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SELENOJALPAITE, Ag_3CuSe_2, A NEW MINERAL SPECIES FROM THE SKRIKERUM Cu–Ag–Tl SELENIDE DEPOSIT, SMÅLAND, SOUTHEASTERN SWEDEN

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ABSTRACT

Selenojalpaite, ideally Ag_3CuSe_2, is a very rare mineral newly identified at the Skrikerum Cu–Ag–Tl selenide deposit, near Valdermarsvik, Småland, southeastern Sweden. It occurs as dark grey anhedral to subhedral grains up to 200 μm across, closely associated with eucairite, altaite, berzelianite and chalcopyrite. Selenojalpaite is opaque with a metallic luster; it possesses a black streak. It is brittle with an uneven fracture; the Vickers microhardness (VHN_{25}) is 37 kg/mm^2 (range 36–40), equivalent to a Mohs hardness of 4–4½. The calculated density is 7.64 g/cm^3 (on the basis of the empirical formula). In plane-polarized reflected light, selenojalpaite is light grey, weakly to moderately bireflectant, and weakly pleochroic from brownish grey to a slightly darker greenish grey. Between crossed polars, it is anisotropic, without characteristic rotation-tints or internal reflections. Values of reflectance in the range 400–700 nm are tabulated; values of R_{min} and R_{max} for the four standard COM wavelengths are 33.5, 37.1 (471.1 nm), 31.8, 35.1 (548.3 nm), 30.4, 34.0 (586.6 nm), and 29.3, 32.4 (652.3 nm), respectively. Its unit-cell parameters were derived by comparison with jalpaite, Ag_3CuS_2, which shows strong chemical and crystallographic similarities. Selenojalpaite is tetragonal, probable space-group $I4_1/amd$, with unit-cell parameters refined from powder data: a 8.939(1), c 11.844(2) Å, V 946.4(2) Å^3, $c : a$ 1.3250, $Z = 8$. The strongest seven powder-diffraction lines [d in Å(I)(hkl)] are: 4.47(60)(200), 2.891(85)(301), 2.813(80)(213), 2.473(75)(204), 2.426(100)(321), 2.162(70)(224) and 2.034(65)(215). Average results of 15 electron-microprobe analyses are Ag 59.20, Cu 11.81, Se 29.01, total 100.02 wt.%, corresponding to $Ag_{2.99}Cu_{1.01}Se_{2.00}$, on the basis of a total of six atoms. The name indicates that it is the Se-dominant analogue of jalpaite, Ag_3CuS_2.

Keywords: selenojalpaite, new mineral species, selenide, electron-microprobe data, reflectance data, X-ray-diffraction data, Skrikerum deposit, Småland, Sweden.

SOMMAIRE

La sélénojalpaïte, de composition idéale Ag_3CuSe_2, est un minéral rarissime nouvellement découvert au gisement de séléniures à Cu–Ag–Tl de Skrikerum, près de Valdermarsvik, Småland, dans le sud-est de la Suède. Elle se présente en grains xénomorphes à sub-idiomorphes gris foncé, atteignant 200 μm de diamètre, en association avec eucairite, altaïte, berzélianite et chalcopyrite. La sélénojalpaïte est opaque avec un éclat métallique; sa rayure est noire. Elle est cassante, et se brise le long de fractures irrégulières. La microdureté de Vickers (VHN_{25}) est 37 kg/mm^2 (intervalle 36–40), ce qui équivaut à une dureté de Mohs de 4–4½. La densité calculée à partir de la formule empirique est 7.64 g/cm^3. En lumière polarisée réfléchie, la sélénojalpaïte est gris pâle, faiblement à modérément biréflectante, et faiblement pléochroïque de gris brunâtre à gris verdâtre légèrement plus foncé. Vue avec polariseurs croisés, elle est anisotrope, sans teintes de rotation ou réflexions internes. Nous donnons les valeurs de réflectance sur l'intervalle 400–700 nm; les valeurs de R_{min} et R_{max} pour les quatre longueurs d'onde standard (COM) sont 33.5, 37.1 (471.1 nm), 31.8, 35.1 (548.3 nm), 30.4, 34.0 (586.6 nm), et 29.3, 32.4 (652.3 nm), respectivement. Les paramètres réticulaires ont été dérivés par comparaison avec ceux de la jalpaïte, Ag_3CuS_2, qui fait preuve de fortes ressemblances chimiques et cristallographiques. La sélénojalpaïte est tétragonale, groupe spatial probable $I4_1/amd$, avec les paramètres suivants affinés à partir des données obtenues par la méthode des poudres: a 8.939(1), c 11.844(2) Å, V 946.4(2) Å^3, $c : a$ 1.3250, $Z = 8$. Les sept raies les plus intenses du spectre de diffraction [d en Å(I)(hkl)] sont: 4.47(60)(200), 2.891(85)(301), 2.813(80)(213), 2.473(75)(204), 2.426(100)(321), 2.162(70)(224) et 2.034(65)(215). Les 15 analyses effectuées avec une microsonde électronique ont donné, en

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moyenne, Ag 59.20, Cu 11.81, Se 29.01, pour un total de 100.02% (poids), correspondant à $Ag_{2.99}Cu_{1.01}Se_{2.00}$ sur une base de six atomes. Le nom choisi indique son analogie à la jalpaïte, Ag_3CuS_2, dont c'est l'équivalent sélénifère.

(Traduit par la Rédaction)

Mots-clés: sélénojalpaïte, nouvelle espèce minérale, séléniure, données à la microsonde électronique, données de réflectance, diffraction X, gisement de Skrikerum, Småland, Suède.

INTRODUCTION

The new mineral species described herein, selenojalpaite, ideally Ag_3CuSe_2, is from the Skrikerum Cu–Ag–Tl selenide deposit, near Valdermarsvik, Småland, southeastern Sweden, a well-known source of rare selenide minerals. The Skrikerum deposit is the type locality for three Cu-bearing selenide phases: berzelianite (Cu_2Se), crookesite (Cu_7TlSe_4) and eucairite (CuAgSe).

The sample containing the new phase was not found *in situ*, but originates from the Mineralogical Collection of the Museo di Storia Naturale, Sezione di Mineralogia e Litologia, Università di Firenze, Italy, where it had been labeled as "eucairite (CuAgSe), Skrikerum, Sweden".

In the Skrikerum Cu–Ag–Tl selenide deposit, the selenides are present as fine anhedral inclusions or as fracture fillings within a calcite vein. Jonsson & Wagner (2002) reported that the calcite vein also contains the following minerals: native copper, Au–Ag alloy, Se-bearing chalcopyrite, Se-bearing bornite, berzelianite, covellite, umangite, athabascaite, klockmannite, ferroselite, eucairite, naumannite, fischesserite, crookesite, bukovite, clausthalite and Se-bearing sphalerite. These authors observed high compositional variability of the Cu-bearing selenides in terms of the ratio Se/(Se + S), as well as considerable nonstoichiometry in terms of the ratio *Me*:(S + Se). Chemical analyses of the stromeyerite and chalcocite associated with selenojalpaite yielded the following formulae (mean result of four analyses): $Cu_{0.97}Ag_{1.03}(S_{0.85}Se_{0.15})$ (stromeyerite), $Cu_{1.98}(S_{0.75}Se_{0.27})$ (chalcocite), thus indicating a Se-rich environment of formation. According to Jonsson & Wagner (2002), the chemical variations observed in the selenides could indicate that the calcite–selenide vein at the Skrikerum deposit formed as a result of multiple episodes of mineralization or from an evolving fluid system.

We have named the new mineral *selenojalpaite* to indicate that it is the Se-dominant analogue of jalpaite, Ag_3CuS_2. The new mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA (2004–48). Type material is housed in the mineralogical collection of the Museo di Storia Naturale, Università di Firenze, Italy, under catalogue number 1768/I.

OCCURRENCE AND PHYSICAL AND OPTICAL PROPERTIES

Selenojalpaite is typically intergrown with eucairite and berzelianite to form aggregates up to several hundred micrometers across (Fig. 1). It also occurs as dark grey anhedral to subhedral grains, up to 200 μm in length, which show no obvious twinning. The other mineral spatially associated with selenojalpaite is chalcopyrite.

The mineral is opaque with a metallic luster and possesses a black streak. It is brittle with an uneven fracture and without cleavage. Unfortunately, the density could not be measured because of the small grain-size; the calculated density is 7.64 g/cm^3 (on the basis of the empirical formula). Micro-indentation measurements carried out with a VHN load of 25 g gave the a mean value of 37 kg/mm^2 (range 36–40), corresponding to a Mohs hardness of 4–4½.

In plane-polarized incident reflected light, selenojalpaite is light grey, weakly to moderately bireflectant, and weakly pleochroic from brownish grey to a slightly darker greenish grey. Between crossed polars, the mineral is anisotropic, without characteristic rotation-tints and internal reflections. Selenojalpaite has a slightly higher reflectance than the associated eucairite.

Reflectance measurements were made in air with a MPM–200 Zeiss microphotometer equipped with a MSP–20 system processor on a Zeiss Axioplan ore microscope. Filament temperature was approximately 3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6, and 652.3 nm). Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Reflectance percentages for R_{min} and R_{max} are reported in the range 400–700 nm with a step of 20 nm in Table 1. The values (R_{min} and R_{max}) for the four standard COM wavelengths are 33.5, 37.1 (471.1 nm), 31.8, 35.1 (548.3 nm), 30.4, 34.0 (586.6 nm), and 29.3, 32.4 (652.3 nm), respectively. Figure 2 shows the reflectance curves obtained for selenojalpaite as well as those reported by Criddle & Stanley (1986) for jalpaite, Ag_3CuS_2, an isotypic mineral (see below).

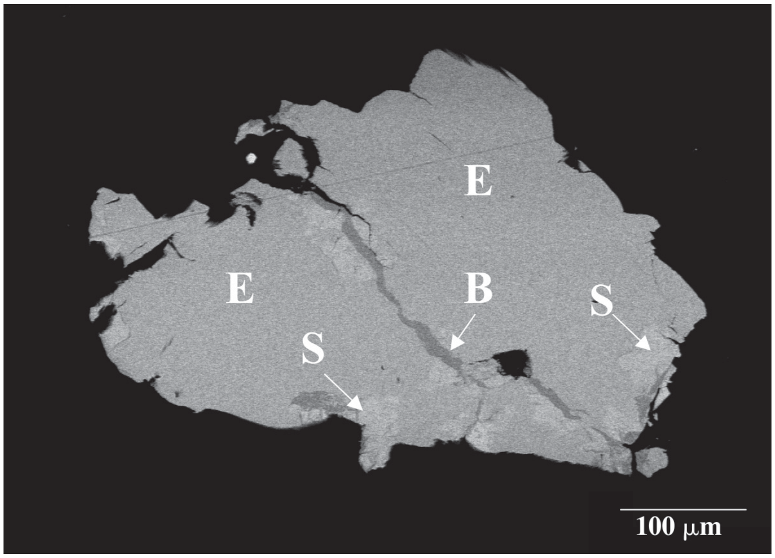

FIG. 1. Back-scattered electron image (SEM) of selenojalpaite (S), associated with eucairite (E) and berzelianite (B). Scale bar: 100 µm.

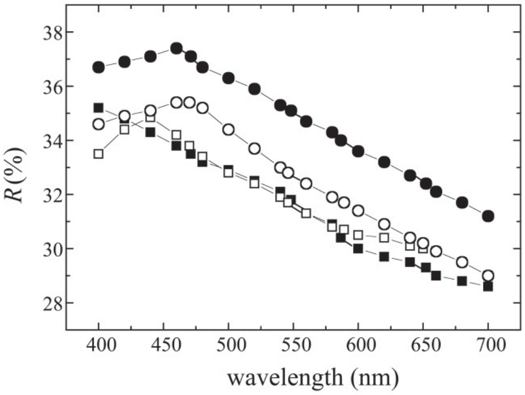

FIG. 2. Reflectance curves for selenojalpaite and jalpaite in air. Open symbols refer to jalpaite (Criddle & Stanley 1986), filled symbols refer to selenojalpaite. Circles and squares refer to R_{max} and R_{min} values, respectively.

TABLE 1. REFLECTANCE DATA FOR SELENOJALPAITE MEASURED IN AIR

λ (nm)	R_{min} (%)	R_{max} (%)	λ (nm)	R_{min} (%)	R_{max} (%)
400	35.2	36.7	560	31.3	34.7
420	34.8	36.9	580	30.9	34.3
440	34.3	37.1	**586.6**	**30.4**	**34.0**
460	33.8	37.4	600	30.0	33.6
471.1	**33.5**	**37.1**	620	29.7	33.2
480	33.2	36.7	640	29.5	32.7
500	32.9	36.3	**652.3**	**29.3**	**32.4**
520	32.5	35.9	660	29.0	32.1
540	32.1	35.3	680	28.8	31.7
548.3	**31.8**	**35.1**	700	28.6	31.2

CHEMICAL COMPOSITION

A preliminary qualitative chemical analysis, made using a scanning electron microscope equipped with an energy-dispersion spectrometer on the same fragment as used for the X-ray study, did not indicate the presence of elements with Z > 9 other than Ag, Cu, Se and very minor to trace amounts of Mn, Fe and S. The quantitative chemical composition was then determined using wavelength-dispersion spectrometry (WDS) by means of a JEOL JXA–8600 electron microprobe. Major and minor elements were determined at an accelerating voltage of 20 kV and a beam current of 40 nA, with variable counting-times: 30 s for Ag, Cu and Se and 60 s for Mn, Fe and S. For the WDS analyses, the following lines were used: Ag*L*α, Cu*K*α, Se second-order *L*α, Fe*K*α, Mn*K*α and S*K*α. The estimated analytical precision (in wt.%) is: ±0.30 for Ag and Se, ±0.20 for Cu, ±0.03 for Fe, Mn and S. The following standards were used: pure Ag (Ag), pure Cu (Cu), synthetic Bi_2Se_3 (Se), bustamite (Mn) and marcasite (Fe, S). The crystal fragment was found to be homogeneous within analytical error. The average chemical composition (15 analyses on different spots of the same grain) and ranges are reported in Table 2. On the basis of a total of six atoms, the empirical formula of selenojalpaite is $Ag_{2.99}Cu_{1.01}Se_{2.00}$. The simplified formula is Ag_3CuSe_2, which requires: Ag 59.37, Cu 11.66, Se 28.97, total 100.00 wt.%.

X-RAY CRYSTALLOGRAPHY

Two fragments, dug out of a polished section, were examined with an Oxford Diffraction Xcalibur^{TM} 2 single-crystal diffractometer (Enhance X-ray source, Mo$K\alpha$ X-ray radiation) fitted with a Sapphire 2 CCD detector. Both fragments gave extremely broad X-ray-diffraction profiles, even if their optical characteristics suggest adequate quality, which thus indicated that a powder-diffraction study was the only possible means of X-ray investigation.

Fully indexed powder-diffraction data obtained with a 114.6 mm Gandolfi camera X-ray (Ni-filtered Cu$K\alpha$ radiation) are presented in Table 3. The intensities were measured with an automated densitometer. The unit-cell parameters were derived by means of the program TREOR (Werner *et al.* 1985) and by comparison with the mineral jalpaite, Ag_3CuS_2 (Johan 1967, Grybeck & Finney 1968, Baker *et al.* 1992), which shows strong similarities with selenojalpaite, both from a chemical and a crystallographic point of view. Selenojalpaite is tetragonal; the refined unit-cell parameters, based on 36 reflections between 7.14 and 1.359 Å, are: a 8.939(1), c 11.844(2) Å, V 946.4(2) Å^3, $c : a$ 1.3250, $Z = 8$. Systematic absences noted among the available reflections (hkl: $h + k + l = 2n$; $hk0$: $h, k = 2n$; $0kl$: $k + l = 2n$; hhl: $2h + l = 4n$; $00l$: $l = 4n$; $h00$: $h = 2n$; $h0$: $h = 2n$) are consistent with the space group $I4_1/amd$.

RELATIONSHIP TO JALPAITE

Other than for slight differences in the intensity of the reflections between selenojalpaite and jalpaite (Baker *et al.* 1992), the X-ray powder data are quite similar. The a and c cell parameters of selenojalpaite [8.939(1) and 11.844(2) Å, respectively] are larger than those observed for jalpaite [8.6705(10) and 11.7573(18) Å, respectively, Baker *et al.* 1992] owing to the greater size of Se with respect to S. By means of a Rietveld crystal-structure refinement, Baker *et al.* (1992) described a structural model for jalpaite that is based on a distorted *bcc* packing of S atoms. These authors found two distinct Ag sites; the first one is surrounded by six S atoms forming a [2 + 4] distorted octahedral environment, whereas the second one is in a distorted tetrahedral environment. Atoms of Cu were found to be linearly coordinated by two S atoms. Considering the close similarity between the intensities in the X-ray-diffraction patterns of selenojalpaite and jalpaite, we hypothesize that all the atoms in selenojalpaite are ordered at the same positions as in jalpaite . Therefore, it seems reasonable to consider selenojalpaite and jalpaite as isotypic phases. Discussion of a structural model for selenojalpaite, however, must await the availability of suitable crystals, since the Cu–Ag–S–Se group of minerals contains many phases that are not isostructural. Amongst this group, acanthite (Ag_2S, space group $P2_1/n$: Frueh 1958) and naumannite (Ag_2Se, space group $P2_12_12_1$: Wiegers 1971), and stromeyerite (CuAgS, space group $Cmc2_1$: Baker *et al.* 1991) and eucairite (CuAgSe, space group *Pmmn*: Frueh *et al.* 1957) are not isostructural, whereas metacinnabar (HgS, space group $F\bar{4}3m$: Aurivillius 1964) and tiemannite (HgSe, space group $F\bar{4}3m$: Earley 1950), and thalcusite ($Cu_2FeTl_2S_4$, space group $I4/mmm$: Makovicky *et al.* 1980) and bukovite ($Cu_2FeTl_2Se_4$, space group $I4/mmm$: Makovicky *et al.* 1980) are isostructural.

TABLE 2. ELECTRON-MICROPROBE DATA FOR SELENOJALPAITE

	wt.%	range	atom ratio
Ag	59.20	58.85 – 59.94	2.99
Cu	11.81	11.51 – 12.08	1.01
Fe	0.00	0.00 – 0.08	0.00
Mn	0.00	0.00 – 0.11	0.00
Se	29.01	28.12 – 29.37	2.00
S	0.00	0.00 – 0.06	0.00
Total	100.02	99.85 – 100.89	

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR SELENOJALPAITE

I/I_0	d_{meas}	d_{calc}	h	k	l	I/I_0	d_{meas}	d_{calc}	h	k	l
45	7.14	7.135	1	0	1	5	1.885	1.884	1	1	6
60	**4.47**	**4.470**	**2**	**0**	**0**	20	1.805	1.806	2	0	6
20	3.79	3.788	2	1	1	35	1.784	1.784	4	0	4
25	3.61	3.612	1	0	3	10	1.768	1.768	4	3	1
15	3.56	3.568	2	0	2	5	1.712	1.713	3	2	5
5	3.16	3.160	2	2	0	10	1.629	1.629	4	3	3
10	2.963	2.961	0	0	4	20	1.600	1.599	4	1	5
85	**2.891**	**2.890**	**3**	**0**	**1**	5	1.581	1.580	4	4	0
80	**2.813**	**2.809**	**2**	**1**	**3**	30	1.531	1.530	5	2	3
50	2.552	2.551	3	1	2	5	1.481	1.481	0	0	8
75	**2.473**	**2.469**	**2**	**0**	**4**	5	1.479	1.480	4	0	6
100	**2.426**	**2.427**	**3**	**2**	**1**	40	1.458	1.458	6	1	1
25	2.375	2.378	3	0	3	20	1.440	1.441	3	3	6
45	2.292	2.290	1	0	5	15	1.427	1.427	4	3	5
40	2.234	2.235	4	0	0	10	1.405	1.405	4	2	6
70	**2.162**	**2.161**	**2**	**2**	**4**	5	1.394	1.394	4	4	4
65	**2.034**	**2.038**	**2**	**1**	**5**	25	1.377	1.377	6	1	3
40	1.986	1.985	3	3	2	5	1.359	1.359	5	2	5

The *d* values are expressed in Å. The strongest seven reflections are shown in **bold**.

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