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OWENSITE, $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$, A NEW MINERAL SPECIES FROM THE WELLGREEN Cu–Ni–Pt–Pd DEPOSIT, YUKON[1]

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Abstract

Owensite is a new mineral species found in samples from the Wellgreen Cu–Ni–Pt–Pd deposit, Kluane District, Yukon Territory. The mineral, which is very rare, occurs as small anhedral grains ranging from 6 × 12 to 43 × 110 μm, and is closely associated with pyrrhotite, magnetite, chalcopyrite and pentlandite. Owensite is opaque, with a metallic luster and a black streak. The mineral is pale brownish grey in plane-polarized reflected light, and isotropic. Reflectance spectra and color values are given. Owensite displays cubic symmetry and has a refined unit-cell parameter a of 10.373(2) Å and a V of 1116.0(3) Å^3, with the following strongest X-ray powder lines [d in Å(I)(*hkl*)]: 3.460(40)(300), 3.281(40)(310), 2.996(90)(222), 2.378(90)(331), 1.835(100)(440) and 1.779(40)(433). Its crystal structure has been determined as cubic, space group *Pm3m* (Szymański 1995). Based on the least-squares-refined unit-cell parameter, a = 10.349(1) Å, with Z = 1, D_{calc} is 4.78 g/cm^3. The average result of electron-microprobe analyses gave: Ba 23.04, Pb 3.58, Cu 25.33, Fe 20.24, Ni 0.25, S 27.11, total 99.55 wt.%, which yields the empirical formula $(Ba_{5.42}Pb_{0.56})_{\Sigma=5.98}(Cu_{12.87}Fe_{11.70}Ni_{0.14})_{\Sigma=24.71}S_{27.31}$, or simply $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$. Structurally, owensite is closely related to djerfisherite $K_6Na(Fe,Ni,Cu)_{24}S_{26}Cl$, but it is totally devoid of the Cl and monovalent metals found in the latter mineral. Owensite honors DeAlton R. Owens (1934–) of the Canada Centre for Mineral and Energy Technology, Ottawa, for his contributions to mineralogy, particularly in the field of electron-microbeam analyses.

Keywords: new mineral species, owensite, $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$, X-ray-diffraction data, electron-microprobe data, reflectance data, Wellgreen deposit, Yukon Territory.

Sommaire

Nous avons découvert une nouvelle espèce minérale, la owensite, dans des échantillons prélevés du gisement à Cu–Ni–Pt–Pd de Wellgreen, du district de Kluane, Territoire du Yukon. Le minéral, qui est d'ailleurs très rare, se présente sous forme de petits grains xénomorphes mesurant de 6 × 12 à 43 × 110 μm; il est étroitement associé à pyrrhotite, magnétite, chalcopyrite et pentlandite. La owensite est opaque, possède un éclat métallique, et sa rayure est noire. Le minéral est gris brunâtre pâle en lumière réfléchie, et isotrope. Nous avons déterminé son spectre de réflectance et ses valeurs de couleur. La owensite est cubique, avec a égal à 10.373(2) Å et V égal à 1116.0(3) Å^3; les six raies les plus intenses [d en Å(I)(*hkl*)] sont 3.460(40)(300), 3.281(40)(310), 2.996(90)(222), 2.378(90)(331), 1.835(100)(440) et 1.779(40)(433). L'ébauche de sa structure cristalline montre qu'il s'agit d'un minéral cubique, groupe spatial *Pm3m* (Szymański 1995); avec un paramètre réticulaire a affiné par la méthode des moindres carrés, 10.349(1) Å, et Z égal à 1, la densité calculée serait égale à 4.78. La moyenne des analyses à la microsonde électronique donne: Ba 23.04, Pb 3.58, Cu 25.33, Fe 20.24, Ni 0.25, S 27.11, total 99.55% par poids, ce qui mène à la formule empirique $(Ba_{5.42}Pb_{0.56})_{\Sigma=5.98}(Cu_{12.87}Fe_{11.70}Ni_{0.14})_{\Sigma=24.71}S_{27.31}$ ou, plus simplement, $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$. La structure de la owensite est étroitement liée à celle de la djerfisherite, $K_6Na(Fe,Ni,Cu)_{24}S_{26}Cl$, malgré l'absence de Cl et de cations monovalents. La owensite honore DeAlton R. Owens (1934–) du Centre Canadien pour la Technologie des Minéraux et de l'Energie, pour ses contributions à la minéralogie, particulièrement dans le domaine d'analyses par micro-faisceau électronique.

Mots-clés: nouvelle espèce minérale, owensite, $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$, données de diffraction X, données de microsonde électronique, données de réflectance, gisement de Wellgreen, Territoire du Yukon.

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INTRODUCTION

A new mineral of the djerfisherite group was discovered during the investigation of a series of samples taken from the Wellgreen Cu–Ni–Pt–Pd deposit (Cabri *et al.* 1993). The Wellgreen deposit is located in the Kluane District of southwestern Yukon, 315 km northwest of Whitehorse and 14 km to the west of the Alaska Highway, at latitude 61°28′N and longitude 139°32′W. The deposit was mined in 1972–73 for Cu and Ni, with the total production amounting to 171,651 t of ore, and in recent years there has been renewed interest in the deposit, with a particular emphasis on the platinum-group element (PGE) content. The deposit is hosted by the Quill Creek Ultramafic Complex of lower Triassic age, which is located in a continuous chain of foothills along the northeastern flank of the St. Elias Mountains, Yukon, known as the "Kluane Ranges" (Campbell 1960, 1977). Three major zones of gabbro-hosted massive and disseminated sulfide mineralization and one minor zone have been discovered to date in the Quill Creek Ultramafic Complex, but the new mineral has, so far, only been found in one of these (the "West Zone").

NAME AND PRESERVATION OF TYPE MATERIAL

The mineral is named owensite in honor of DeAlton R. Owens (1934–) of the Canada Centre for Mineral and Energy Technology, in Ottawa, for his contributions to mineralogy, particularly in the field of electron-microbeam analyses. The mineral and the mineral name were approved by the IMA Commission on New Minerals and Mineral Names in March 1994. Type material, consisting of polished sections, is deposited in the Systematic Reference Series of the National Mineral Collection, housed at the Geological Survey of Canada, Ottawa, under catalogue number NMC 67326, and at The Natural History Museum, London, U.K. (E.1495, BM 1994,54).

OCCURRENCE

The new mineral was found in drill-core rejects from sample D1 (disseminated sulfides in peridotite) and from sample EII (disseminated sulfides in chilled gabbro – pegmatitic gabbro), both from the West Zone of the Quill Creek Ultramafic Complex. Owensite is a rare mineral that occurs as small anhedral grains (6×12 to a maximum of 43×110 μm in size) within pyrrhotite (Fig. 1), closely associated with magnetite, chalcopyrite and pentlandite. Associated minerals are pyrite, cobaltite–gersdorffite, arsenopyrite, ullmannite, violarite, chromite, ilmenite, sphalerite, argento-pentlandite, breithauptite, covellite, marcasite, nickeline, galena, rutile, barite, hessite, Au–Ag alloys;

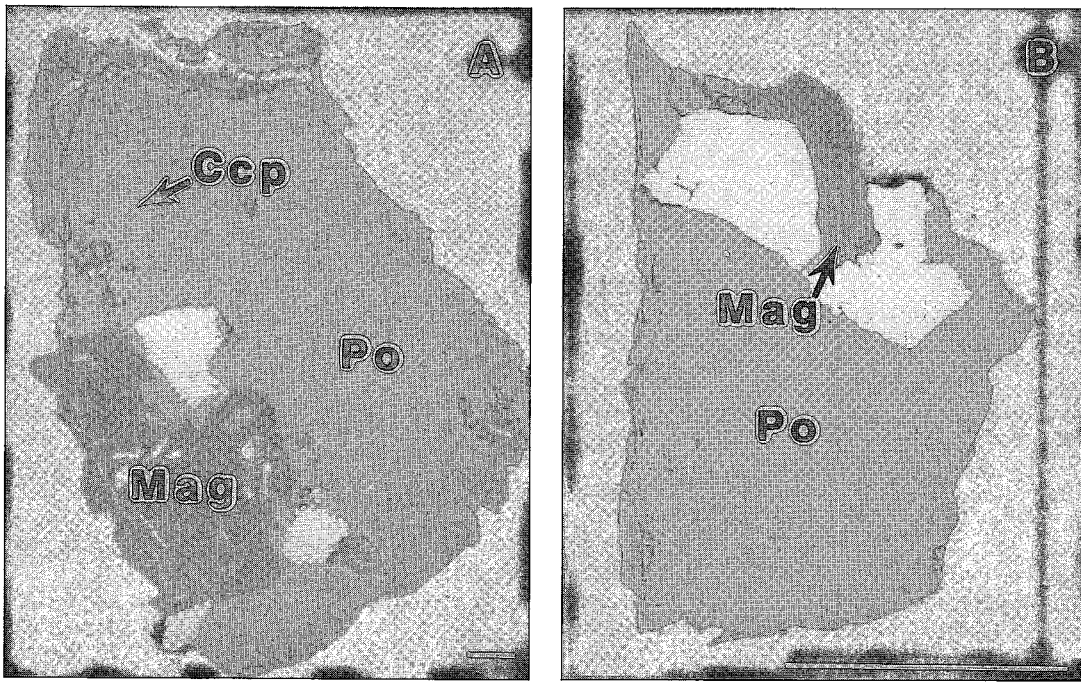

FIG. 1. SEM photomicrographs. A) Anhedral grains of owensite (white) in contact with magnetite (Mag) and enclosed in pyrrhotite (Po) with minor chalcopyrite (Ccp). Scale bar represents 10 μm. B) Subhedral grain of owensite (white) in contact with magnetite (Mag) and enclosed in pyrrhotite (Po). Scale bar represents 100 μm.

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

$I_{(est.)}$	dÅ$_{(meas)}$	dÅ$_{(calc.)}$	*hkl*	$I_{(est.)}$	dÅ$_{(meas)}$	dÅ$_{(calc.)}$	*hkl*
40*	3.460	3.458	300	15*	1.994	1.996	511
40*	3.281	3.280	310	10*	1.927	1.926	520
20*	3.124	3.127	311	10*	1.892	1.894	521
90*	2.996	2.994	222	100*	1.835	1.834	440
10*	2.876	2.877	320	10*	1.806	1.806	522,441
10*	2.518	2.516	410	40*	1.779	1.779	433
5	2.449	2.445	330	5	1.750	1.753	531
90*	2.378	2.380	331	20*	1.728	1.729	600
5	2.317	2.319	420	10*	1.621	1.620	443
5	2.259	2.263	421	5	1.597	1.600	541
5	2.212	2.211	332	10*	1.565	1.564	622
5	2.112	2.117	422	20*	1.545	1.546	630,542
15*	2.074	2.074	500	10*	1.528	1.529	631
5	2.029	2.034	510,431				

114.6 mm Gandolfi camera; Cu radiation, Ni filter (λ CuKα 1.54178 Å); intensities estimated visually; not corrected for shrinkage and no internal standard; indexed on a 10.373 Å (slightly different from single-crystal value of a 10.349(1) Å). * = used in unit-cell refinement

the platinum-group minerals: sperrylite, moncheite, sudburyite, testibiopalladite, kotulskite, mertieite II, stibiopalladinite, geversite, undefined Pd(Bi,Te), undefined $Pd_3Ni(Sb,Te,Bi)_5$, undefined $(Pd,Ni)_3(Te,Sb,Bi)_4$; the PGE-bearing minerals: Pd–Pt-bearing melonite and undefined $(Ni,Pd)_2(Te,Sb)_3$ (Cabri *et al.* 1993).

Analytical Methods

Heavy-mineral separates were mounted in araldite, with special care being taken during mounting and grinding stages to maintain a monolayer of grains. Polishing was done on lead laps with diamond powders, and finished using 0.05 μm γ-Al_2O_3 on a cloth lap. Chemical analyses were done by wavelength-dispersion spectrometry on a JEOL 733 electron microprobe, using the following X-ray lines and standards: Cu$K\alpha$, Fe$K\alpha$, S$K\alpha$ (chalcopyrite, Western Mines); Pb$L\alpha$ (synthetic PbS); Ba$L\alpha$ (synthetic $BaSO_4$) and Ni$K\alpha$ (Ni metal). The analyses were performed at 20 kV with a beam current of 20 nA (cup reading) and a 20-second count rate. Raw data were corrected using the ZAF program supplied by Tracor Northern (NORAN).

Reflectance values were measured in air and in oil (Zeiss oil, n_D = 1.515, DIN 58.884 at 20°C) using a Zeiss MPM 03 microscope-photometer. The measurements were made against a SiC standard (Zeiss no. 472).

The X-ray powder-diffraction pattern (Table 1) was obtained with a 114.6-mm Gandolfi camera employing Ni-filtered Cu$K\alpha$ radiation (λ 1.54178 Å) without an internal standard; the pattern was not corrected for film shrinkage. A single anhedral fragment, extracted from a polished section, was mounted and studied by single-crystal precession methods employing Zr-filtered Mo radiation.

Physical and Optical Properties

Owensite has a microhardness VHN_{10} of 137; only one indentation was possible owing to the paucity of material, and it corresponds to a calculated Mohs hardness of 3½. The mineral is opaque with a metallic luster and a black streak. The new mineral takes a very good polish; in reflected plane-polarized light in air, it is pale brownish grey, with no discernible bireflectance or pleochroism. The reflectance spectra (Fig. 2) of three separate grains of owensite, all included in grains of pyrrhotite, were measured in polished mount E.1495. By comparison with the appearance of pyrrhotite, owensite is much lower reflecting, brownish grey in air and greenish-brownish grey in oil. As the measured spectra for the three grains were found to be so nearly identical, Table 2 shows the reflectance data collected in air and in oil and color values for the largest grain only. These data are in accord with the subjective appearance of the mineral. Owensite tarnishes quite rapidly (in the air of London, U.K.), losing about 1% (absolute) in reflectance in 36 hours. Data for the untarnished mineral (Fig. 3) are compared with R spectra for djerfisherite (Genkin *et al.* 1969), thalfenisite (Rudashevskiy *et al.* 1979) and the mineral

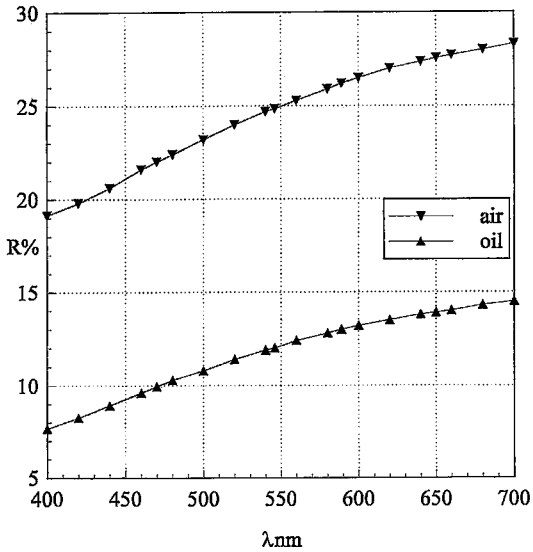

FIG. 2. Reflectance spectra of owensite between 400 and 700 nm, in air and in oil.

TABLE 2. REFLECTANCE DATA AND COLOR VALUES FOR OWENSITE

REFLECTANCE VALUES					
λnm	*R*	^{in}R	λnm	*R*	^{in}R
400	19.15	7.67	560	25.3	12.4
420	19.8	8.26	580	25.9	12.8
440	20.6	8.93	589	26.2	13.0
460	21.6	9.62	600	25.5	13.2
470	22.0	9.95	620	26.95	13.5
480	22.4	10.3	640	27.35	13.8
500	23.2	10.8	650	27.55	13.9
520	24.0	11.4	660	27.7	14.0
540	24.7	11.9	680	28.0	14.3
546	24.9	12.0	700	28.3	14.5

COLOR VALUES					
Illuminant A:			Illuminant C:		
x	0.464	0.472	*x*	0.330	0.341
y	0.413	0.415	*y*	0.336	0.346
Y%	25.75	12.7	*Y*%	25.3	12.3
λ_d	587	587	λ_d	578	578
P_e%	15.3	22.4	P_e%	10.7	16.2

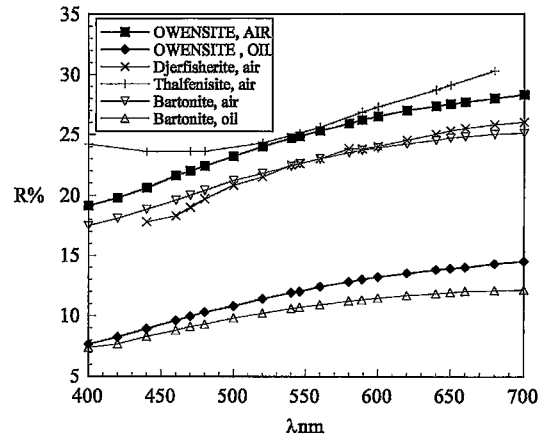

FIG. 3. Comparative reflectance spectra of owensite, djerfisherite (Genkin *et al.* 1969), thalfenisite (Rudashevskiy *et al.* 1979) and bartonite (QDF3.35, Criddle & Stanley 1993).

bartonite (QDF3.35, Criddle & Stanley 1993). As expected, there are strong similarities in the reflectance spectra of these minerals. The bartonite data are included because, as originally described by Czamanske *et al.* (1981), the mineral is ideally Cl-free, $K_3Fe_{10}S_{14}$, but may contain up to 1.38 wt% Cl, and a range of compositions was found between it and djerfisherite. This points to some interesting questions about the essential nature of Cl in the formulae of members of the djerfisherite "group".

CHEMICAL DATA

Nine grains were quantitatively analyzed with the electron microprobe (Table 3). The mean analytical results (and ranges) are: Ba 23.04(21.93–24.25), Pb 3.58(0.89–5.18), Cu 25.33(24.42–27.29), Fe 20.24(18.93–21.42), Ni 0.25(0.16–0.60), S 27.11(26.74–27.46), total 99.55 wt%. The average empirical formula, based on 58 atoms as determined from the crystal-structure study (Szymański 1995), is $(Ba_{5.42}Pb_{0.56})_{\Sigma=5.98}(Cu_{12.87}Fe_{11.70}Ni_{0.14})_{\Sigma=24.71}S_{27.31}$ or, ideally, $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$. All the grains

TABLE 3. ELECTRON-MICROPROBE DATA FOR OWENSITE

Anal.		Weight per cent*							Atomic proportions							
no.	*n*	Ba	Pb	Cu	Fe	Ni	S	Totals	Ba	Pb	Σ	Cu	Fe	Ni	Σ	S
1	5	22.02	5.18	26.15	19.25	0.25	26.74	99.59	5.22	0.82	6.04	13.41	11.23	0.14	24.78	27.18
2	6	23.15	3.73	24.42	20.81	0.26	27.26	99.63	5.44	0.58	6.02	12.40	12.02	0.14	24.56	27.43
3	4	21.93	5.13	24.54	20.38	0.23	27.16	99.37	5.18	0.80	5.98	12.54	11.85	0.13	24.52	27.50
4	5	22.54	4.36	25.23	19.94	0.16	27.20	99.43	5.32	0.68	6.00	12.86	11.57	0.09	24.52	27.48
5	3	23.12	3.53	24.90	20.45	0.18	27.12	99.30	5.45	0.55	6.00	12.68	11.85	0.10	24.63	27.37
6	2	22.90	3.87	24.75	21.42	0.22	26.96	100.12	5.36	0.60	5.96	12.53	12.34	0.12	24.99	27.05
7	2	23.48	3.43	25.58	19.97	0.17	27.46	100.09	5.49	0.53	6.02	12.92	11.48	0.09	24.49	27.49
8	2	23.98	2.11	25.12	21.04	0.19	27.02	99.46	5.62	0.33	5.95	12.72	12.12	0.10	24.94	27.11
9	3	24.25	0.89	27.29	18.93	0.60	27.11	99.07	5.67	0.14	5.81	13.80	10.89	0.33	25.02	27.17
Average		23.04	3.58	25.33	20.24	0.25	27.11	99.55	5.42	0.56	5.98	12.87	11.70	0.14	24.71	27.31

1. 50 x 90 μm, with very minor chalcopyrite, gangue and galena attached; 2. 45 x 55 μm in pyrrhotite; 3. 30 x 70 μm in pyrrhotite with minor magnetite; 4. 55 x 70 μm with minor pentlandite and magnetite in pyrrhotite; 5. 43 x 110 μm with minor magnetite in pyrrhotite; 6. 15 x 22 μm in pyrrhotite; 7. 20 x 45 μm with minor chalcopyrite in pyrrhotite; 8. 18 x 22 μm with minor chalcopyrite, magnetite in pyrrhotite; 9. 19 x 62 μm, within pyrrhotite; all the grains are from sample D1 with exception of (9) which is from sample EII.

*Cl was sought for, but was not detected (minimum detection level of 0.013 wt%).

analyzed show fairly good homogeneity. Because of some similarities with the minerals djerfisherite and thalfenisite (see Szymański 1995), Cl was specifically sought but not detected (minimum detection-level of 0.013 wt%, corresponding to <0.012 Cl atoms per formula unit).

X-Ray Powder and Single-Crystal Study

A single anhedral fragment, measuring 50 × 90 μm, was mounted and studied by single-crystal precession methods employing Zr-filtered Mo radiation. The fragment was mounted with a^* parallel to the dial axis. The levels of the reciprocal lattice collected were: $hk0 \rightarrow hk2$, $h0l \rightarrow h2l$, 011* Λ a^* and 021* Λ a^*. Owensite displays cubic symmetry and has a measured unit-cell parameter a of 10.422 Å. No systematic absences were noted on precession films, and the observed diffraction-symmetry is $m3m$ (*i.e.*, $hk = kh$ reflections); these factors dictate that the permissible space-groups are $Pm3m$ (221), $P432$ (207) or $P\bar{4}3m$ (215) (diffraction aspect P^*3^*). The correct space-group, as determined by crystal-structure analysis (Szymański 1995), is $Pm3m$.

The refined unit-cell parameter a 10.373(2) Å and volume V 1116.0(3) Å^3 are based on 19 reflections, between 3.460 and 1.528 Å, in the X-ray powder pattern for which unambiguous indexing was possible. All possible reflections down to 1.5 Å were visually examined on single-crystal precession films. Fully indexed X-ray powder data, obtained with a 114.6-mm Gandolfi camera, are presented in Table 1. It should be noted that the grain used for the single-crystal study was also used for both the X-ray powder study and the crystal-structure analysis. The powder pattern superficially resembles those of djerfisherite (a 10.465 Å) and thalfenisite (a 10.29 Å). Owensite is thus a new member of the djerfisherite group. The crystal-chemical implications of $(Ba,Pb)^{2+}$ substitution for $(K,Na)^{1+}$ and Tl^{1+} are further discussed by Szymański (1995).

Assuming the empirical formula derived from the electron-microprobe analyses and $Z = 1$, the calculated density for owensite is 4.78 g/cm^3.

Discussion

Owensite is the first Ba sulfide (actually a Ba base-metal sulfide) to be found in nature. The crystallization of this unusual mineral must be ascribed to the extremely high concentrations of Ba (~5000 ppm) found in all mineralized and unmineralized lithologies within the Quill Creek Complex (Cabri *et al.* 1993); this is in direct contrast to normal concentrations of Ba found in rocks of tholeiitic composition (<350 ppm). This enrichment in Ba also is reflected in the occurrence of barite and Ba-bearing feldspars in the ultramafic rocks of the Quill Creek Complex; it may be ascribed to significant contamination of the magma(s) that gave rise to the complex; this is supported by the isotopic values of $\delta^{34}S$, $^{187}Os/^{186}Os$ and $^{87}Sr/^{86}Sr$ (L. Hulbert, in prep.).

Another unusual feature of this new mineral is the fact that the original interpretation of the stoichiometry was M_9S_8, based on the electron-microprobe results. It was only possible to understand the true stoichiometry after a crystal-structure study (Szymański 1995).

Finally, the possible relation with the djerfisherite structure was only investigated following comments made by voting members of the Commission on New Minerals and Mineral Names, IMA. As discussed in detail by Szymański (1995), though owensite is closely related to djerfisherite, it is different in that it contains none of the monovalent metals characteristic of djerfisherite and is also devoid of Cl, considered to be an essential element in djerfisherite (Clarke *et al.* 1994).

TABLE 4. COMPARISON OF OWENSITE AND DJERFISHERITE-GROUP MINERALS

	Djerfisherite	Thalfenisite	Owensite
a Å	10.465	10.29	10.373(2)
V Å^3	[1146.09]	1089.55	1116.0(3)
Idealized formula	$K_6Na(Fe,Cu)_{24}S_{26}Cl$	$Tl_6(Fe,Ni,Cu)_{25}S_{26}Cl$	$(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$
D_{calc} (g/cm^3)	[3.64]	5.26	4.78
Symmetry	cubic	cubic	cubic
Space Group	$Pm3m$	ND*	$Pm3m$
Z	1	1	1
References	Dmitrieva *et al.* (1979)	Rudashevskiy *et al.* (1979)	This study

* ND: not determined or given; D_{meas} not determined or given. [ ]: calculated in present study.

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