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 Ag₂S to Ag₈S₆₆₆, aguilarite Ag₄S₅₅₆₅₈ to Ag₄S₅₅₆₅₈, and naumannite Ag₂Se to Ag₈S₆₆₆, respectively.

While studying a silver ore from the Guanajuato area, Mexico (Petruk & Owens 1974), some difficulty was encountered in defining acanthite (Ag₂S), aguilarite (Ag₄SeS), and naumannite (Ag₂Se) 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).

The Ag₅S - Ag₄Se minerals in the Guanajuato ore: 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 Ag₅S - Ag₄Se 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 C₁), acanthite with small aguilarite inclusions (Fig. 1B, Sample Guanajuato C₂), acanthite-aguilarite intergrowths (Fig. 1C, Sample Guanajuato A₁), 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 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.
Properties of Acanthite, Aguilarite and Naumannite

Polymorphs

Acanthite is the low-temperature monoclinic polymorph of Ag₅S 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 Ag₅Se and it inverts to a high-temperature cubic polymorph at 133°C (Conn & Taylor 1969). Aguilarite is the low-temperature cubic polymorph of Ag₅S.
ature orthorhombic polymorph of Ag₃Se, 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 significant 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 etched grains could be analyzed. Expanded beam and low specimen current were used for selenium values remained approximately 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.

Electron microprobe analyses on the Guanajuato samples show that the acanthite contains gaspanini (1969). However, the beam size had to be reduced and only etched grains were analyzed. 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 etched grains could be analyzed. Silver metal was used as a standard for silver, chalcostibite (CuSbS₂) for sulphur, and synthetic CuSe for selenium. The data were processed using the computer program of Rucklidge & Naumannite contains 25 wt.% Se and 1.3 wt.% S (Table 1). For the Silver City sample, 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), aguilarite (Guanajuato B), naumannite (Silver City), aguilarite with minor aguilarite inclusions (Guanajuato A), and synthetic Ag₃Se 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 1. Chemical Composition of Acanthite, Aguilarite and Naumannite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>Composition (wt %)</th>
<th>Atomic Prop.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guanajuato A</td>
<td>Acanthite</td>
<td>85.1 12.0 2.2</td>
<td>99.4 0.6</td>
</tr>
<tr>
<td>Guanajuato B</td>
<td>Acanthite</td>
<td>66.4 12.0 16.3</td>
<td>100.0 0.0</td>
</tr>
<tr>
<td>Guanajuato C</td>
<td>Acanthite</td>
<td>85.4 12.3 2.2</td>
<td>99.4 0.6</td>
</tr>
<tr>
<td>Theoretical</td>
<td>Acanthite</td>
<td>87.06 12.94 0.00</td>
<td>100.0 0.0</td>
</tr>
<tr>
<td>Guanajuato C**</td>
<td>Intergrowth</td>
<td>83.7 10.6 5.1</td>
<td>99.4 0.8</td>
</tr>
<tr>
<td>Guanajuato A**</td>
<td>Intergrowth</td>
<td>82.9 9.7 8.4</td>
<td>100.5 0.7</td>
</tr>
<tr>
<td>Guanajuato A***</td>
<td>Intergrowth</td>
<td>80.5 7.8 14.7</td>
<td>100.0 0.0</td>
</tr>
<tr>
<td>Guanajuato A</td>
<td>Aguilarite</td>
<td>80.7 7.1 13.4</td>
<td>101.2 0.3</td>
</tr>
<tr>
<td>Guanajuato B</td>
<td>Aguilarite</td>
<td>81.6 7.4 15.2</td>
<td>101.2 1.1</td>
</tr>
<tr>
<td>Theoretical</td>
<td>Aguilarite</td>
<td>75.50 5.91 14.99</td>
<td>100.0 0.0</td>
</tr>
<tr>
<td>Silver City*</td>
<td>Naumannite</td>
<td>74.8 1.3 25.1</td>
<td>101.1 0.1</td>
</tr>
<tr>
<td>Theoretical</td>
<td>Naumannite</td>
<td>73.16 0.00 25.86</td>
<td>100.0 0.0</td>
</tr>
</tbody>
</table>

*Obtained with a 57.3 mm Debye-Scherrer camera, Co Kα, Fe filter.
The x-ray diffraction powder pattern for the ancanthite with minor aguilarite inclusions (Sample Guanajuato C) did not contain any lines that could be identified as belonging to the pattern of aguilarite, and was therefore indexed as ancanthite with a cell of \( a = 4.23 \), \( b = 6.90 \), \( c = 7.89 \) Å and \( \beta = 99.47^\circ \). The powder pattern for the ancanthite-aguilarite intergrowths (Sample Guanajuato A) resembled the aguilarite pattern but could not be indexed until specific lines were attributed to the presence of ancanthite.

The x-ray diffraction pattern for synthetic Ag\(_8\)Se 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\(_8\)S\(_{0.91}\)Se\(_{0.09}\)). The aguilarite, however, contains ancanthite inclusions which could indicate non-equilibrium conditions for the aguilarite-ancanthite, or possibly non-stoichiometry of one or more of the minerals.

The presence of ancanthite, ancanthite-aguilarite intergrowths, and aguilarite in the Guanajuato samples suggests that a two-phase field exists between ancanthite and aguilarite. Our data indicate that one-phase ancanthite contains up to 2.2 wt.% Se, and that the ancanthite-aguilarite mixtures contain more than 5.1 wt.% Se. Therefore, the boundary between ancanthite and the two-phase field lies between these values. Kieft & Oen (1973) reported that ancanthite from Salida, Indonesia, contains up to 4% Se, but they do not report having etched it to determine whether it is one-phase ancanthite or an ancanthite-aguilarite intergrowth. Nevertheless, it is possible that their material is one-phase ancanthite and that this ancanthite has the maximum Se content possible for the species. Therefore, it is suggested that the boundary between ancanthite and the two-phase field is Ag\(_8\)S\(_{0.80}\)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 ancanthite-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\(_8\)S\(_{0.38}\)Se\(_{0.62}\) (Se 13.2% wt.%) is suggested.

![Speculative phase diagram for the low temperature minerals of the Ag\(_8\)S - Ag\(_8\)Se system.](image-url)
On the basis of this study, the acanthite composition varies from $\text{Ag}_2\text{S}$ to $\text{Ag}_2\text{Se}_{0.86}\text{Se}_{1.18}$, the aguilardite composition from, perhaps, $\text{Ag}_2\text{S}_{0.55}\text{Se}_{1.05}$ to about $\text{Ag}_2\text{S}_{1.10}\text{Se}_{0.80}$ and the naumannite composition from $\text{Ag}_2\text{Se}$ to about $\text{Ag}_2\text{S}_{0.80}\text{Se}_{0.88}$. A speculative phase diagram for the $\text{Ag}_2\text{S}$-$\text{Ag}_2\text{Se}$ 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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