamict amorphous state. An annealed (1000°C, 24 h in air) fragment gave a pattern with 14 discernible reflections above $d = 1.50 \text{ \AA}$. These reflections do not represent a single phase, revealing that the mineral did not recrystallize to its original structure during annealing. Chernovite-(Y), YAsO_4 , is definitely one of the heating products. A rutile phase of the ilmenorutile type is present as is probably also a pyrochlore phase. Heating in an inert gas, maybe at various temperatures and pressures, could possibly regain the original structure of the mineral and produce crystals suitable for structure determination.

Analytical details

Wavelength-dispersive electron-microprobe analyses were performed in October 2001 with a Cameca Camebax instrument at the Mineralogical-Geological Museum in Oslo, operating at 20 kV and with 18.5 nA probe current. The counting time was 10 s for peak and background. The probe standards and measured peaks were: MnTiO_3 (Mn- $K\alpha$ and Ti- $K\alpha$), Fe_2O_3 (Fe- $K\alpha$), REEPO_4 (Y- $L\alpha$, Yb- $L\alpha$, Lu- $L\alpha$), GaAs (As- $L\alpha$), Nb and Ta metals (Nb- $L\alpha$, Ta- $M\alpha$) and Sb_2O_3 (Sb- $L\alpha$). Areas measuring $5 \times 5 \mu\text{m}$ were scanned during analysis. The elements Er, Pb, U and Th were sought but found to be below the detection limit. Since the mineral occurs in a metamict state, it was unexpected not to detect U or Th. However, EDS scans of another sample of the mineral did show a small U peak.

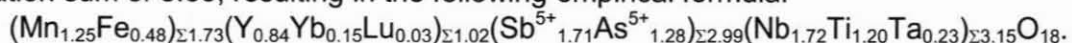
Discussion of chemical formula

A back-scatter electron (BSE) image of the analysed sample is shown in Fig. 2. The major part of the fragment is chemically homogeneous. The dark, irregular areas are due to incipient alteration along cracks. The mean analytical results for both areas are displayed in Table 1.

The dark areas have a lower total compared to the light areas, most likely caused by the introduction of water during the alteration process. It should be noted that the mean content of As is higher in the altered parts, whereas all other elements show lower mean values (except for Yb and Lu, but these differences are not significant). The chemical composition of the dark areas will not be discussed any further.

It is reasonable to assume that iron, in association with manganese, occurs in its divalent state. However, the valence states of As and Sb, which may be trivalent or pentavalent, are problematic issues. Pentavalent As and Sb are assumed in the left part of Table 1. The resulting analytical total for the light areas (96.97 wt%) is reasonable for a metamict mineral containing some water of metamictization. Furthermore, electron-microprobe analyses of small grains embedded in epoxy usually give analytical sums somewhat below 100%.

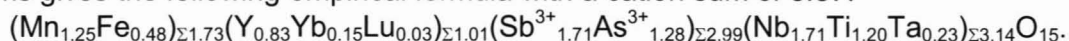
Based on a total of 18 oxygen atoms, the mean analytical data of the light areas give a cation sum of 8.89, resulting in the following empirical formula:



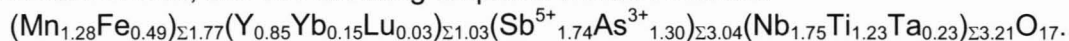
This grouping of cations results in fairly acceptable summation coefficients. It should be noted that a ratio of cations to oxygen equal to 1:2 occurs in a number of other metamict Nb-Ta-Ti oxide minerals (aeschynite group, euxenite group and samarskite group) as well as in the columbite group.

The case of regarding both As and Sb as trivalent is also shown in Table 1. The resulting total of only 92.63 wt% seems to be unrealistic, unless a high content of

water or light elements like Be and B are involved. We have not had the opportunity to check the presence of these two elements, but such small cations are not known to occur in other metamict oxide minerals. Calculation based on a total of 15 oxygen atoms gives the following empirical formula with a cation sum of 8.87:



A third possibility with trivalent As and pentavalent Sb is given in Table 1. The resulting total of 95.08 wt% may be acceptable. Based on a total of 17 oxygen atoms, the cation sum is 9.05, and the following empirical formula ensues:



The case of pentavalent As and trivalent Sb (not shown in Table 1; the analytical total is 94.52 wt%) is discussed at the end of this chapter.

The various formula calculations shown above must now be discussed in the light of the crystal-chemical behaviour of As and Sb and by comparison with other As- and Sb-bearing minerals, especially with those occurring in the Tennvatn pegmatite.

A starting point would be a table of ionic radii (in Å) for As and Sb as a function of coordination numbers [n] (taken from Shannon 1976):

	[3]	[4]	[5]	[6]
As ³⁺	–			0.58
As ⁵⁺		0.335 ¹		0.46
Sb ³⁺	–	0.76 ²	0.80	0.76
Sb ⁵⁺				0.60

¹ tetrahedral (As⁵⁺ at the centre of a tetrahedron)

² Sb³⁺ at the apex of a four-sided pyramid

The association of As⁵⁺ and Sb⁵⁺ in six-fold coordination is the first possibility considered in Table 1 and in the corresponding formula presented above. The ionic radii are seen to be favourable for this case. A commonly occurring site position for trivalent As and Sb is in three-fold coordination, with As and Sb at the apex of flat trigonal pyramids, attributed to the presence of a lone electron pair on the cation. No radius data are given for this situation ([3] in the table). The association of As³⁺ and Sb³⁺, whether in three- or six-fold coordination, is the second choice in Table 1. The third possibility in Table 1 is a combination of six-fold coordinated As³⁺ and Sb⁵⁺, which is seen to be a good match in terms of ionic radii.

A complicating factor in the assessment of a correct formula for the Tennvatn mineral is the possibility of mixed valences of both As and Sb, as well as their presence at differently coordinated sites. This is elucidated by showing some mineral examples below. For the sake of brevity, references are generally not cited; it is referred to the literature quotations in Strunz & Nickel (2001).

Arsenic in oxygen-containing minerals is mostly pentavalent and tetrahedrally coordinated; this is the large class of arsenate minerals with (AsO₄)³⁻ groups. A limited subclass of minerals comprises arsenites and antimonites, with trivalent As and Sb at the apex of a flat trigonal pyramid, i.e. (XO₃)³⁻ groups, as explained above. Examples

of simple oxides with $^{[3]}(\text{As,Sb})^{3+}$ are arsenolite and claudetite (polymorphs of As_2O_3), senarmontite and valentinite (polymorphs of Sb_2O_3), as well as the recently described stibioclaudetite, AsSbO_3 , with ordered distribution of As and Sb (Origlieri et al. 2009).

Some examples of minerals with six-coordinated Sb^{5+} are swedenborgite, $\text{NaBe}_4\text{Sb}^{5+}\text{O}_7$, brizziite, $\text{NaSb}^{5+}\text{O}_3$, and byströmite, $\text{MgSb}^{5+}_2\text{O}_6$. A combination of $^{[3]}\text{Sb}^{3+}$ and $^{[6]}\text{Sb}^{5+}$ is found in cervantite, $\text{Sb}^{3+}\text{Sb}^{5+}\text{O}_4$. In pyrochlore structures, Sb^{3+} may enter the eight-coordinated (!) A site and Sb^{5+} the six-coordinated B site, the most extreme case being stibiconite, $\text{Sb}^{3+}\text{Sb}^{5+}_2\text{O}_6(\text{OH})$.

Hematolite, $(\text{Mn}^{2+},\text{Mg},\text{Al})_{15}(\text{AsO}_3)(\text{AsO}_4)_2(\text{OH})_{23}$, and several related minerals (mcgovernite, dixenite, synadelphite and arakiite) have a combination of $(\text{As}^{3+}\text{O}_3)^{3-}$ and $(\text{As}^{5+}\text{O}_4)^{3-}$ groups. Such groups are also present in hundholmenite-(Y) (Raade et al. 2007).

A combination of Sb^{5+} and As^{5+} in the form of SbO_6 octahedra and AsO_4 tetrahedra is found in manganostibite, $\text{Mn}^{2+}_7\text{Sb}^{5+}\text{As}^{5+}\text{O}_{12}$, and parwelite, $(\text{Mn}^{2+},\text{Ca},\text{Mg})_5\text{Sb}^{5+}(\text{As}^{5+}\text{O}_4)(\text{SiO}_4)\text{O}_4$.

The structure of richelsdorfite, $\text{Ca}_2\text{Cu}_5\text{Sb}^{5+}(\text{AsO}_4)_4\text{Cl}(\text{OH})_6\cdot 6\text{H}_2\text{O}$, contains AsO_4 tetrahedra and $\text{Sb}(\text{OH})_6$ octahedra.

Stenhuggarite, $\text{CaFe}^{3+}(\text{As}^{3+}\text{O}_2)(\text{As}^{3+}\text{Sb}^{3+}\text{O}_5)$, has a unique combination of AsO_3 trigonal pyramids and SbO_4 square pyramids.

Pentavalent Sb does not seem to occur in tetrahedral coordination, as opposed to As^{5+} . Cualstibite was first formulated as $\text{Cu}_6\text{Al}_3(\text{SbO}_4)_3(\text{OH})_{12}\cdot 10\text{H}_2\text{O}$, suggesting the presence of SbO_4 tetrahedra. Recent structure determinations of cualstibite and the related zincalstibite (Bonaccorsi et al. 2007) have shown that the minerals contain $\text{Sb}(\text{OH})_6$ octahedra, the revised formula of cualstibite being $\text{Cu}_2\text{AlSb}^{5+}(\text{OH})_{12}$. The current formula of theisite, $\text{Cu}_5\text{Zn}_5(\text{AsO}_4,\text{SbO}_4)_2(\text{OH})_{14}$, also suggests the presence of SbO_4 tetrahedra, although $\text{Sb}(\text{OH})_6$ groups are more likely (the structure is not known). The structure of sabelliite, $(\text{Cu},\text{Zn})_2\text{Zn}[(\text{As},\text{Sb})\text{O}_4](\text{OH})_3$, contains an AsO_4 tetrahedron and a square pyramid partly occupied by mixed $(\text{As},\text{Sb})^{5+}$.

Quite recently, As-rich fergusonite-beta-(Y) was described from Mount Cervandone, Italy (Guastoni et al. 2010). Fergusonite-beta-(Y), the monoclinic polymorph of YNbO_4 , has six-coordinated Nb, and As^{5+} substitutes at the Nb site. Nearly 30% substitution of As^{5+} for $^{[6]}\text{Nb}^{5+}$ (ionic radius 0.64 Å) is interesting in the light of the composition of the metamict Tennvatn mineral. It should be noted that Cherbadung, the type locality of asbecasite, belongs to the same area and is situated on the Swiss side of the border. As noted above, asbecasite sometimes occurs in association with the metamict mineral at Tennvatn.

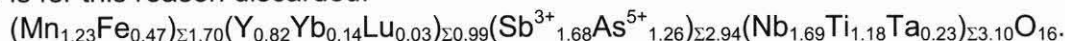
This review leads to the conclusion that it is not possible to attach a definite chemical formula to the metamict Tennvatn mineral at present. The combination of six-coordinated Sb^{5+} and As^{5+} does not seem to have been reported in minerals before, as is also the case for six-coordinated As^{3+} and Sb^{5+} . However, it cannot be concluded that these alternatives are unrealistic. Allocating As and Sb to a common site simplifies the discussion and results in acceptable cation coefficients for the three alternatives mentioned above. Of course, As and Sb could occupy individual sites with different coordinations, either with different valences or with the same valence. Dealing with such diverse options is rather complicated and would not seem to result in nice formula subscripts.

Finally, a survey of other As- and Sb-bearing minerals in the Tennvatn pegmatite is useful. The arsenate minerals bergslagite, chernovite-(Y), gasparite-(Ce), mimetite,

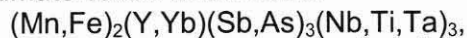
pharmacosiderite and svabite have been identified. Antimony-bearing minerals are stibiocolumbite (SbNbO_4 with Sb^{3+}O_3 pyramids) and asbecasite. In the latter mineral, with formula $\text{Ca}_3(\text{Ti,Fe,Sn})(\text{As,Sb})_6(\text{Be,B,Al})_2\text{Si}_2\text{O}_{20}$, trivalent As and Sb are present in trigonal pyramids (Cannillo et al. 1969, Sacerdoti et al. 1993). A qualitative SEM-EDS analysis showed major As and minor Sb in the Tennvatn asbecasite (A.O. Larsen 1990, *Interne notater, Geologisk Museum*, 158-160).

Of these minerals, asbecasite, chernovite-(Y), pharmacosiderite, stibiocolumbite and svabite are associated with the metamict mineral. The latter four minerals are, however, considerably younger and can not be regarded as cogenetic with the metamict mineral. Asbecasite is also younger, but is more likely cogenetic. This might indicate the presence of trivalent As and Sb in the metamict mineral.

As a last alternative, a combination of As^{5+} and Sb^{3+} in the metamict mineral is considered, based on the presence of these cations in the associated minerals. However, a calculation based on these two cations, situated at different sites, does not result in a formula with nice subscripts. Combining the two cations at a six-coordinated site gives a formula similar to those noted above but is probably not feasible owing to the relatively large difference in ionic radii (see the preceding table) and is for this reason discarded:



It is thought to be of importance that the formula calculations shown here lead to empirical formulae with whole numbers of oxygen atoms and the following approximate cation coefficients:



where Sb and As may be $(\text{Sb}^{5+},\text{As}^{5+})$, $(\text{Sb}^{3+},\text{As}^{3+})$ or $(\text{Sb}^{5+},\text{As}^{3+})$. Based on the association with asbecasite, the option with trivalent Sb and As is the most likely, although the low summation seemingly speaks against this alternative. Measurement of the water content of the metamict mineral and a check for the light elements Be and B should be the next steps in the investigation of the mineral.

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Table 1. Averages of electron-microprobe analyses (wt%) of unknown, metamict mineral (UK-2) from Tennvatn.

	Light area		Dark area		Light area		Light area	
	wt% n = 5	sd	wt% n = 3	sd	As ³⁺ Sb ³⁺		As ³⁺ Sb ⁵⁺	
MnO	8.21	0.26	7.24	0.19	MnO	8.21	MnO	8.21
FeO	3.18	0.18	3.06	0.44	FeO	3.18	FeO	3.18
Y ₂ O ₃	8.70	0.27	7.08	0.44	Y ₂ O ₃	8.70	Y ₂ O ₃	8.70
Yb ₂ O ₃	2.67	0.23	3.02	0.23	Yb ₂ O ₃	2.67	Yb ₂ O ₃	2.67
Lu ₂ O ₃	0.52	0.11	0.62	0.03	Lu ₂ O ₃	0.52	Lu ₂ O ₃	0.52
TiO ₂	8.88	0.26	8.63	0.23	TiO ₂	8.88	TiO ₂	8.88
As ₂ O ₅	13.59	0.16	16.19	1.09	As ₂ O ₃	11.70	As ₂ O ₃	11.70
Nb ₂ O ₅	21.05	0.49	19.45	0.89	Nb ₂ O ₅	21.05	Nb ₂ O ₅	21.05
Sb ₂ O ₅	25.47	0.64	23.06	0.62	Sb ₂ O ₃	23.02	Sb ₂ O ₅	25.47
Ta ₂ O ₅	4.70	0.46	4.20	0.16	Ta ₂ O ₅	4.70	Ta ₂ O ₅	4.70
Sum	96.97	0.86	92.54	1.21	Sum	92.63	Sum	95.08

n – number of single analyses; sd – standard deviation (calculated in spite of the small number of point analyses)



Fig. 1. SEM-BSE picture of unknown, metamict oxide mineral (UK-2) from Tennvatn. Taken by Harald Folvik and enhanced with Corel Photo-Paint by G. Raade.

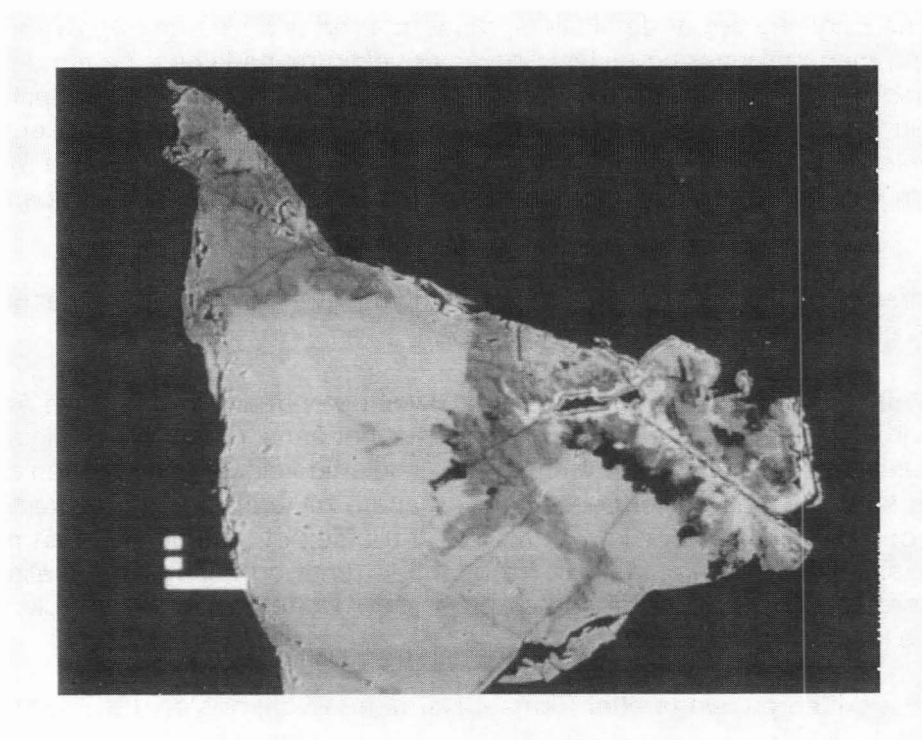


Fig. 2. BSE image of a polished section of UK-2, a metamict mineral from Tennvatn. The scale bar is 100 μm . Analytical data for the light and dark areas are found in Table 1.