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OBSERVATIONS ON ACANTHITE, AGUILARITE AND NAUMANNITE

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ABSTRACT

The relationships between acanthite, aguilarite and naumannite were investigated by studying acanthite and aguilarite in an ore suite from Guanajuato, Mexico, naumannite, aguilarite, and acanthite in a sample from Silver City, Idaho, and a synthetic naumannite. Results obtained by electron microprobe and *x*-ray diffraction analyses, and by etching with 10% KCN confirm that naumannite, aguilarite and acanthite are distinct mineral species. The compositional limits suggested for these minerals are: acanthite Ag_2S to $Ag_2S_{0.85}Se_{0.15}$; aguilarite $Ag_4S_{0.95}Se_{1.05}$ to $Ag_4S_{1.10}Se_{0.90}$; and naumannite Ag_2Se to $Ag_2S_{0.12}Se_{0.88}$.

INTRODUCTION

While studying a silver ore from the Guanajuato area, Mexico (Petruk & Owens 1974), some difficulty was encountered in defining acanthite (Ag_2S), aguilarite (Ag_4SeS), and naumannite (Ag_2Se) on the basis of electron microprobe and *x*-ray diffraction data. A literature survey failed to reveal the compositional ranges for these minerals; consequently an investigation of them was undertaken by studying acanthite and aguilarite in an ore suite from Guanajuato, Mexico, naumannite, aguilarite, and acanthite in a naumannite sample from Silver City, Idaho (Sample No. X-40568, National Mineral collection, Geological Survey of Canada), and synthetic naumannite prepared by Canadian Copper Refiners Limited (Rowland 1962).

MODE OF OCCURRENCE OF THE MINERALS

The Ag_2S - Ag_2Se minerals in the Guanajuato ores occur as separate grains, 2 to 250 microns in diameter (mean 20 microns), disseminated in dark grey quartz in three different ore types (Petruk & Owens 1974). The minerals could not be differentiated optically, but they were defined by etch tests combined with electron microprobe and *x*-ray diffraction analyses. The results show that different minerals of the Ag_2S - Ag_2Se system occur in samples from different ore types. Type 1 ore, which occurs at the lowest elevation above sea level, contains only acanthite (Sample Guanajuato H). Type 2 ore, which occurs at an intermediate elevation, contains separate acanthite grains (Fig. 1A, Sample Guanajuato C_1), acanthite with small aguilarite inclusions (Fig. 1B, Sample Guanajuato C_2), acanthite-aguilarite intergrowths (Fig. 1C, Sample Guanajuato A_1), and, in vugs, the acanthite with aguilarite inclusions is bordered by naumannite (Fig. 1D). Type 3 ore, which occurs at higher elevations, contains separate grains of of acanthite and aguilarite (Samples Guanajuato B and Guanajuato 1).

The naumannite sample from Silver City, Idaho, consists of massive naumannite with aguilarite lamellae which, in turn, contain acanthite inclusions (Fig. 1F). An analysis with image-analysis equipment (Quantimet) shows that the naumannite encloses 15% aguilarite plus acanthite.

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Properties of Acanthite, Aguilarite and Naumannite

Polymorphs

Acanthite is the low-temperature monoclinic polymorph of Ag_2S which, on heating, reversibly inverts at 176°C to argentite, the high-temperature cubic polymorph (Kracek 1946). Naumannite is the low-temperature orthorhombic polymorph of Ag_2Se and it inverts to a high-temperature cubic polymorph at 133°C (Conn & Taylor 1969). Aguilarite is the low-temper-

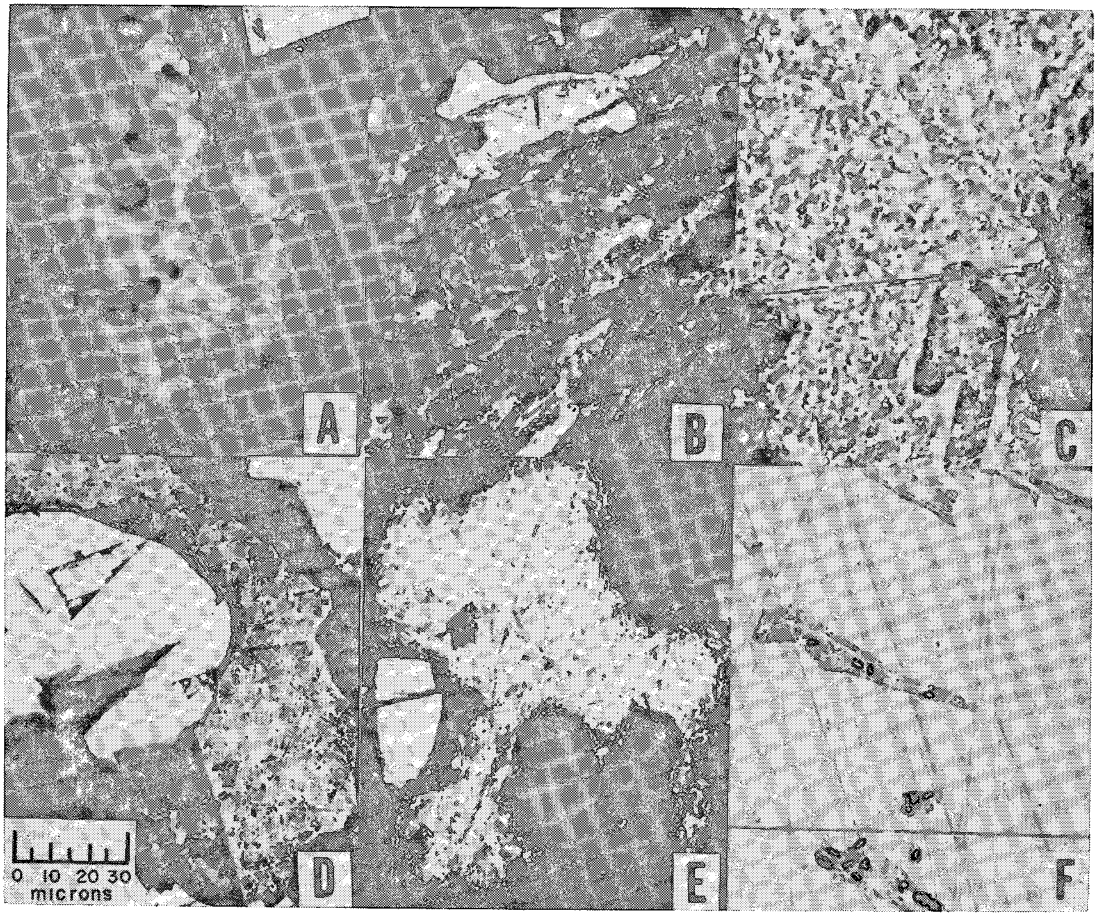

FIG. 1A An acanthite grain embedded in araldite resin and etched 1 minute with 10% KCN. The mineral etches irregularly. The most intensely etched areas are dark grey, the less intensely etched ones light grey, and the pits are black (Sample Guanajuato C_1).

FIG. 1B Acanthite with two aguilarite inclusions and a galena grain. The white grain at the top of the field is galena and the weakly etched one directly below it is aguilarite. The acanthite etched preferentially along a crystallographic direction (NE-SW) so that some parts etched deeply (dark grey to black) and other parts appear as narrow unetched zones (Sample Guanajuato C_2).

FIG. 1C Acanthite-aguilarite intergrowth. The acanthite appears as dark grey irregular spots and the aguilarite is white (Sample Guanajuato A_1).

FIG. 1D Acanthite-aguilarite intergrowth (irregularly etched) bordered by naumannite (unetched). The unetched grain on the left is galena.

FIG. 1E Aguilarite embedded in araldite resin and etched for 1 minute with 10% KCN. The unetched grain on the left is pyrite (Sample Guanajuato B).

FIG. 1F Naumannite from Silver City, Idaho, etched for 15 seconds. The naumannite is unetched, aguilarite lamellae are partly etched, and the acanthite inclusions in aguilarite are deeply etched. The acanthite inclusions are outlined in ink to enhance contrast.

ature orthorhombic polymorph of Ag_4SSe, and Main *et al.* (1972) have shown, by differential thermal analysis, that it inverts at 122°C ± 1°C, presumably to a high-temperature cubic polymorph.

Etch tests

A 10% solution of KCN, applied to the Guanajuato samples for 1 minute and to the Silver City sample for 15 seconds, clearly differentiated the mineral species. Acanthite etched strongly, aguilarite moderately, and naumannite remained unetched (Figs. 1A, 1D, 1E and 1F). Microprobe analyses on etched grains have significantly lower values for silver than were obtained on the same grains prior to etching, but the sulphur and selenium values remained approximately the same. This is probably due to differential dissolution by KCN.

Compositions of the minerals

The mineral compositions were determined by microprobe analyses using an expanded beam, 15 to 80 microns in diameter, and a specimen current of 0.02 amps at 25 kv on a MAC (Materials Analysis Company) microprobe. The expanded beam and low specimen current were used because acanthite dissociates under a small beam and high specimen current. On small grains, however, the beam size had to be reduced and only qualitative information could be obtained. Silver metal was used as a standard for silver, chalcostibite ($CuSbS_2$) for sulphur, and synthetic CuSe for selenium. The data were processed with the computer program of Rucklidge & Gasparrini (1969).

Electron microprobe analyses on the Guanajuato samples show that the acanthite contains 1.2 to 2.2 wt.% Se and 12.0 to 12.3 wt.% S, acanthite-aguilarite intergrowths contain 5.1 to 11.1 wt.% Se and 7.4 to 10.6 wt.% S, and the aguilarite contains 13.4 wt.% Se and 7.1 wt.% S (Table 1). For the Silver City sample, the naumannite contains 25 wt.% Se and 1.3 wt.% S, and aguilarite contains 15.2 wt.% Se and 6.4 wt.% S. Qualitative microprobe data confirmed that the minute inclusions in the Silver City aguilarite are acanthite.

X-ray diffraction

X-ray powder diffraction patterns of microprobed acanthite (Guanajuato C_1), aguilarite (Guanajuato B), naumannite (Silver City), acanthite with minor aguilarite inclusions (Guanajuato C_2), acanthite-aguilarite intergrowths

TABLE 1. CHEMICAL COMPOSITION OF ACANTHITE, AGUILARITE AND NAUMANNITE

Sample	Mineral	Composition (wt %)				Atomic Prop.		
		Ag	S	Se	Total	Ag	S	Se
Guanajuato 1	Acanthite	85.1	12.0	1.2	98.3	2.03	0.96	0.04
Guanajuato C_1*	Acanthite	86.4	12.0	1.6	100.0	2.03	0.95	0.05
Guanajuato H	Acanthite	85.4	12.3	2.2	99.9	1.93	0.93	0.07
Theoretical	Ag_2S	87.06	12.94	0.00	100.00	2.00	1.00	0.00
Guanajuato C_2**	Intergrowth	83.7	10.6	5.1	99.4	1.97	0.84	0.16
Guanajuato A***	Intergrowth	82.9	9.0	8.6	100.5	1.98	0.72	0.28
Guanajuato G	Intergrowth	80.9	7.4	11.1	99.4	2.03	0.62	0.38
Guanajuato B*	Aguilarite	80.7	7.1	13.4	101.2	1.92	0.53	0.47
Silver City	Aguilarite	79.6	6.4	15.2	101.2	1.89	0.51	0.49
Theoretical	Ag_4SeS	79.50	5.91	14.59	100.00	2.00	0.50	0.50
Silver City*	Naumannite	74.8	1.3	25.0	101.1	1.94	0.11	0.89
Theoretical	Ag_2Se	73.15	0.00	26.85	100.00	2.00	0.00	1.00

*See Table 2 for *x*-ray powder diffraction data.
**Only acanthite detected by *x*-ray diffraction, but etch shows aguilarite inclusions in acanthite (Fig. 1B).
***Both acanthite and aguilarite detected by *x*-ray diffraction and by etching (Fig. 1C).

(Guanajuato A), and synthetic Ag_2Se prepared by Canadian Copper Refiners Limited (Rowland 1962) were obtained with a 57.3 mm Debye-Scherrer camera using Fe-filtered Co radiation. The acanthite pattern was indexed on the basis of a monoclinic cell (Swanson *et al.* 1960), and the naumannite pattern using an orthorhombic cell (Weigers 1971). The aguilarite pattern was indexed using a naumannite-type cell. All cell parameters were refined on the measured *d*-values (Table 2) using the PARAM program of Stewart *et al.* (1972).

TABLE 2. X-RAY DIFFRACTION PATTERNS*

Mono-clinic Indices	Acanthite (Guanajuato C_1) a=4.20, b=6.91 c=7.88Å, β=99.98°			Ortho-rhombic Indices	Aguilarite (Guanajuato B_2) a=4.33, b=7.09 c=7.76Å			Naumannite (Silver City) a=4.31, b=7.02 c=7.71Å		
hkl	I	d_{obs}	d_{calc}	hkl	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}
$\bar{1}11$	2	3.42	3.43							
				111	1	3.33	3.34	2	3.29	3.31
111	3	3.06	3.06							
$\bar{1}12$	5	2.84	2.84	102	5	2.88	2.89	3	2.87	2.87
$\bar{1}20$	2	2.66	2.65	112	2	2.67	2.68	10	2.65	2.66
$\bar{1}21$	10	2.59	2.60	121	2	2.59	2.59	10	2.56	2.57
112	7	2.45	2.45	013	10	2.43	2.43	4	2.42	2.41
$\bar{1}03$	4	2.39	2.39							
031	3	2.21	2.21	031	3	2.23	2.24	6	2.23	2.22
				113		--	--	2	2.10	2.10
122	4	2.09	2.09	023 201	1	2.09	2.09	4	2.08	2.07
				211	1	2.00	2.00	4	2.00	2.00
				123	1	1.88	1.88	3	1.87	1.87
				132		--	--	½	1.81	1.81
213	3	1.72	1.72							
				041	3	1.73	1.73	½	1.74	1.76
				114		--	--	1	1.71	1.71
				222		--	--	½	1.65	1.66
$\bar{1}41$	2	1.58	1.58							
				133		--	--	3	1.61	1.61
				230	2	1.60	1.60	1	--	--
$\bar{1}05$	1	1.55	1.55	231	2	1.56	1.56	1	1.55	1.55
015	1	1.51	1.52	223		--	--	½	1.50	1.50
$\bar{1}34$	1	1.46	1.46	232	4	1.48	1.48		--	--
025	1	1.41	1.42	214		--	--	3	1.41	1.41
				302	2	1.35	1.35		--	--
240	1	1.33	1.33							
				044	1	1.31	1.31		1.29	1.29
				152	1	1.28	1.28	2	1.26	1.26
				053		--	--	3	1.23	1.23
				243		--	--	2	1.20	1.20
				153		--	--	1	1.18	1.18
				332		--	--	2	1.17	1.17
				160		--	--	1	1.13	1.13
				017	1	1.09	1.09	3	1.09	1.09
				117		--	--	3	1.05	1.05
				254	1	1.01	1.01		--	--
				164		--	--	2	0.98	0.98
				172	1	0.96	0.96	1	0.95	0.95
				246		--	--	2	0.94	0.93

*obtained with 57.3 mm Debye-Scherrer camera, Co rad., Fe filter

The *x*-ray diffraction powder pattern for the acanthite with minor aguilarite inclusions (Sample Guanajuato C_2) did not contain any lines that could be identified as belonging to the pattern of aguilarite, and was therefore indexed as acanthite with a cell of $a = 4.23$, $b = 6.90$, $c = 7.89$ Å and $\beta = 99.47°$. The powder pattern for the acanthite-aguilarite intergrowths (Sample Guanajuato A) resembled the aguilarite pattern but could not be indexed until specific lines were attributed to the presence of acanthite.

The *x*-ray diffraction pattern for synthetic Ag_2Se is the same as that quoted by Berry & Thompson (1962) for naumannite, but Berry & Thompson include a line at $d = 4.15$Å which we believe may be a grease line. The naumannite pattern of Berry & Thompson gives a calculated cell of $a = 4.33$, $b = 7.04$, and $c = 7.75$Å.

Discussion

The occurrence of aguilarite lamellae in the Silver City naumannite shows that these two minerals are separate species, even though their powder patterns can be indexed on essentially the same orthorhombic cell. It also suggests that, for the depositional conditions of this ore, the naumannite has a maximum sulphur content for this species (1.3% S, *i.e.* $Ag_2S_{0.11}Se_{0.89}$). The aguilarite, however, contains acanthite inclusions which could indicate non-equilibrium conditions for the aguilarite-acanthite, or possibly non-stoichiometry of one or more of the minerals.

The presence of acanthite, acanthite-aguilarite intergrowths, and aguilarite in the Guanajuato samples suggests that a two-phase field exists between acanthite and aguilarite. Our data indicate that one-phase acanthite contains up to 2.2 wt.% Se, and that the acanthite-aguilarite mixtures contain more than 5.1 wt.% Se. Therefore, the boundary between acanthite and the two-phase field lies between these values. Kieft & Oen (1973) reported that acanthite from Salida, Indonesia, contains up to 4% Se, but they do not report having etched it to determine whether it is one-phase acanthite or an acanthite-aguilarite intergrowth. Nevertheless, it is possible that their material is one-phase acanthite and that this acanthite has the maximum Se content possible for the species. Therefore, it is suggested that the boundary between acanthite and the two-phase field is $Ag_2S_{0.85}Se_{0.15}$ (approx. 4.7 wt.% Se). Similarly, our data indicate that one-phase aguilarite contains at least 13.4 wt.% Se, and the acanthite-aguilarite intergrowth, a maximum of 11.1 wt.% Se; therefore, the boundary between aguilarite and the two-phase field lies between these values and the composition $Ag_2S_{0.55}Se_{0.45}$ (Se 13.2% wt.%) is suggested.

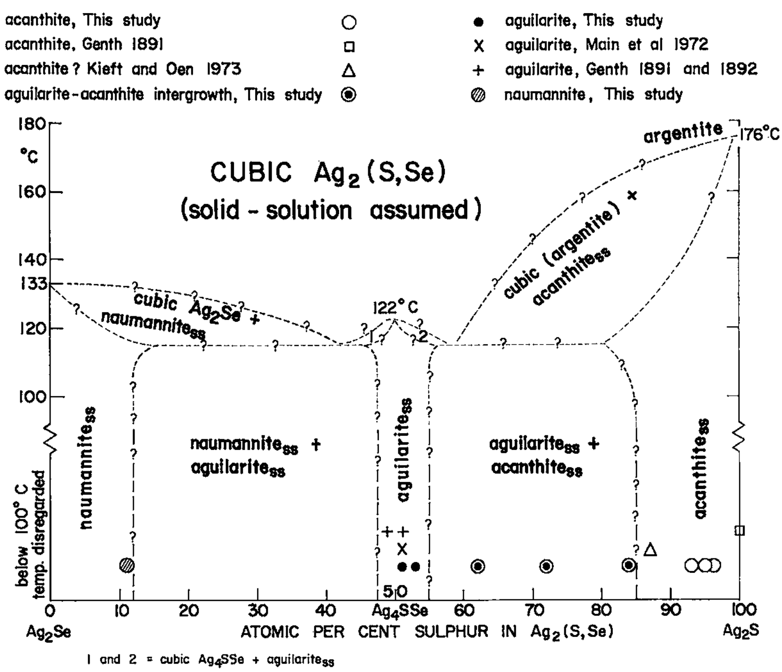

FIG. 2 Speculative phase diagram for the low temperature minerals of the Ag_2S - Ag_2Se system.

On the basis of this study, the acanthite composition varies from Ag_2S to $Ag_2S_{0.85}Se_{0.15}$, the aguilarite composition from, perhaps, $Ag_4S_{0.95}Se_{1.05}$ to about $Ag_4S_{1.10}Se_{0.90}$ and the naumannite composition from Ag_2Se to about $Ag_2S_{0.12}Se_{0.88}$. A speculative phase diagram for the Ag_2S-Ag_2Se system below 200°C, as interpreted from the results of this study and from data reported in the literature, is given in Figure 2.

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