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OENITE, CoSbAs, A NEW MINERAL SPECIES FROM THE TUNABERG Cu–Co-SULFIDE SKARNS, BERGSLAGEN, SWEDEN

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ABSTRACT

Oenite, ideally CoSbAs, is a new mineral species from the Tunaberg Cu–Co-sulfide skarns, southeastern Bergslagen, Sweden. It occurs as up to 300 μm silver-white anhedral aggregates in chalcopyrite as replacements of cobaltite and löllingite. Oenite is further associated with allargentum, bismuth, bornite, breithauptite, gudmundite, nisbite and tetrahedrite. Oenite is opaque with a metallic luster, grey streak and uneven fracture. The calculated density D_{calc} for oenite is 7.91 g cm^{-3} ($Z = 4$); $VHN_{100} = 599$. In reflected plane-polarized light, the mineral is silver-white; a weak bireflectance and pleochroism from white to slightly darker creamish white are only visible in oil on grain boundaries. Anisotropism, in reddish brown and purplish colors, is distinct in air and in oil. Reflectance values (nm, $R_2\%/R_1\%$): 470, 58.2/55.5; 546, 56.8/55.6; 589, 55.8/55.5; 650, 55.0/55.5. On the basis of results of eighty electron-microprobe analyses on six samples, oenite shows continuous solid-solution in the system CoSbAs–FeSbAs–NiSbAs between CoSbAs and (Fe,Ni)SbAs, an unnamed (Fe,Ni)-rich member with Fe > Co. The relatively constant chemical composition of oenite in a chalcopyrite-rich specimen was chosen as representative; the mean values for 21 analyses are (in wt.%): Co 15.4(1.3), Fe 5.6(1.5), Ni 2.7(0.9), Cu 0.1(0.1), Sb 47.4(1.0), As 26.9(2.1), S 2.0(1.2), sum 100.1(0.7). The average chemical formula is $(Co_{0.65}Fe_{0.24}Ni_{0.11})_{\Sigma1.00}(Sb_{0.96}As_{0.04})_{\Sigma1.00}(As_{0.85}S_{0.15})_{\Sigma1.00}$ or, ideally, CoSbAs. The most Co-rich composition of oenite corresponds to $(Co_{0.86}Fe_{0.04}Ni_{0.10})_{\Sigma1.00}Sb_{1.00}(As_{0.89}Sb_{0.07}S_{0.04})_{\Sigma1.00}$. The unit cell is orthorhombic, space group unknown, *a* 3.304(6), *b* 6.092(8), *c* 10.258(13) Å, $V = 206.5(8)$ Å^3. The strongest seven X-ray powder reflections [*d* in Å(I)(*hkl*)] are 2.63(10)(022), 2.53(8)(112), 1.942(10)(015), 1.730(4)(130), 1.640(4)(016 or 132), 1.396(4)(222), and 1.118(8)(240 or 137 or 152). This XRD pattern is almost identical with that of synthetic CoSbAs (in prep.). The name honors Professor Ing Soen Oen, Amsterdam, for his important contributions to ore geology and ore mineralogy.

Keywords: oenite, new mineral species, unnamed (Fe,Ni)SbAs, electron-microprobe analyses, system CoSbAs–NiSbAs–FeSbAs, Tunaberg Cu–Co-sulfide skarns, Bergslagen, Sweden.

SOMMAIRE

L'oenite, nouvelle espèce minérale dont la composition idéale est CoSbAs, a été découverte dans les skarns minéralisés en sulfures de Cu et de Co de Tunaberg, dans le sud-est du Bergslagen, en Suède. On la trouve en agrégats de couleur blanc argenté 300 μm de diamètre dans la chalcopyrite, en remplacement de la cobaltite et de la löllingite. L'oenite est aussi associée aux phases allargentum, bismuth, bornite, breithauptite, gudmundite, nisbite et tétraédrite. C'est un minéral opaque ayant un éclat métallique, une rayure grise et une cassure inégale. La densité calculée D_{calc} est 7.91 ($Z = 4$); $VHN_{100} = 599$. En lumière réfléchie, nicols non croisés, l'oenite est blanc argenté, avec une faible biréflectance et un pléochroïsme allant du blanc au blanc légèrement crémeux, visible seulement dans l'huile en bordure des grains. L'anisotropie, en couleurs brun rougeâtre à violacée, est distincte dans l'air comme dans l'huile. Les valeurs de réflectance (nm, $R_2\%/R_1\%$) sont 470, 58.2/55.5; 546, 56.8/55.6; 589, 55.8/55.5; 650, 55.0/55.5. D'après les résultats de quatre-vingt analyses à la microsonde électronique, prélevées sur six échantillons, l'oenite fait preuve d'un solution solide continue dans le système CoSbAs–FeSbAs–NiSbAs, entre CoSbAs et (Fe,Ni)SbAs, membre sans nom dans lequel la proportion du Fe dépasse celle du Co. La composition relativement constante de l'oenite dans un échantillon riche en chalcopyrite a été choisie représentative de l'espèce. Les résultats moyens de 21 analyses (en %, poids) sont: Co 15.4(1.3), Fe 5.6(1.5), Ni 2.7(0.9), Cu 0.1(0.1), Sb 47.4(1.0), As 26.9(2.1), S 2.0(1.2), total 100.1(0.7). La formule chimique représentative est $(Co_{0.65}Fe_{0.24}Ni_{0.11})_{\Sigma1.00}(Sb_{0.96}As_{0.04})_{\Sigma1.00}(As_{0.85}S_{0.15})_{\Sigma1.00}$ ou, idéalement, CoSbAs. La composition la plus riche en Co correspond à $(Co_{0.86}Fe_{0.04}Ni_{0.10})_{\Sigma1.00}Sb_{1.00}(As_{0.89}Sb_{0.07}S_{0.04})_{\Sigma1.00}$. La maille élémentaire

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est orthorhombique, mais le groupe spatial est méconnu; *a* 3.304(6), *b* 6.092(8), *c* 10.258(13) Å, $V = 206.5(8)$ Å^3. Les sept raies les plus intenses du spectre de diffraction [*d* en Å(I)(*hkl*)] sont 2.63(10)(022), 2.53(8)(112), 1.942(10)(015), 1.730(4)(130), 1.640(4)(016 ou 132), 1.396(4)(222), et 1.118(8)(240 ou 137 ou 152). Ce spectre est presqu'identique à celui de l'équivalent synthétique CoSbAs. Le nom honore Ing Soen Oen, professeur à Amsterdam, pour ses contributions importantes à la géologie des gîtes minéraux et à la minéralogie des minerais.

(Traduit par la Rédaction)

Mots-clés: oenite, nouvelle espèce minérale, (Fe,Ni)SbAs, analyses à la microsonde électronique, système CoSbAs–NiSbAs–FeSbAs, skarns à sulfures de Cu–Co, Tunaberg, Bergslagen, Suède.

INTRODUCTION

The Tunaberg Cu–Co sulfide skarns containing the new mineral species oenite, ideally CoSbAs, occur in a felsic metatuffite formation, in the upper part of an Early Proterozoic (1.88–1.83 Ga; Dobbe *et al.* 1995) volcanosedimentary sequence metamorphosed to the upper amphibolite facies. The Tunaberg polymetallic sulfide deposits, in south-central Sweden, are located in the southeastern part of the Bergslagen metallogenic province (16°55' East and 58°39' North), about 100 km southwest of Stockholm. The mineralization in the upper metatuffite formation shows a central zone of Cu–Co sulfide skarns hosted by intercalated skarn-altered marbles, and a peripheral zone of Zn–Pb sulfides hosted by graphite slates, metatuffites and marbles (Dobbe & Oen 1993, 1994). Two sulfide assemblages in Cu–Co sulfide diopside – hedenbergite – hornblende skarns of the central zone are recognized (Dobbe & Oen 1994): pyrrhotite – cubanite – chalcopyrite of assemblage 1 originally crystallized as a pyrrhotite – *iss* (intermediate solid-solution) assemblage at temperatures above 500°C, whereas chalcopyrite – bornite – galena of assemblage 2 crystallized from Cu-enriched evolved fluids at lower temperatures. Stages of differentiation in assemblage 2 are characterized by subassemblages of (Co,Ni,Fe) (sulf)arsenides (2A), (Co,Ni,Fe) (sulf)antimonides (2B), (Co,Ni,Fe) sulfides (2C), Bi–Sb–Ag–Au–Hg–Te as native elements and alloys (2D), tetrahedrite (2E), sulfosalts and Bi–Sb–Ag–Mn–Cd–Sn-sulfides (2F), and oxides (2G).

Oenite (pronounced *oonite*) is named after Dr. Ing Soen Oen (1928–1996), Professor of Petrology, Mineralogy and Ore Geology at the University of Amsterdam and at the Vrije Universiteit at Amsterdam, in recognition of his important contributions to the geology and mineralogy of ore deposits. The mineral and the mineral's name have been approved by the Commission on New Minerals and Mineral Names, IMA. The type material, consisting of several hand specimens, polished sections and polished thin sections, is preserved in the mineral collection of the Instituut voor Aardwetenschappen, Vrije Universiteit, Amsterdam.

OCCURRENCE OF OENITE

Oenite was found in polished sections of arsenide and antimonide-rich chalcopyrite – bornite – galena associations collected from the dumps at the abandoned mine in Cu–Co sulfide skarns of the central zone. Oenite forms anhedral, polycrystalline aggregates up to 300 μm across in chalcopyrite, usually along contacts with cobaltite (Fig. 1). Chalcopyrite in oenite-bearing specimens is a host for minerals of subassemblages 2B, D, E and F. Gudmundite (locally Co,As-bearing; Dobbe & Oen 1994) in chalcopyrite is separated from cobaltite by an oenite-rich zone. Cobaltite is replaced by chalcopyrite and oenite. In magnetite-bearing chalcopyrite–galena samples, a 10–60 μm-wide rimming aggregate of oenite grains occur as a replacement of löllingite enclosed in chalcopyrite (Fig. 2A), whereas löllingite enclosed in galena is replaced by (Fe,Ni)-rich oenite and unnamed (Fe,Ni,Co)SbAs (Fig. 2B). Oenite may contain inclusions of native bismuth, dyscrasite or allargentum, breithauptite, chalcopyrite and idiomorphic sphalerite; the mineral is rimmed by native bismuth, dyscrasite or allargentum, breithauptite, nisbite, and tetrahedrite. Other minerals identified in oenite-bearing specimens are acanthite, antimony, arsenopyrite, cobalt pentlandite, (para)costibite, cubanite, kieftite ($CoSb_3$: Dobbe *et al.* 1994), mackinawite, pyrrhotite, stannoidite and uraninite.

CHEMICAL COMPOSITION

Electron-microprobe analyses were performed with a Cambridge Instruments Microscan-9 operated at an acceleration potential of 15 kV and at a beam current of 40 nA. Counting times were 15 s. The intensity of *K*α lines were measured for Co, Ni, Fe, Cu, S, of *L*α lines for Sb, As, and of *M*α lines for Bi. Pure metals (Co, As), heazlewoodite (Ni), troilite (Fe), chalcopyrite (Cu), stibnite (Sb, S), and bismuthinite (Bi, S), were used as standards. A ZAF correction procedure was applied using Berger's & Selzer's J/Z value (Reed 1993).

Analytical results for oenite illustrate extensive solid-solution between CoSbAs and (Fe,Ni)SbAs

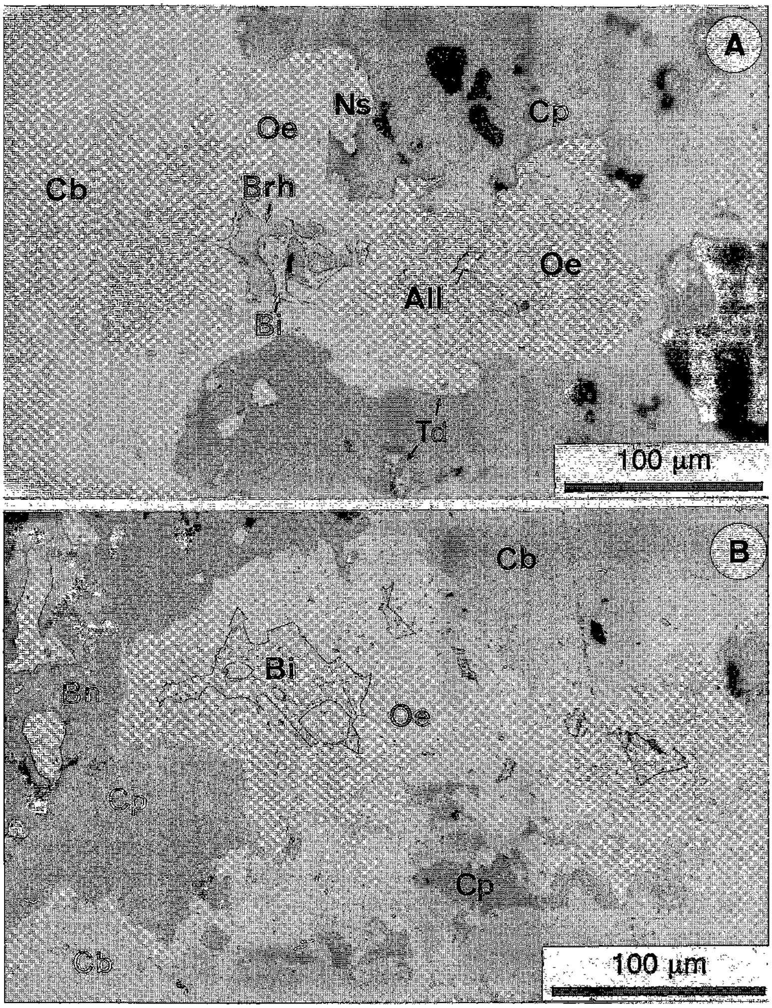

FIG. 1. A–B. Rimming aggregates of oenite (Oe) along contacts with cobaltite (Cb) and chalcopyrite (Cp). Oenite with inclusions of native bismuth (Bi), breithauptite (Brh) and allargentum (All). Nisbite (Ns) and tetrahedrite (Td) also occur as an overgrowth on oenite. Cobaltite in B is corroded and replaced by oenite and chalcopyrite. Bn: bornite. Parallel nicols and 470 nm filter to enhance contrast between oenite and cobaltite. Specimen RD–90.600A.

(Fig. 3, Table 1). A similar, extensive coupled replacement of cobalt by iron and nickel in (Co,Ni,Fe)–(sulf)arsenides from Tunaberg occurs in cobaltite–gersdorffite and safflorite–löllingite solid solutions (Dobbe & Oen 1994). According to the nomenclature of solid solutions in ternary systems (Nickel 1992), (Fe,Ni)SbAs with Fe > Co can be regarded as an unnamed Fe–Ni-rich member in the CoSbAs–FeSbAs–NiSbAs system. Twenty-one analyses carried out on specimen RD–90.600A, (col. 1–6, Table 1) were selected as representatives of the chemical composition of oenite. On the basis of 3 atoms in the unit cell and assuming that S substitutes for As (see below), the average composition of oenite is $(Co_{0.65}Fe_{0.24}Ni_{0.11})_{\Sigma1.00}(Sb_{0.96}As_{0.04})_{\Sigma1.00}(As_{0.85}S_{0.15})_{\Sigma1.00}$ or, ideally, CoSbAs. The most Co-rich composition corresponds to $(Co_{0.86}Fe_{0.04}Ni_{0.10})_{\Sigma1.00}Sb_{1.00}(As_{0.89}Sb_{0.07}S_{0.04})_{\Sigma1.00}$. The most (Fe,Ni)-rich compositions of unnamed (Fe,Ni)SbAs corresponds to $(Fe_{0.52}Ni_{0.37}Co_{0.13})_{\Sigma1.02}(Sb_{0.99}As_{0.01})_{\Sigma1.00}(As_{0.88}S_{0.10})_{\Sigma0.98}$.

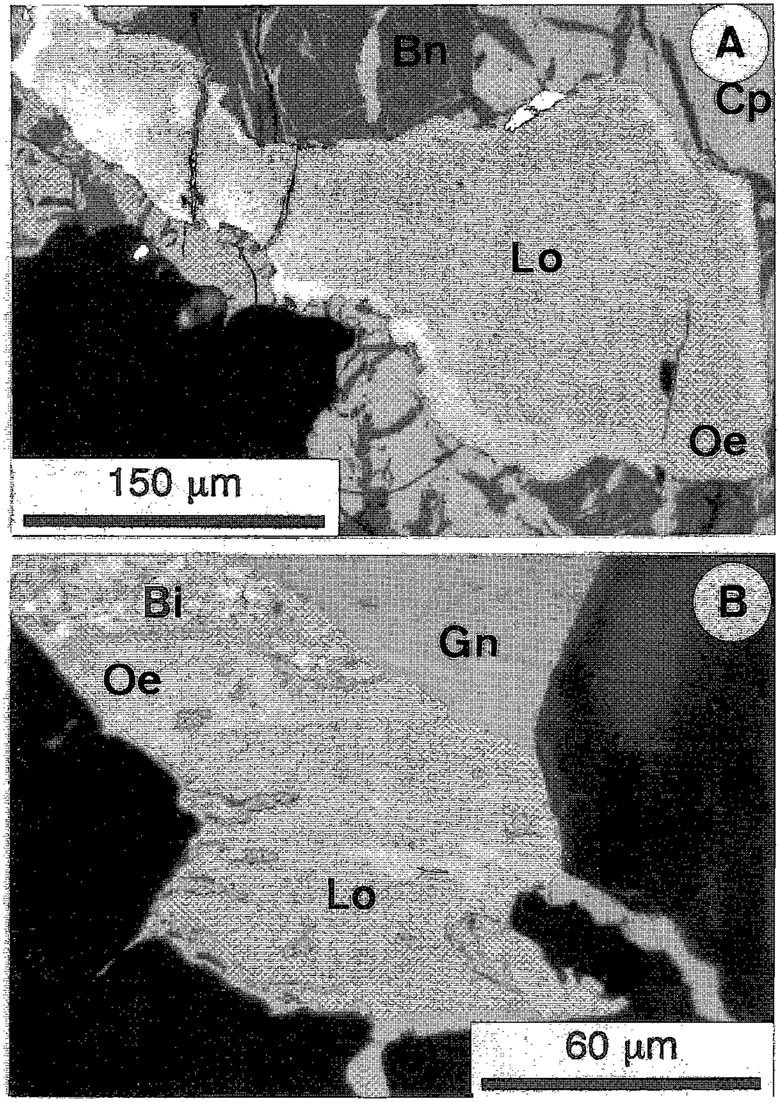

FIG. 2. A. Löllingite (Lo) with rim and overgrowth of oenite (Oe) in chalcopyrite (Cp) and bornite (Bn). Black: gangue. Bi: native bismuth. B. Overgrowth of (Fe,Ni)-rich oenite and unnamed (Fe,Ni)SbAs on löllingite (Lo) in galena (Gn) and gangue (black). Bi: native bismuth. Parallel nicols. Specimen RD–608B.

The proportion of arsenic shows a strong negative correlation with that of S, which suggests that S substitutes for As; the proportions of Sb and S show no correlation. The majority of the compositions plot within the ranges 0.75–0.99 *apfu* (atoms per formula unit) As, 0.94–1.02 *apfu* Sb and 0.05–0.27 *apfu* S. The range of Sb for (As + S) substitution in natural oenite is very similar to that in synthetic $CoSb_{0.75-1.18}As_{0.80-1.24}$ in the Co–Sb–As (= 1:1:1) system (in prep.).

Limited substitution of Fe + Ni for Co occurs in oenite in chalcopyrite-rich specimens RD–90.600A and PV–5772. Locally, the Fe-content of oenite increases with S/As values, whereas Ni tends to decrease (Table 1, anal. 1 to 6).

Extensive substitution of Fe + Ni for Co occurs in (Fe,Ni)-rich oenite and unnamed (Fe,Ni)SbAs in galena-rich specimens RD–608B and Dobbe 1, 3 and 4 (Fig. 3). This has no significant effect on the ratio S/As.

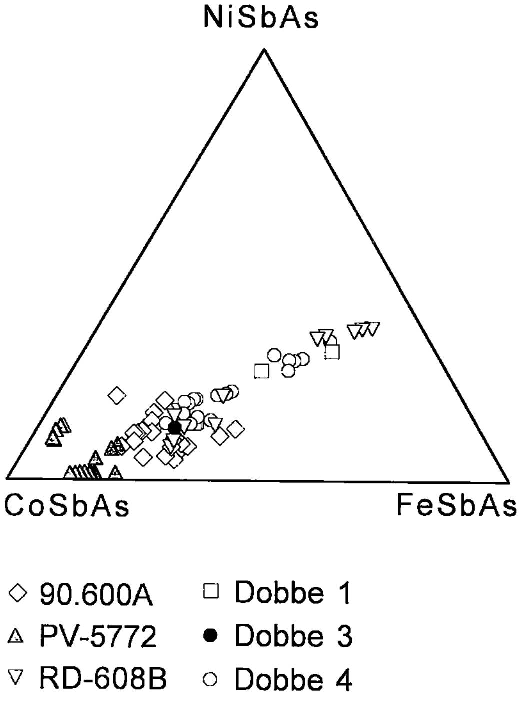

FIG. 3. CoSbAs–FeSbAs–NiSbAs diagram showing extensive solid-solution between oenite and unnamed (Fe,Ni)SbAs.

Regular patterns between Co-rich and (Fe,Ni)-rich parts were only found in grain 4A of specimen Dobbe 1, which consists of alternating zones of oenite, (Co,Fe,Ni)SbAs, and (Fe,Ni,Co)SbAs. Compositions 15 and 16 (Table 1) represent the most Co- and (Fe,Ni)-rich zones in grain 4A, respectively.

Cobaltite in specimen RD–90.600A (Fig. 1) has an average composition $(Co_{0.65}Ni_{0.22}Fe_{0.17})AsS$; löllingite in specimens RD–608B, Dobbe 1 and Dobbe 4 (Fig. 2) has an average composition $(Fe_{0.61}Co_{0.35}Ni_{0.07})As_2$.

PHYSICAL AND OPTICAL PROPERTIES

In hand specimens, oenite is opaque with a metallic luster and silver-white color. The mineral is characterized by a grey streak and brittle, uneven fracture without cleavage. Crystals and aggregates show irregular forms; twinning is not observed. One indentation gave a VHN_{100} microhardness value of 599. The polishing hardness of oenite is higher than for chalcopyrite, nisbite, breithauptite, sphalerite and tetrahedrite, and lower than for cobaltite and safflorite–löllingite; it is close to that of gudmundite.

In reflected, plane-polarized light, oenite is silver-white in air, and white with a faint yellowish or creamy tint in oil. Neither bireflectance nor reflectance pleochroism is seen in air; a weak bireflectance and pleochroism from white to slightly darker creamy white is only noticeable at its own grain boundaries in

TABLE 1. CHEMICAL COMPOSITION OF OENITE AND UNNAMED (Fe,Ni)SbAs

Anal. No	1	2	3	4	5	6	7*	8*	9*	10*	11	12	13	14	15	16	17	18	19	20
Specimen	RD-90.600A						PV-5772				RD-608B				Dobbe 1		Dobbe 4			
Grain code	--- A ---		--- B ---		--- D ---		--- ZG ---		--- ZH ---		A	B	C	J	4A		17A	21A	--- 16A ---	
Co, Wt%	16.0	15.7	16.5	16.1	15.5	14.9	19.9	18.7	20.3	17.2	15.4	13.9	5.3	3.0	13.7	5.0	13.1	11.2	7.1	13.2
Fe	4.5	6.5	4.3	7.0	4.9	6.7	0.8	0.8	2.6	3.7	6.3	5.6	9.7	11.7	6.8	10.9	5.8	7.3	9.4	6.7
Ni	2.9	2.1	2.7	1.5	2.8	2.2	2.3	2.9	0.1	2.1	2.1	4.0	8.0	8.7	3.4	7.4	4.4	4.9	6.7	3.6
Cu	n.d.	n.d.	0.1	n.d.	0.5	0.4	n.d.	n.d.	0.9	0.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sb	47.0	48.2	46.7	48.5	47.2	46.7	51.0	54.0	49.0	47.4	47.7	45.7	47.7	48.3	47.9	48.2	44.8	47.2	47.6	46.6
As	28.7	25.0	29.5	24.6	27.8	26.5	25.9	23.3	24.3	28.2	26.4	29.1	27.9	26.6	27.4	26.5	30.7	28.0	27.0	27.5
S	1.1	2.9	1.0	3.6	1.3	3.0	0.5	0.4	1.9	0.8	1.9	0.6	0.7	1.3	1.0	1.5	0.9	1.2	1.3	0.7
Total	100.2	100.4	100.8	101.3	100.0	100.4	100.4	100.1	99.1	100.1	99.8	98.9	99.3	99.6	100.2	99.5	99.7	99.8	99.1	99.3
Co, form. unit	0.68	0.64	0.69	0.65	0.65	0.61	0.86	0.83	0.86	0.73	0.64	0.60	0.23	0.13	0.58	0.21	0.55	0.47	0.30	0.56
Fe	0.20	0.28	0.19	0.30	0.22	0.29	0.04	0.04	0.12	0.17	0.28	0.25	0.44	0.52	0.30	0.49	0.26	0.33	0.42	0.30
Ni	0.12	0.09	0.12	0.06	0.12	0.09	0.10	0.13		0.09	0.09	0.17	0.34	0.37	0.14	0.31	0.19	0.21	0.29	0.15
Cu					0.02	0.02			0.04	0.03										
Sb	0.96	0.96	0.95	0.95	0.97	0.92	1.07	1.16	1.01	0.97	0.97	0.95	0.99	0.99	0.98	0.99	0.91	0.97	0.98	0.95
As	0.95	0.81	0.97	0.78	0.92	0.85	0.89	0.81	0.82	0.94	0.87	0.98	0.94	0.89	0.92	0.88	1.02	0.93	0.91	0.91
S	0.09	0.22	0.08	0.26	0.10	0.22	0.04	0.03	0.15	0.07	0.15	0.05	0.06	0.10	0.08	0.12	0.07	0.09	0.10	0.13

Bi not detected; n.d. = not detected; (*) Analyst: W.J. Lustenhouwer.
Anal. No. 1, 3, 5: S-poor oenite. Anal. No. 2, 4, 6: S-rich oenite.
Anal. No. 1, 2: oenite in Fig. 1B. Anal. No. 11: oenite in Fig. 2A. Anal. 13: unnamed (Fe.Ni,Co)SbAs in Fig. 2B.

TABLE 2. X-RAY POWDER DATA FOR OENITE

*I*est	*d*meas	*d*calc	*hkl*	*I*est	*d*meas	*d*calc	*hkl*
2	3.28	3.30	100	3	1.576	1.576	211
2	2.90	2.90	110			1.573	202
3	2.78	2.79	111	1	1.520	1.523	040
		2.78	102			1.523	212
10	2.63	2.62	022			1.519	106
8	2.53	2.53	112	2	1.4906	1.4909	026
2	2.36	2.36	014	1	1.4439	1.4433	035
2	2.27	2.27	023	4	1.3963	1.3974	222
10	1.942	1.944	015	2	1.1362	1.1373	046
4	1.730	1.730	130			1.1362	151
2	1.702	1.706	131	8	1.1182	1.1198	240
		1.702	025			1.1182	137
4	1.640	1.646	016			1.1158	152
		1.639	132				

– 114.6 mm Debye-Scherrer camera employing Fe-filtered Co radiation ($\lambda CoK\alpha$ = 1.7902 Å)

– intensities estimated visually

– (*d*) calculated for orthorhombic cell: a_o 3.3044, b_o 6.0922, c_o 10.2583 Å

– chalcopyrite reflections have been deleted

oil. Oenite is weakly to distinctly anisotropic with reddish brown (darker than the yellowish brown of adjoining löllingite) to darker pale violet rotation tints (brighter than the blue of löllingite). With the analyzer uncrossed by 2°, the rotation tints are brownish red to purplish blue. The rotation tints are more intense in oil. Reflectance measurements were made in air against the tungsten carbide standard Zeiss WC–6: (nm, R_2%, R_1%): 470, 58.2, 55.5; 546, 56.8, 55.6; 589, 55.8, 55.5; 650, 55.0, 55.5. Flat R_1 and negative R_2 spectral curves converge, with crossings above 550 nm. The reflectance of oenite is higher than for cobaltite, safflorite–löllingite and gudmundite, and lower than for nisbite.

X-RAY STUDIES

Single crystals suitable for X-ray studies have not been found. X-ray powder-diffraction data were obtained with a 57.3 mm diameter Gandolfi-type camera on grains removed from polished sections with a microscope-mounted drill (Verschure 1978). Several experiments were performed on fragments of oenite to minimize contaminations with cobaltite, bornite and chalcopyrite. Finally, a 30 × 20 × 20 μm grain was found; it gave only three of the strongest reflections of chalcopyrite.

The results presented in Table 2 were obtained with a 114.6 mm Debye–Scherrer camera on the same grain of oenite; its polycrystalline nature resulted in smooth and continuous reflections of the oenite, in contrast to the three reflections of chalcopyrite, which have a grainy appearance. The chalcopyrite reflections have been deleted from Table 2, but were used as an internal standard to verify the accuracy of the pattern of oenite.

Indexing and refinement of the pattern were performed with the program SCANIX 2.20. A fully indexed powder pattern between 3.28 and 1.1182 Å is given in Table 2. The unit-cell parameters, based on 11 reflections in the X-ray powder pattern for which unambiguous indexing was possible, are: *a* 3.304(6), *b* 6.092(8), *c* 10.258(13) Å, *V* 206.5(8) Å^3 and *a*:*b*:*c* 0.5424:1:1.6838. With Z = 4, the calculated density for $(Co_{0.65}Fe_{0.24}Ni_{0.11})_{\Sigma1.00}(Sb_{0.96}As_{0.04})_{\Sigma1.00}(As_{0.85}S_{0.15})_{\Sigma1.00}$ is 7.91 g/cm^3. The XRD pattern of oenite is almost identical to that of synthetic CoSbAs (in prep.). Oenite is isoelectronic with the members of the marcasite group: safflorite, costibite and clinosafflorite.

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