

A selenium-rich sulphide assemblage in the Caledonides of northern Norway

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Chemical analyses of a sulphide assemblage from Russeholmen, Nordreisa, North Norway, reveal a selenium content of 0.65 wt % in molybdenite, 0.12 wt % in pyrite and 0.10 wt % in chalcopyrite. These are among the highest selenium concentrations reported for these minerals from Norwegian localities. Selenium to sulphur ratios are calculated, and a distribution factor for selenium between the minerals is established. The molybdenite contains 240 ppm rhenium. The mineralization occurs in a Precambrian amphibolite belonging to the Caledonian Nabar Nappe. Chemical analyses were done by inductively coupled plasma optical emission spectrometry, X-ray fluorescence spectrometry and electron microprobe – X-ray spectrometry.

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In 1964 the Geological Survey of Norway carried out follow-up investigations of claims in Nordreisa community, Troms county (Trøften 1964). These investigations, which also included X-ray fluorescence analyses, led to the discovery of an occurrence of molybdenite with an exceptionally high content of selenium. On further examination, the molybdenite proved to be associated with minor amounts of pyrite and chalcopyrite, these also showing high contents of selenium. The exact locality of the claim, which was staked by Lars S. Henriksen in 1897, is Russeholmen on the farm Loppevollen in Nordreisa community, Troms county, map-sheet 1734 IV and coordinates E052 N452 (Fig. 1).

Selenium is a rare element in the earth's crust, with abundance values well below 1 ppm in most rocks. However, due to a close crystallochemical similarity with sulphur, the radii of Se^{2-} and S^{2-} being respectively 1.91 Å and 1.74 Å, selenium can replace sulphur in many sulphides. Some sulphides and selenides are isomorphous and even form complete solid solutions.

Very few selenium minerals are reported from Norway. Minerals belonging to the galena (PbS)-clausthalite (PbSe) solid solution series are described from Numedal (Heier 1953), and from the Kisgruva sulphide deposit in the Kongsberg area (Foslie 1982). This last locality is also reported to carry the minerals altaite and tetradyomite.

The Se-rich molybdenite from Russeholmen is the only occurrence so far known from Norway.

Until 1965 only one similar occurrence was described in the literature, namely that from a uranium mine at Shinkolobwe in Zaire (Derriks & Vaes 1955). Häkli et al. (1965) have since described two Se-rich molybdenites from Kuusamo in Finland, also in association with a uranium mineralization.

Goldschmidt & Strock (1935) found that molybdenites on average contain the highest Se-concentrations among the sulphides, and Goldschmidt had predicted that molybdenum diselenide, MoSe_2 , might exist as a natural mineral and eventually form a solid solution series with molybdenite, MoS_2 (Kvalheim, pers.comm. 1964).

In the early seventies a new mineral which proved to be molybdenum diselenide was discovered in a uranium deposit at Kapijimpanga, southeast of Solwezi in Zambia (Čech et al. 1973). The mineral was given the name drysdallite and found to be identical with synthetic MoSe_2 , the structure of which had been determined by James & Lavik (1963). According to Čech et al. (1973), the phase relations between MoS_2 and MoSe_2 had not been studied experimentally; this would reveal whether extensive solid solution really exists. However, cell parameter data for the two molybdenites from Kuusamo (Häkli et al. 1965) plotted as a function of composition, together with the corresponding data for molybdenite, drysdallite and synthetic MoSe_2 , indicate that extensive solid solution is likely.

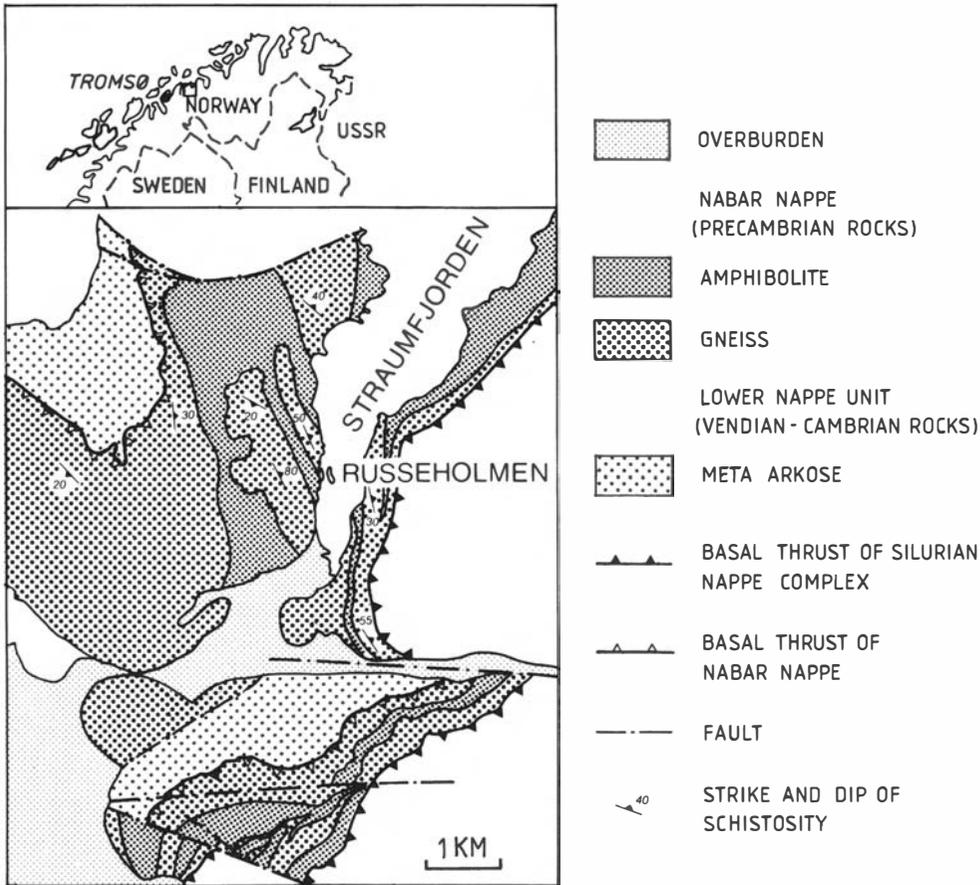


Fig. 1. Schematic geological map of the Straumfjorden area. After Bakke et al. (1975).

Geological overview

The Nordreisa area constitutes a part of the northern extremity of the Caledonides in Scandinavia, and is built up of several nappe complexes. The Straumfjord area is underlain by the Nabar Nappe belonging to the Kalak Nappe Complex (Zwaan & Roberts 1978). The Nabar Nappe, which covers most of the Nordreisa area, consists of two different rock units; a basal unit of Precambrian gneisses and amphibolites, unconformably overlain by Vendian to Cambrian metasediments. The metamorphic grade of the Precambrian rocks is amphibolite facies, and this is partly overprinted by Caledonian upper greenschist facies metamorphism with ductile deformation. The molybdenite mineralization occurs in the Precambrian amphibolite, which sup-

posedly is derived by metamorphism of basic igneous rocks.

Occurrence and mineral assemblages

The molybdenite occurs in amphibole-calcite-quartz veins in the amphibolite. A petrographic examination shows amphibole as the major vein constituent together with approximately 15 % calcite, 5 % quartz and 1 % sulphides. The texture is coarse-grained and equigranular with aggregates of molybdenite up to 15 mm in size. The only detected sulphide minerals, apart from molybdenite, are pyrite and chalcopyrite. Pyrite occurs as well-developed crystals of up to some tenths of a millimetre in size scattered through-

out the rock and in some places also in contact with the molybdenite (Fig. 2). Chalcopyrite occurs mainly in contact with pyrite or as small inclusions in the pyrite (Fig. 3). Neither pyrite nor chalcopyrite has been found as inclusions in the molybdenite.

Chemical analyses

Se-rich sulphide assemblages are suitable for studying the distribution of selenium between coexisting sulphide minerals. The distribution of selenium between the sulphide minerals pyrite, sphalerite and chalcopyrite in the Se-rich Kisgruva sulphide deposit was studied by Foslie (1982). Se-rich molybdenites have not been reported to be associated with other sulphides, and the Russeholmen deposit therefore provides an opportunity to study the distribution of selenium between molybdenite, pyrite and chalcopyrite.

Chemical analysis of the pyrite and chalcopyrite was made possible by microprobe techniques. The microprobe technique was also applied to the molybdenite, mainly to test for zonal distribution. The molybdenite was available in quantities of several grams, and was therefore also analysed by X-ray fluorescence spectrometry (XRF) and inductively coupled plasma optical emission spectrometry (ICP-OES).

Since molybdenite is a typical host mineral for rhenium, and especially since no analysis of rhenium seems to exist for the very few known selenium-rich molybdenites, a rhenium analysis of the molybdenite was carried out by the plasma technique. An independent rhenium analysis of this material was carried out at the United States Geological Survey in Denver by XRF after pre-concentration based on acid distillation and sulphide precipitation.

A composite sample of the vein minerals calcite, quartz and amphibole was subjected to a tentative analysis for gold by graphite furnace atomic absorption technique, the underlying reason being the close association which often exists between selenium, tellurium and gold. Alluvial gold deposits occur at different places in this part of the country, but the origin of the gold is still unknown. The fact that the selenium-rich mineralization is associated with veins of calcite and quartz, and also occurs in a rock type of Proterozoic or possible Archean age, which is very common in the areas where alluvial gold is found, are additional reasons for a test for gold. As a matter

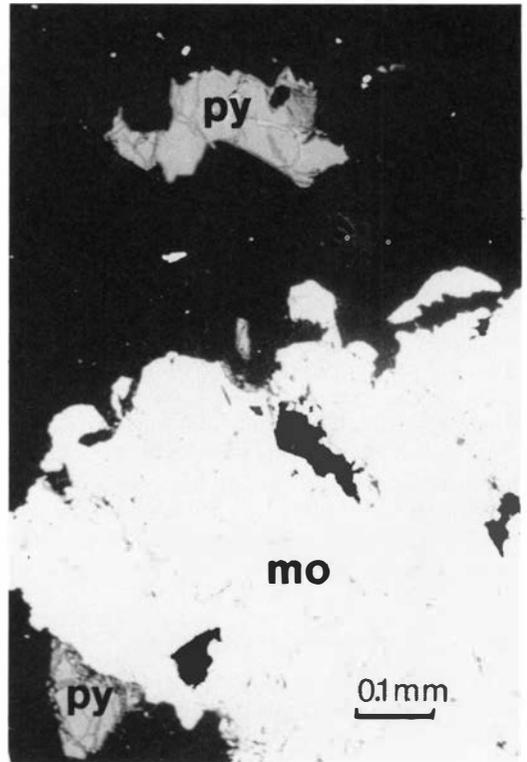


Fig. 2. SEM photograph showing molybdenite (mo) imbedded in amphibolite (dark). Pyrite (py) occurs both in contact with molybdenite and scattered throughout the amphibolite.

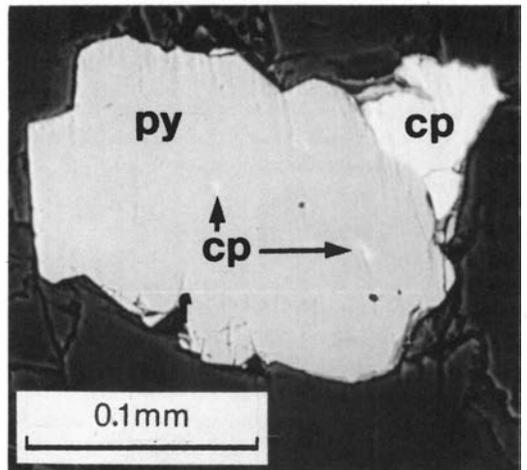


Fig. 3. SEM photograph showing chalcopyrite (cp) both in contact with pyrite (py) and as inclusions in pyrite.

of curiosity it can also be mentioned that some of the spherulites of Se-rich molybdenite found at Kuusamo in Finland contained a grain of native gold as a nucleus (Häkli et al. 1965).

A qualitative analysis of the molybdenite was done by means of d.c. arc optical emission spectrography.

Optical d.c. arc spectrography

The molybdenite sample was mixed with 2 parts of carbon powder and analysed on a quartz prism spectrograph of Mannkopff construction with d.c. arc excitation. Aside from inclusions of surrounding rock material, which also appear on Fig. 2, the spectrogram shows a relatively pure molybdenite. In addition to Mo, small amounts of Cu (<0.1 %) and Pb (<0.05 %) are the only typical chalcophile elements which have been detected with certainty.

X-ray fluorescence spectrometry

For quantitative X-ray fluorescence determination of selenium in the molybdenite, a Philips PW 1540 X-ray spectrometer with W-tube operated at 40 kV and 18 mA was used. The analysing crystal used was a LiF (200) and intensities were measured with a scintillation counter.

The molybdenite was analysed in triplicate with 1 gram samples against synthetic standards prepared by mixing SeO₂ into a base of spectrochemically pure MoO₃. Molybdenum was used as reference element (variable internal standard), and background correction was carried out. The results obtained were 0.57 %, 0.60 % and 0.63 % Se, with an average of 0.60 % Se. From experience, the total reproducibility of sample preparation and measurements is in the order of 1–3 %, which may indicate that slight inhomogeneities exist in the sample material.

Inductively coupled plasma optical emission spectrometry

For quantitative determination of selenium and rhenium by the plasma technique we used a Jarrell-Ash Model 975 ICAP AtomComp with pneumatic cross flow nebulizer and a Plasma-Therm RF generator type HFP 2000 D operating at 27.13 MHz. Since neither selenium nor rhenium is included in the fixed element programme of the polychromator, these two elements were determined with an external Jarrell-Ash 0.5 m

Model 82–000 monochromator. The operating system parameters were:

Forward power: 1.1 kW

Reflected power: < 10 W

Argon coolant gas flow rate: 17.500 l/min.

Argon sample gas flow rate: 0.650 l/min.

Argon plasma gas flow rate: 0.300 l/min.

Sample uptake: 1.2 ml/min.

Observation zone: 16 mm above the induction coil

Exposure time: 10 sec.

Analytical lines (I = atomic line, II = ionic line):

Se: 196,0 nm (I)

Re: 197.3 nm (II) and 227.5 nm (II)

Preparation of solutions for analysis was done by dissolving in duplicate 0.1 g molybdenite in 5 ml of fuming nitric acid and diluting to a final volume of 50 ml.

Standards were made from stock solutions prepared by dissolution in acids of SeO₂, MoO₃ and metallic Re. The duplicate Se-determinations obtained were 0.65 % Se and 0.68 % Se, with the average of 0.67 % Se.

Determination of rhenium was carried out by use of the line Re 197.3 nm. The results were controlled with the line Re 227.5 nm because of interference from molybdenum.

Due to careful matching of the standards with molybdenum, the two analytical lines gave identical results. The results of the duplicate analyses obtained were 270 ppm Re and 250 ppm Re, with an average of 260 ppm Re.

The result obtained by the laboratories of the USGS in Denver was 220 ppm Re, an agreement which is acceptable at this concentration level and on this kind of material.

Electron microprobe

The quantitative analyses of selenium in molybdenite, pyrite and chalcopyrite by the microprobe technique were carried out at the Continental Shelf Institute (IKU) with a Jeol Superprobe 733 and with the wavelength dispersive system for X-ray detection. Natural minerals were available as zero standards, namely molybdenite, marcasite and chalcopyrite.

A scan across the molybdenite with measurements at 9 positions indicated Se-concentrations between 0.43 % and 0.71 %, with an average of 0.59 % Se. The spread of the analyses can be explained by relief effects, which can be considerable on soft materials like molybdenite, by

zoning and by statistical spreading. An average of several determinations will in all these cases improve the analysis, and the value of 0.59 % Se agrees well with the XRF and ICP-OES determinations. No indications of zonal structures in the molybdenite were detected.

The analyses of selenium in pyrite were made on several crystals and in several positions within each individual crystal. Selenium concentrations determined by measurements at 14 positions ranged between 0.08% and 0.17 % with an average of 0.12 % Se. The concentration of selenium in the small scattered pyrite crystals seemed to be independent of their position in relation to the molybdenite. Likewise, no significant difference seemed to exist in Se-concentration within each individual crystal.

Analysis of the chalcopyrite was carried out on the largest grain shown in Fig. 3 and on one of the small inclusions of chalcopyrite in the pyrite. Four analyses showed Se-concentrations of 0.09 %, 0.06 %, 0.09 % and 0.14 %, giving an average of 0.10 % Se. The small inclusion of chalcopyrite showed 0.09 % Se. This is close to the average, and chalcopyrite trapped in pyrite apparently does not differ in Se-concentration from that of the grain in contact with pyrite.

Summary of the analyses

The analytical results for selenium in molybdenite obtained with three independent methods are in good agreement. The results obtained by the plasma technique are considered to be the most reliable, mainly because of the close matching of standards and samples. By transforming the samples from a crystalline to an amorphous state, in this case by dissolution with nitric acid, chemical as well as physical effects are more easily controlled.

Physical effects might well have caused a minor bias in the XRF-determinations of selenium, since crystalline sulphidic mineral samples were analysed against amorphous oxidic standards. The microprobe determinations are based on small sample areas and are therefore often subject to inhomogeneity problems. Even if this is to a certain degree outweighed by replicate determinations, the plasma analyses based on 0.1 g samples are considered to be the more accurate. Thus, with major weight on the plasma analyses, the value of 0.65 % Se is considered as the average for the molybdenite. The following Se-

concentrations are thus established: molybdenite 0.65 % Se, pyrite 0.12 % Se and chalcopyrite 0.10 % Se.

Discussion

Tischendorf (1966) gives the most common concentrations of selenium in the three sulphides as follows: molybdenite 32–265 ppm Se, pyrite 20–150 ppm Se and chalcopyrite 20–200 ppm Se. These values are based on available analyses up to that time without regard to sulphide mineral assemblage. The values therefore provide no information on the mutual distribution of selenium between the minerals of one particular sulphide mineral assemblage.

In the present sulphide assemblage, containing the three minerals molybdenite, pyrite and chalcopyrite, the following distribution ratio for selenium has been established:

$$\begin{array}{l} \text{molybdenite} : \text{pyrite} : \text{chalcopyrite} = \\ 6.5 \quad : \quad 1.2 \quad : \quad 1.0 \end{array}$$

The weight ratios of selenium to sulphur in the three sulphides have been calculated to 1:62 for molybdenite, 1:445 for pyrite and 1:349 for chalcopyrite.

One interesting feature relating to selenium-rich molybdenites is the close association which appears to exist between selenium-rich molybdenites and uranium mineralizations. The three previously mentioned occurrences of such molybdenites are all closely connected with uranium mineralization. A search for uranium by XRF and by radioactivity measurements gave negative results on sample material from the Russeholmen deposit, and no immediate connection with uranium mineralizations therefore seems to exist at this locality.

In future investigations of uranium mineralizations, systematic analysis for selenium would be of interest, not only in this area but also elsewhere. Pyrite could possibly prove to be a suitable sulphide mineral for such investigations, both because pyrite is a common accessory sulphide mineral in many rocks, and because it has been shown in this work that pyrite can contain appreciable amounts of selenium when it occurs together with selenium-rich molybdenite.

One uranium mineralization, the Orrefjell deposit, situated far from Russeholmen and apparently without any geologic connection, is reported to carry a sulphide mineral paragenesis con-

sisting of molybdenite, pyrite and pyrrhotite (Rindstad 1982, Lindahl 1983). Selenium analyses of these sulphides would be of interest. Another uranium mineralization, the Nabar deposit, which occurs in the same type of rock as the selenium-rich sulphides at Russeholmen (Zwaan et al. 1975), would seem to be of particular interest for selenium investigations. If a relationship can be found between uranium mineralizations and selenium, selenium could be an important indicator for the presence of uranium.

The tentative analysis for gold of the vein minerals calcite, quartz and amphibole gave as result 20 ppb Au. This value is well above the concentrations of gold normally found in most rocks, but cannot be characterized as anomalous. A possible elevated level of gold in this rock type could be one conceivable primary source for alluvial gold. Voronin et al. (1972) described a theory for the formation of placer deposits, where electrochemical processes in the rivers are responsible for the redeposition of gold which has been brought into solution from some primary gold source.

The average value for rhenium in the molybdenite from Russeholmen is 240 ppm. This concentration is significantly higher than what is found in purely molybdenite assemblages. The content of rhenium corresponds to the lower range of what is normally found in molybdenites from chalcopyrite-bearing assemblages of the porphyry Cu-Mo type (Giles & Schilling 1972). The role of selenium in the distribution of rhenium seems to be little studied. It has, however, been claimed that rhenium and selenium are closely associated in some molybdenites (Mogarovski 1963). No general correlation between rhenium and selenium is seen to exist when different deposits of molybdenite are compared. Thus, a molybdenite from Ørdsalen containing 440 ppm Re, analysed by the laboratories of the USGS in Denver, showed no detectable selenium.

The relatively high content of rhenium in the molybdenite from Russeholmen could be of interest for radiometric dating after the Re-Os method. This would hopefully reveal whether the molybdenite mineralization is pre-thrusting or not.

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