

# Selenium-bearing minerals from the Kongsberg Silver District

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## Introduction

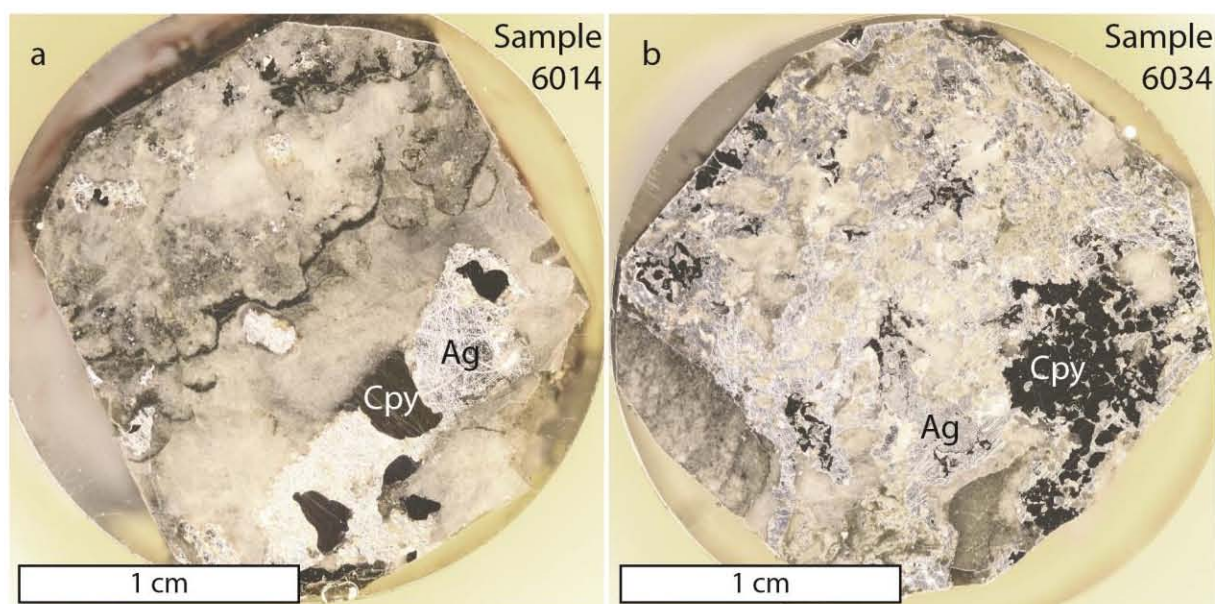
The silver mines at Kongsberg are famous for spectacular samples of wire silver exhibited in numerous mineralogical museums around the world. In addition to native silver, a large number of other minerals have been reported from the deposit, including native elements (Au, As, Cu, S, C), sulphides, sulphosalts, selenides, arsenides, carbonates, sulphates, arsenates and halides, and a range of silicate minerals (Neumann 1944; Johnsen 1986, 1987; Bancroft *et al.* 2001). Very little research has been carried out on the Kongsberg silver deposits since the work of Neumann (1944). Kullerud *et al.* (2016) and Kotková *et al.* (in press), however, contributed to the understanding of mineralizing processes focusing mainly on antimony-mercury-silver minerals using modern methods. The present study focuses on selenium-bearing minerals from the Kongsberg silver deposits.

## Selenium

Selenium (Se) is a non-metal with atomic number 34. In the periodic table, selenium is positioned below sulfur and above tellurium. Selenium readily substitutes for sulfur in sulfides, where it occurs as a trace element. However, selenium also occurs as a mineral-forming element in a substantial number of minerals, *e.g.* in selenides. Furthermore, selenium is taken up by plants and the concentration can be high in coal and other organic-rich deposits, such as black shales. Most selenium that is exploited is produced as a byproduct of copper refining from copper ores (Butterman & Brown 2004).

## Samples studied

During ongoing studies of samples from the Norwegian Mining Museum's collection from the Kongsberg silver deposits, selenium-bearing minerals were observed in two samples from the Southern Vinoren area, about 7 km north of the Jondalen Valley. One of the samples comes from the Norske Løve Mine (sample 6014), while the other one was labelled Southern Vinoren (sample 6034), indicated that it can be from the Norske Løve Mine or one of the other mines in the area. Sample 6014 is composed of a light-green host rock with disseminated grains of native silver and sulfides. Some veins of calcite with native silver and sulfides crosscut the host rock. Isolated silver grains are up to 5 mm in diameter (Fig. 1a). The surface of the sample is covered by erythrite. Sample 6034 is a fragment from a calcite vein with abundant native silver forming a network, and with sulfides, in particular chalcopyrite (Fig. 1b).



**Fig. 1.** Polished slabs of the studied samples, showing the textural relationships between native silver (bright shining), chalcopyrite (dark) and calcite (white).

### Textural occurrences of the Se-bearing minerals

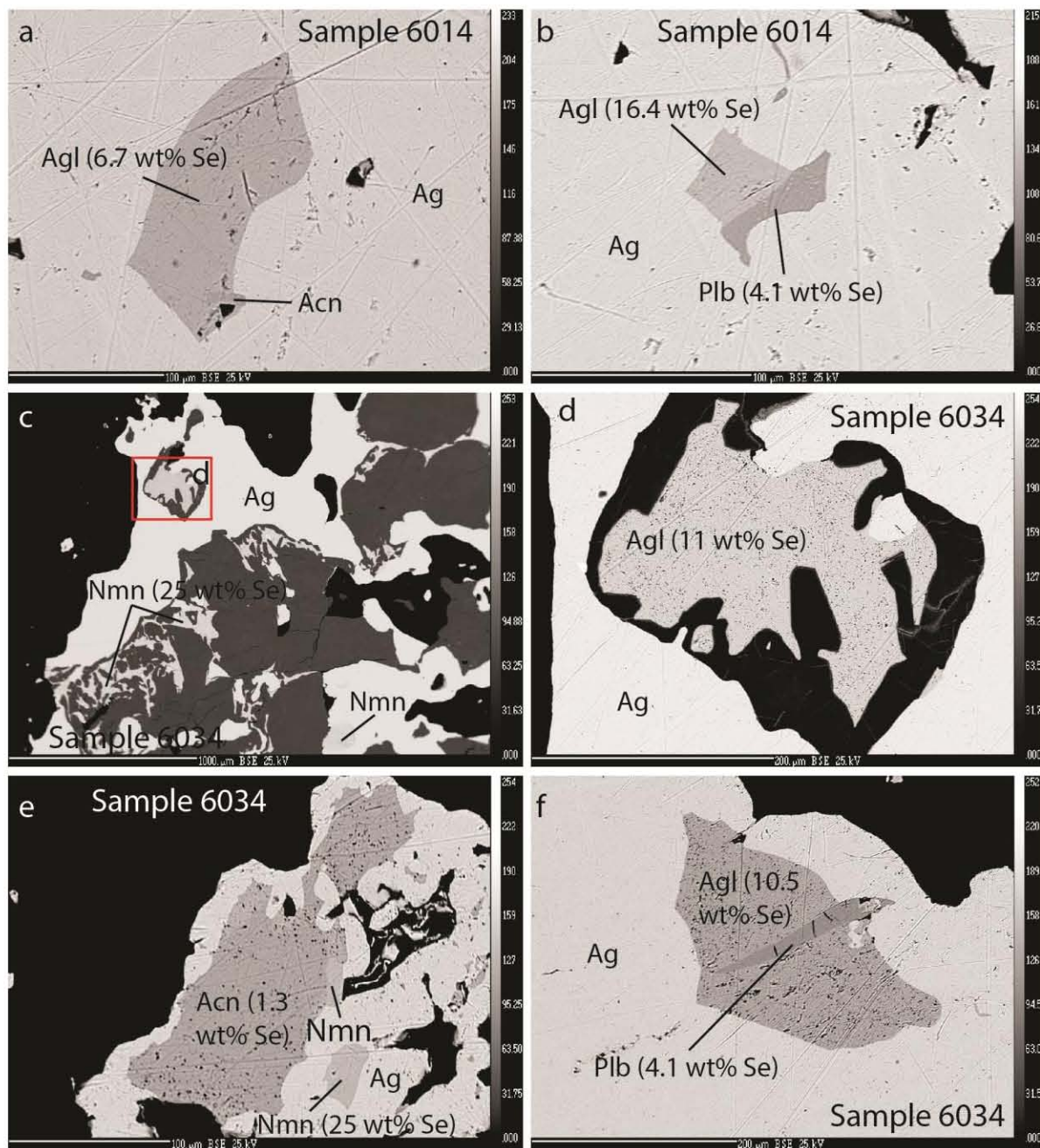
In sample 6014, the Se-bearing minerals occur as small (< 100  $\mu\text{m}$  in diameter) inclusions in native silver. The Se-bearing minerals include aguilarite, naumannite, polybasite and acanthite (see Table 1 for the general formulae of the minerals). Most of the inclusions are mono-mineralic, but inclusions of aguilarite + acanthite (Fig. 2a), and aguilarite + polybasite (Fig. 2b) can be observed.

Figure 2c-d shows naumannite and aguilarite closely associated with chalcopyrite, enclosed in native silver from sample 6034. This sample also contains inclusions in native silver of naumannite + acanthite (Fig. 2e) and aguilarite + polybasite (Fig. 2f).

The contact relationships between silver and the inclusions in silver shown in Fig. 2 suggest that mineral assemblages Ag + acanthite + aguilarite (Fig. 2a), Ag + acanthite + naumannite (Fig. 2e) and Ag + aguilarite + polybasite (Fig. 2b and f) all were in chemical equilibrium.

**Table 1.** General formulae of ore minerals mentioned in the text.

Acanthite	$\text{Ag}_2\text{S}$
Aguilarite	$\text{Ag}_4\text{SeS}$ $= \text{Ag}_2\text{Se}_{0.5}\text{S}_{0.5}$
Naumannite	$\text{Ag}_2\text{Se}$
Polybasite	$(\text{Ag,Cu})_{16}\text{Sb}_2\text{S}_{11}$



**Fig. 2.** Textural occurrences of the studied Se-bearing minerals. See text for discussion. Abbreviations of mineral names: Ag = native silver, Acn = acanthite, Agl = agularite, Nmn = naumannite, Plb = polybasite.

### Mineral compositions

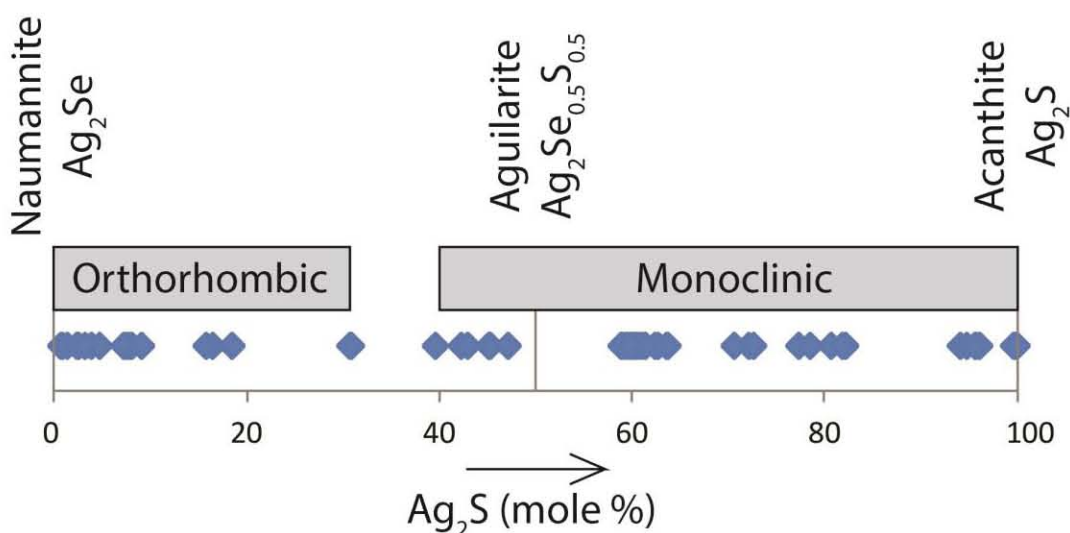
Chemical compositions of the minerals were determined by the use of the CAMECA SX100 electron microprobe at the Masaryk University in Brno, Czech Republic.

Detailed studies of acanthite, naumannite and agularite have shown that there are two distinct solid solution series along the  $\text{Ag}_2\text{S}$ - $\text{Ag}_2\text{Se}$  join: a monoclinic ‘acanthite-like’  $\text{Ag}_2\text{S}$ - $\text{Ag}_2\text{S}_{0.4}\text{Se}_{0.6}$  series; and



an orthorhombic ‘naumannite-like’  $\text{Ag}_2\text{S}_{0.3}\text{Se}_{0.7}$ - $\text{Ag}_2\text{Se}$  series (Pingitore *et al.* 1992, 1993; Bindi & Pingitore 2013).

The compositions of acanthite, aguilarite and naumannite from the Southern Vinoren deposits show large variations along the binary join  $\text{Ag}_2\text{S}$  -  $\text{Ag}_2\text{Se}$  (Fig. 3). For naumannite, Se varies in the range 18.6 – 26.7 wt%, corresponding to 0.69 – 1 Se atom per formula unit. Aguilarite contains up to 16.4 wt% Se, corresponding to 0.6 atoms per formula unit. Polybasite contains up to 4.1 wt% Se.



**Fig. 3.** Variations in the Se-content of naumannite, aguilarite and acanthite from Southern Vinoren. The monoclinic and orthorhombic solid solution series are from Pal'yanova *et al.* (2014).

## Discussion and conclusions

The presence of naumannite, aguilarite, polybasite and acanthite as inclusions in native silver in the studied samples from the Southern Vinoren area suggests that these minerals formed during the earliest stage of ore formation. We have not observed Se-bearing minerals in samples from other areas in the Kongsberg Silver District, where native silver characteristically contains inclusions of Se-free acanthite and Se-free polybasite (Kotková *et al.* in press). The distribution of Se-bearing minerals in the district can be explained as a result of local variations in the selenium/sulfur activity ratio of the ore-forming fluid, with a much higher selenium/sulfur activity ratio in the Southern Vinoren area than elsewhere.

Whereas monoclinic acanthite and aguilarite, and orthorhombic naumannite are stable at low temperatures, their high-temperature polymorphs are all cubic. Argentite, which is the cubic polymorph of  $\text{Ag}_2\text{S}$ , is stable at temperatures above about 176 °C (Vaughan & Craig 1978). In one of the studied samples, we observed an inclusion of  $\text{Ag}_2\text{S}$  in native silver with a cubic shape, indicating that  $\text{Ag}_2\text{S}$  initially crystallized as argentite at a temperature above 176 °C. Likewise, the cubic polymorph of naumannite is stable at temperatures above 135 °C (Feng *et al.* 2013). Pal'yanova *et al.* (2014) argue that at temperatures between about 176 °C and 592 °C, there is a complete solid solution series between  $\text{Ag}_2\text{S}$  and  $\text{Ag}_2\text{Se}$ . The silver deposits at Kongsberg formed at temperatures above 176 °C (*e.g.* Johansen & Segalstad 1985; Kotková *et al.* in press). It is therefore inferred that acanthite,

naumannite and aguilarite initially crystallized as cubic minerals, notated as  $\gamma\text{-Ag}_2\text{S}_{1-x}\text{Se}_x$  by Pal'yanova *et al.* (2014). The Se-content of the minerals was controlled by the selenium/sulfur activity ratio of the ore-forming fluid during mineral growth. Whether acanthite, naumannite or aguilarite formed during cooling of their cubic polymorph depended solely on the initial Se-content of the cubic phase.

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