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EYSELITE, $Fe^{3+}Ge^{4+}{}_3O_7(OH)$, A NEW MINERAL SPECIES FROM TSUMEB, NAMIBIA

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Abstract

Eyselite, ideally $Fe^{3+}Ge^{4+}{}_3O_7(OH)$, is orthorhombic with a *P* lattice, and unit-cell parameters refined from powder data: *a* 8.302(4), *b* 9.718(4), *c* 4.527(2) Å, *V* 365.2(3) Å^3, *a*:*b*:*c* 0.8543:1:0.4658, *Z* = 2. The strongest eight lines of the X-ray powder-diffraction pattern [*d* in Å (*I*)(*hkl*)] are: 4.105(40)(011), 3.681(100)(111), 3.121(60b)(220,121), 2.921(100)(211), 2.512(40)(131), 2.403(90)(320), 1.646(80)(322) and 1.624(50)(142). The mineral occurs on a single specimen originating from the Tsumeb mine, Tsumeb, Namibia, as very fine-grained aggregates in vugs of massive renierite – germanite – tennantite ore. There are no other associated secondary phases. Individual subhedral to rarely euhedral crystals are platy to very thin prismatic, elongate [001], with a length-to-width ratio of approximately 3:1 and not exceeding 20 µm in maximum length. Typical crystals are 20 × 14 × 1 µm in size. Forms are {100} major, very thin {010}, rounded {011}, and very thin rounded {001} minor. Crystals show growth steps on {100} and are partly hollow. The mineral is dirty brown-yellow (aggregates) to yellow-tan (crystals), opaque (aggregates) to transparent (crystals), with a brownish yellow streak, and vitreous luster. Eyselite is brittle, with an uneven fracture, and is nonfluorescent. The aggregates are soft; *D* (calc.) is 3.639 g/cm^3 for the empirical formula. It is biaxial positive, and two indices of refraction exceed 1.80; 2*V* (meas.) is large; pale yellow in plane-polarized light, with no pleochroism, low birefringence, moderate anisotropy, and length-fast. Averaged results of electron-microprobe analyses yield CaO 0.06, Fe_2O_3 18.54, Ga_2O_3 1.01, GeO_2 77.75, H_2O [2.64] (by difference), total [100.00] wt.%. The empirical formula, on the basis of O = 8, is $(Fe^{3+}_{0.93}Ga^{3+}_{0.04})_{\Sigma 0.97}Ge^{4+}_{2.98}O_{6.90}(OH)_{1.17}$. The infrared-absorption spectrum shows bands for structural (OH). A micro-XAS study shows that all the Fe is trivalent, and the Ge atoms are probably in octahedral coordination. The mineral's name honors the late Walter H. Eysel, Professor of Crystallography, Ruprecht-Karls-Universität, Heidelberg, Germany, for his contributions to the study of germanates and for his numerous contributions to the Powder Diffraction File.

Keywords: eyselite, new mineral species, iron germanium oxide hydroxide, X-ray powder data, electron-microprobe data, infrared spectroscopy, micro-XAS study, selected-area electron diffraction, Tsumeb mine, Tsumeb, Namibia.

Sommaire

La eyselite, dont la formule idéale est $Fe^{3+}Ge^{4+}{}_3O_7(OH)$, est orthorhombique avec une maille *P*, et possède les paramètres réticulaires suivants, affinés à partir de données en diffraction X obtenues sur poudre: *a* 8.302(4), *b* 9.718(4), *c* 4.527(2) Å, *V* 365.2(3) Å^3, *a*:*b*:*c* 0.8543:1:0.4658, *Z* = 2. Les huit raies les plus intenses du spectre de diffraction, méthode des poudres [*d* en Å (*I*)(*hkl*)] sont: 4.105(40)(011), 3.681(100)(111), 3.121(60b)(220,121), 2.921(100)(211), 2.512(40)(131), 2.403(90)(320),

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1.646(80)(322) et 1.624(50)(142). Le minéral, découvert sur un seul échantillon provenant de la mine Tsumeb, en Namibie, se présente en aggrégats de grains infimes dans des cavités d'un minerai à renierite – germanite – tennantite massif. Aucune autre phase secondaire ne lui est associée. Les cristaux individuels sub-idiomorphes à rarement idiomorphes sont des plaquettes ou des prismes très minces, allongés selon [001], avec un rapport longueur à largeur d'environ 3:1, et n'atteignant que 20 μm au maximum. Les cristaux typiques sont 20 × 14 × 1 μm. Les formes sont {100} majeure, {010} très mince, {011} arrondie, et {001} mineure, très mince et arrondie. Les cristaux montrent des paliers de croissance sur {100} et sont en partie caverneux. Ils sont brun jaunâtre sale (aggrégats) à jaune brunâtre (cristaux), opaques (aggrégats) à transparents (cristaux), avec une rayure jaune brunâtre et un éclat vitreux. La eyselite est cassante, avec une fracture inégale, et non fluorescente. Les aggrégats sont mous; D (calc.) est 3.639 g/cm^3 pour la formule empirique. Elle est biaxe positive, et deux des indices de réfraction dépassent 1.80; $2V$ (mesuré) est grand; jaune pâle en lumière polarisée, sans pléochroïsme, faible biréfringence, anisotropie modérée, et allongement positif. Les résultats moyens des analyses faites avec une microsonde électronique donnent CaO 0.06, Fe_2O_3 18.54, Ga_2O_3 1.01, GeO_2 77.75, H_2O [2.64] (par différence), pour un total de [100.00]% (poids). La formule empirique, sur une base de O = 8, est $(Fe^{3+}_{0.93}Ga^{3+}_{0.04})_{\Sigma 0.97}Ge^{4+}_{2.98}O_{6.90}(OH)_{1.17}$. Le spectre d'absorption infrarouge montre des bandes attribuées à l'hydroxyle structural. Une étude en micro-absorption des rayons X montre que tout le fer est trivalent, et les atomes de Ge seraient en coordinence octaédrique. Le nom choisi honore feu Walter H. Eysel, professeur de Cristallographie, Ruprecht-Karls-Universität, Heidelberg, Germany, pour ses nombreuses contributions à l'étude des germanates et à la banque de données en diffraction X sur poudres.

(Traduit par la Rédaction)

Mots-clés: eyselite, nouvelle espèce minérale, oxyde hydroxylé de fer et germanium, diffraction X sur poudre, données de microsonde électronique, spectroscopie infrarouge, spectroscopie micro-XAS, diffraction des électrons sur aire choisie, mine Tsumeb, Tsumeb, Namibie.

INTRODUCTION

The Tsumeb mine, Tsumeb, Namibia (lat. 19°13'S, long. 17°43'E) has been, over the years, a prolific source of new mineral species. Herein, we describe another new phase, eyselite, from this classic locality. The specimen on which the new mineral occurs was acquired in 1977 by one of us (T.M.S.), from a collection of altered Ge-bearing ore samples in the possession of the late Sid Pieters of Windhoek, Namibia. The secondary phase on the ore sample was X-rayed by routine powder-diffraction methods in the early 1990s, but was unidentified and remained so until a portion of the material was sent to the senior author for further characterization in late 2002.

The mineral is named *eyselite* in honor of the late Walter Hans Eysel (1935–1999), Professor of Crystallography at the Ruprecht-Karls-Universität, Heidelberg, Germany, for his contributions to the study of germanates (as models for silicates) and for his numerous contributions to the Powder Diffraction File produced by the International Centre for Diffraction Data (ICDD). A fitting tribute to Dr. Eysel was published by Pentinghaus & Tovar (2000). The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA (2003–52). A small portion of the holotype specimen used for study (3 × 1.5 × 1.5 cm) is housed in the Systematic Reference Series of the National Mineral Collection at the Geological Survey of Canada, Ottawa, Ontario, under catalogue number 68093. The larger matrix sample and the electron-microprobe mount have been retained by T.M.S.

OCCURRENCE AND ASSOCIATED MINERALS

Eyselite was identified in a vug (4 × 5 mm) on a single specimen (1.6 × 2.3 × 3.5 cm) of renierite – germanite ore with minor associated tennantite. The new mineral is very rare, and we estimate that only 10 mg of pure eyselite remains for further study. The mineral has formed from the alteration of the Ge-bearing sulfide minerals by aqueous solutions (*i.e.*, groundwaters) migrating through the Tsumeb orebody. No other secondary mineral occurs in the vug in direct association with eyselite.

PHYSICAL AND OPTICAL PROPERTIES

Eyselite occurs on the holotype specimen within the 4 × 5 mm vug as loosely attached, very fine-grained aggregates of tiny crystals (Fig. 1) coating the sulfide phases that host the cavity. A SEM photomicrograph (Fig. 2) shows that the megascopically anhedral aggregates are composed of randomly oriented subhedral to rarely euhedral crystals that generally do not exceed 20 μm in size and average approximately 20 × 14 × 1 μm. Individual crystals are platy to very thin prismatic, elongate along [001], with a length-to-width ratio that does not exceed 3:1. The dominant forms are {100} major, with minor {010}, {011} and {001}; the latter two are usually somewhat rounded in appearance. Growth steps are present on the {100} face, and crystals appear to be partly hollow if viewed down the [001]. The color of the mineral varies from dirty brown-yellow (aggregates) to yellow-tan (crystals), and the streak is brownish yellow. The luster is vitreous, and crystals are transparent, whereas aggregates are opaque. Eyselite is brittle, with an uneven fracture, and is nonfluorescent under both long- and short-wave ultraviolet light. Twinning and cleavage were not observed. Individual crystals are too small to accurately measure hardness, though aggregates are soft. The density could not be measured because of the small size of available crystals and the dearth of material. The density calculated, on the basis of the empirical formula and unit-cell parameters refined from powder data, is 3.639 g/cm^3.

Optically, eyselite is very pale yellow in plane-polarized light and has a low birefringence, moderate anisotropy, parallel extinction, and it is length-fast (negative). It is nonpleochroic, biaxial positive, with a large $2V$ and with at least two indices of refraction greater than 1.80. The crystal size (10–20 μm grains) did not allow us to acquire more precise optical data.

CRYSTALLOGRAPHY

Eyselite, at least those samples that have been examined to date, is unsuitable for study by traditional X-ray single-crystal techniques. A single-crystal precession study was attempted, but failed; the crystals are too small to adequately diffract. Even multiple crystallites did not diffract with sufficient intensity on orientation films. Therefore, hand-picked material was subjected to convergent beam electron-diffraction (CBED) study with a TEM, and the resulting microdiffraction pattern gave an orthogonal two-dimensional lattice with averaged spacings of 9.76 and 4.46 Å and no systematic extinction conditions. Using the results of the CBED study, the X-ray powder-diffraction pattern (Table 1) was successfully indexed by the Ito method on a primitive orthorhombic unit-cell. Regarding potential space-group choices, inspection of the indexed powder data given in Table 1 suggests that if the systematic absence condition $h0l$ with $h + l = 2n$ is present, then the permissible space-group choices are $Pmnm$, $Pmn2_1$ or $P2_1nm$ (diffraction aspect $P{*}n{*}$). However, if there is no systematic $h0l$ absence condition, then the highest symmetry-related primitive orthorhombic space-group is $P2_12_12_1$, which would indicate only systematic absence extinctions along the principal axial directions. It should be noted that the size of the individual crystals, coupled with the presence of growth steps on the predominant face, and the partly hollow nature of the crystals, precluded an attempt at a CCD-based crystal-structure determination (F.C. Hawthorne, pers. commun., 2003). There is most certainly too little material available for an *ab initio* Rietveld refinement.

FIG. 1. Photomicrograph of eyselite aggregates. Scale bar: 0.5 mm.

Eyselite is thus orthorhombic with a P lattice, and the refined unit-cell parameters, a 8.302(4), b 9.718(4), c 4.527(2) Å, V 365.2(3) Å^3, a:b:c 0.8543:1:0.4658, Z = 2, are based on 22 powder reflections, representing d values between 4.105 and 1.350 Å for which unambiguous indexing was possible. The powder data are unique and bear no resemblance to any germanate, silicate or any other inorganic phase listed in the Powder Diffraction File. The only other Fe–Ge-oxy compounds found in nature are brunogeierite $(Ge^{2+},Fe^{2+})Fe^{3+}{}_2O_4$ and stottite $Fe^{2+}Ge^{4+}(OH)_6$.

CHEMICAL COMPOSITION

Electron-microprobe study

Aggregates of eyselite were mounted in polished section and chemically analyzed with a Cameca SX–50 electron microprobe, using an operating voltage of 15 kV, a beam current of 10 nA, and a beam diameter of 0.2 to 0.5 μm. The following standards were used: wollastonite (Ca), hematite (Fe), synthetic GaAs (Ga) and synthetic GeO_2 (Ge). An energy-dispersion scan indicated the absence of any other elements with atomic number greater than 9, except those reported here. The paucity of material prevented quantitative determination of the amount of H_2O. However, the presence of H as (OH) was confirmed by powder infrared-absorption study; the amount of H_2O was therefore calculated by difference. Germanium was assumed to be Ge^{4+}, as this is the most common valence state for the element at Tsumeb. Iron was assumed to be Fe^{3+} on the basis of the color of the mineral and of its occurrence as a secondary mineral within a supergene ore zone. This assumption was subsequently confirmed by a qualitative micro-XAS study (see below), which unambiguously indicated that all iron is Fe^{3+}. The average of nine determinations (and ranges) gave CaO 0.06 (0.03–0.09), Fe_2O_3 18.54 (16.97–20.55), Ga_2O_3 1.01 (0.73–1.31), GeO_2 77.75 (75.65–79.61), H_2O [2.64], total [100.00] wt.%. With O = 8, the empirical formula is $(Fe^{3+}_{0.93}Ga^{3+}_{0.04})_{\Sigma 0.97}Ge^{4+}_{2.98}O_{6.90}(OH)_{1.17}$. The ideal formula, $Fe^{3+}Ge^{4+}_3O_7(OH)$, requires Fe_2O_3 19.83, GeO_2 77.93, H_2O 2.24, total 100.00 wt.%. Because precise values of the indices of refraction could not be determined, a meaningful index of compatibility could not be calculated.

Micro-X-ray absorption spectroscopy (*XAS*) *study*

The polished section used for quantitative electron-microprobe analyses was sent to the Advanced Light Source (ALS) facility in Berkeley, California for further study to determine the valence state of the Fe atom in eyselite. Analytical characterization by micro-XRD, micro-XRF (X-ray fluorescence), and micro-XAS were done at Beamline 10.3.2 [see Manceau *et al.* (2002) for a comprehensive review of the equipment and procedures available at ALS]. Micro-XRD patterns were taken with a 16 × 7 μm spot size, at an operating voltage of 14 keV, and showed that the eyselite grains are mosaic, with a spread of several degrees, without detectable (*h*0*l*) reflections. Micro-XRF mapping was done with a 5 × 5 μm beam spot size at operating voltages of 12 and 14 keV. The study revealed that the Fe:Ge ratio is constant between grains and within each grain. The results are consistent with a daltonide (stoichiometric) compound. Minor amounts of Ca and Ga were detected (as previously determined by electron probe); in addition, trace amounts of Rb and Sr also were detected. Micro-XAS was carried out at both the Fe*K* and Ge*K* edges. For the near-edge (XANES) region of Fe, goethite, fayalite and metallic Fe (alloy addition in aluminum tape) were used as standards. The XANES (X-ray Absorption Near-Edge Spectroscopy) results are shown in Figure 3, and demonstrate that the Fe in eyselite is trivalent. Magnetite, ZnO and α-GeO_2 were used as EXAFS (extended X-ray absorption edge fine structure) standards. EXAFS measurements at the Fe *K*-edge yielded an average Fe–O first-shell average distance of 2.00(2) Å, which is consistent with that in other Fe^{3+} oxides. EXAFS measurements at the Ge edge yielded a Ge–O first-shell average distance of 1.88 Å, which is considerably larger that that found in α–GeO_2 (1.74 Å), but is close to that found in β–GeO_2 (1.86 Å). These two polymorphs of GeO_2 differ in that the α-form has Ge in tetrahedral coordination, and the β-form has Ge in octahedral coordination. Thus we can postulate that the Ge atoms in eyselite are most likely in octahedral coordination. For both the Fe and Ge edges, several higher shells are visible; this feature suggests that the mineral is structurally well ordered.

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR EYSELITE

	$I_{est.}$	dÅ$_{(meas.)}$	dÅ$_{(calc.)}$	*hkl*		$I_{est.}$	dÅ$_{(meas.)}$	dÅ$_{(calc.)}$	*hkl*
*	40	4.105	4.103	011	*	5	1.722	1.724	312
*	100	3.681	3.679	111	*	20	1.656	1.656	042
	60b	3.121	3.156	220	*	80	1.646	1.648	322
			3.076	121	*	50	1.624	1.624	142
*	100	2.921	2.918	211	*	10b	1.561	1.559	501
*	30	2.631	2.634	031		30	1.539	1.541	332
*	5	2.591	2.589	221				1.539	511
*	40	2.512	2.511	131				1.538	242
*	30	2.430	2.430	040		15	1.500	1.501	351
*	90	2.403	2.405	320				1.500	161
*	5	2.332	2.332	140		3	1.466	1.468	113
*	20	2.294	2.294	311	*	10	1.432	1.431	261
*	10	2.263	2.263	002		10	1.404	1.405	531
*	30	2.227	2.224	231				1.403	213
*	10	2.143	2.141	041	*	20	1.397	1.398	360
*	15	2.122	2.124	321		15	1.384	1.384	600
	3	2.070	2.076	400				1.383	432
			2.073	141		5	1.368	Num.	Num.
	3	1.988	1.992	122	*	10	1.350	1.350	133
			1.987	202		10	1.328	Num.	Num.
	15	1.852	1.855	032		20	1.312	Num.	Num.
			1.852	411		20	1.302	1.301	352
	10	1.745	1.748	430				1.301	162
			1.746	151					

114.6 mm Debye-Scherrer powder camera; Cu radiation and Ni-filter (λCu*K*α = 1.54178 Å); intensities estimated visually, b: broad line; not corrected for shrinkage, and no internal standard; * : lines used for unit-cell refinement; indexed with *a* 8.302(4), *b* 9.718(4), *c* 4.527(2) Å. Num.: numerous lines.

INFRARED SPECTROSCOPY

The procedures for acquiring the infrared-absorption spectrum of eyselite are identical to those reported by Roberts *et al.* (1994). The sample was analyzed using a Bomen Michelson MB–100 FTIR spectrometer equipped with a wide-band mercury–cadmium telluride detector. The transmittance spectrum (Fig. 4) shows a medium-intensity, somewhat shallow absorption band with a peak at 2957 and a distinct shoulder at 3389 cm^{-1}, attributable to O–H stretching in the hydroxyl group. There is no evidence of a band in the 1600–1700 cm^{-1} region, which would be characteristic of H–O–H bending in structural H_2O. Bands at 1007, 1085 and 1230 cm^{-1} are unassigned, but are inferred to pertain to Ge–O interactions.

ACKNOWLEDGEMENTS

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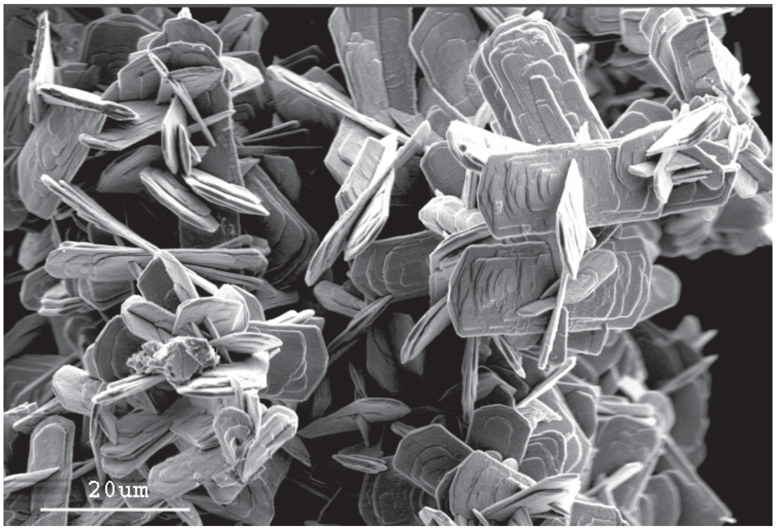

FIG. 2. SEM photomicrograph showing individual crystals of eyselite. Scale bar: 20 μm.

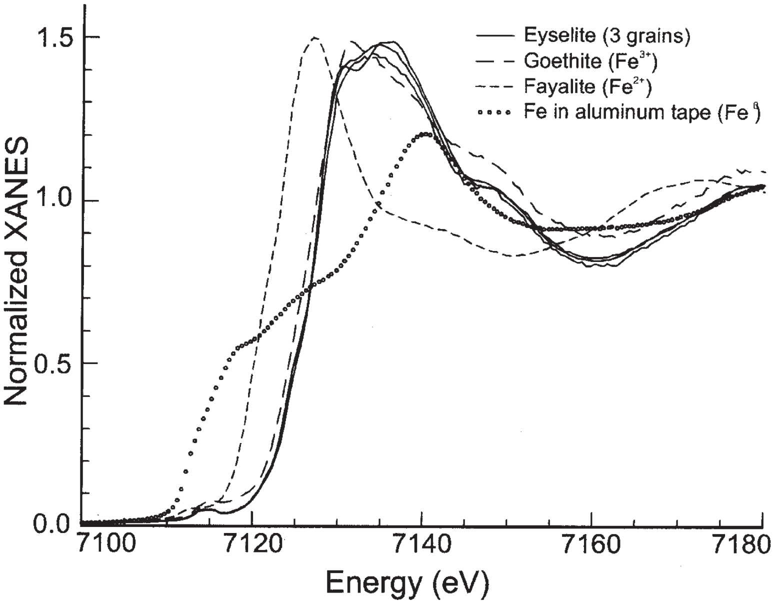

FIG. 3. XANES plots for three individual grains of eyselite (solid lines), goethite (dashed lines), fayalite (fine dashed lines) and metallic Fe (symbols). The differences between eyselite grains may be due to polarization effects.

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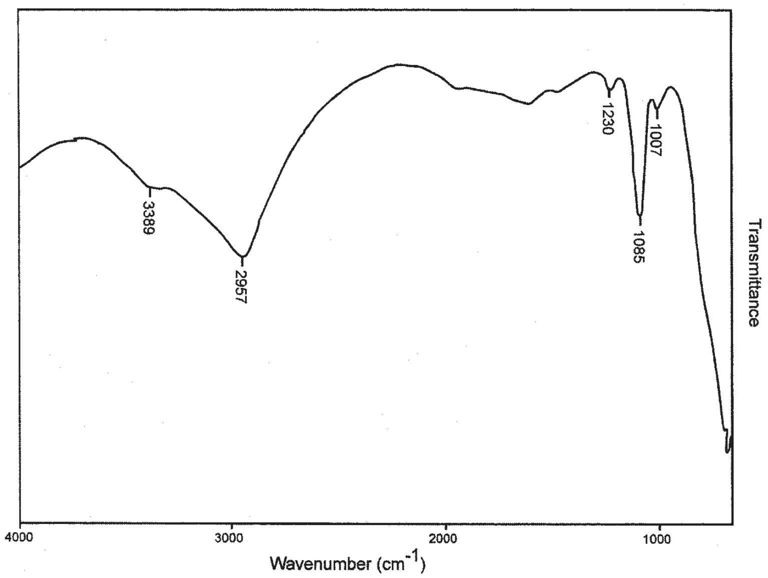

FIG. 4. Infrared-absorption spectrum for eyselite.

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