# BEHAVIOR OF SELENIUM AND SULFUR IN SVECOKARELIAN SULFIDE-RICH ROCKS

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Selenium content is high and the S/Se ratio low in the economically most important sulfide ores which are situated in the Svecokarelian schist belt. The S/Se ratio is like that in Middle Precambrian (1.4—2.5 Ga) Svecokarelian carbonaceous and argillaceous schists, indicating that the sulfides originated in those schists and, after sedimentation, were separated from them by metamorphic and magmatic processes.

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## Introduction

Selenium is a chalcophile element which under endogenic conditions does not become incorporated into silicates; most of it is found therefore in sulfides (Koljonen 1974 a). During exogenic processes Se partly separates from S (*cf.* Dyachkova & Khodakoviskiy 1968): $S^{2-}$ is mostly oxidized to sulfate which migrates easily, while $Se^{2-}$ changes to elemental form or to selenite ion. Se migrates with difficulty because it is adsorbed onto colloids and is enriched into hydrolysates and oxidates. Se as nutrient is removed by organisms from soil solutions and enriched in organic remains. During the decomposition of organic matter, Eh and pH in soil decrease and thus further hinder the migration of Se (Koljonen 1974 b, c, 1975 a).

The S/Se ratio changes during sedimentary processes and characterizes thereby the sediments formed and the rocks derived from them. The total content of Se decreases during metamorphism but rocks seem to maintain its ratio with S because the small amount of selenium present under endogenic conditions, in reduced form, is incorporated with sulfur into sulfides. During metamorphic or magmatic processes some variation in the ratio probably occurs, because some sulfides preferentially incorporate Se (*cf.* Sindeeva 1964; Tischendorf 1966), some of the sulfide-forming cations (*e.g.* $Fe^{2+}$, $Ni^{2+}$, $Cu^{1+}$) separate out, and the oxidation state changes ($Fe^{2+}/Fe^{3+}$). The predominant feature is that the S/Se ratio decreases during differentation of rocks because Se tends to be enriched together with mobile elements into late high temperature solutions (*cf.* Kaplan *et al.* 1969; Zies 1929). Se is absent from the low temperature sulfate and carbonate-rich thermal waters.

In the following the Se content and S/Se ratio

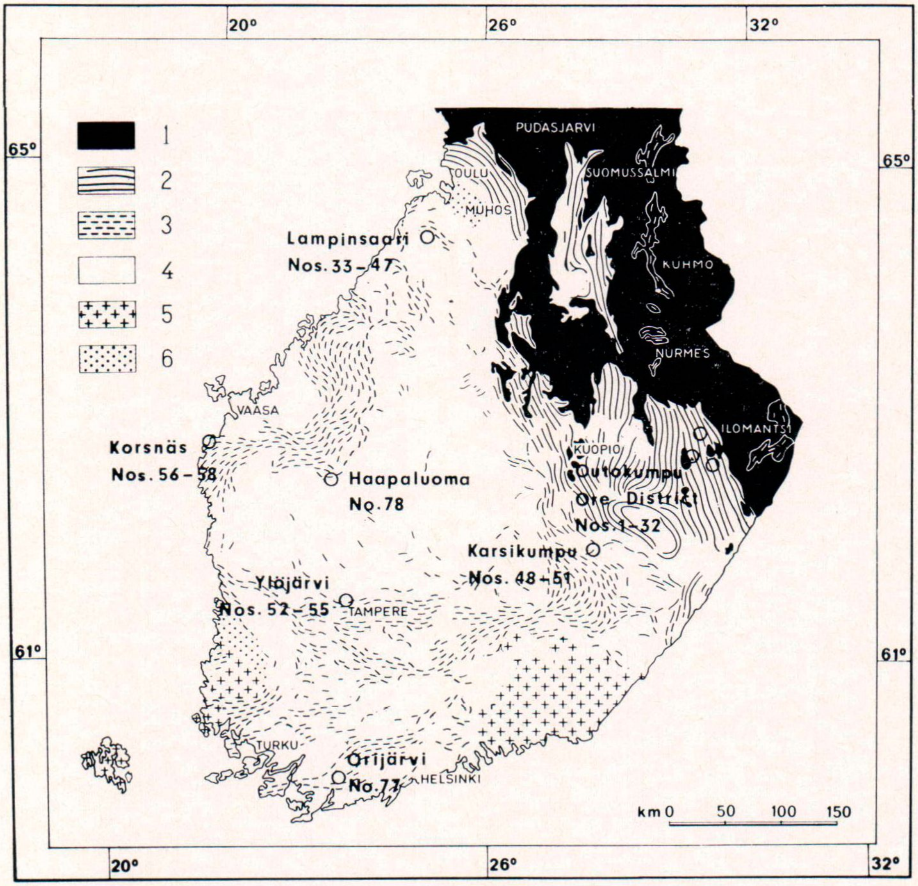


Fig. 1. The sites of investigated ore deposits presented on the geological map of Finland (Simonen 1971) Presvecokarelian rocks (2.6—2.8 Ga): 1. Orthogneiss. Svecokarelian rocks (1.8—1.95 Ga): 2. Karelian schist belt; 3. Svecofennian schist belt; 4. Orogenic plutonic rocks. Later Precambrian postorogenic rocks: 5. Rapakivi intrusions; 6. Jotnian sedimentary rocks. The numbers indicate samples in Table 1.

are studied in ore deposits and metamorphic schists. A short description of the studied Finnish deposits, which are situated in Middle Precambrian rocks (1.4—2.5 Ga, Rankama & Welin 1972), can be found in the index compiled by Kahma (1974). A comprehensive bibliography is also given in his study.

## The sulfide ores in the Karelian zone

Fe, Cu, Co, Zn, and S ores in the Outokumpu Ore District (Fig. 1, Table 1, Nos. 1—32).

The economically most important ore in this district is the Outokumpu deposits (Nos. 1—2) which are situated about 30 km SE of the Luikonlahti mineralization (Nos. 3—25).

Se contents have increased in most rocks compared with the averages in magmatic and metamorphic rocks. The S/Se ratio is 2 000—8 000 in magnitude.

The total Se content in skarn rocks is high but the S/Se ratio is greater than the average in Outokumpu ore, carbonaceous schists, or quartz schist. Under endogenic conditions Se seems to be more mobile than S in Ca-rich rocks, just as during exogenic processes it migrates as selenite in areas where limestone prevails. Also the low Se content in alkalic rocks, carbonatites, and anorthosites (Koljonen 1974 a) and the absence of Se minerals from them indicate increased mobility of this element in iron-poor rocks rich in bases.

In Tuusniemi (Nos. 26—32) commercially valuable anthophyllite asbestos lenses are found in the same district as the copper ores. Se content is high, and the S/Se ratio is like that in the Outokumpu and Luikonlahti ores. Possibly this indicates that the hydrothermal solutions (*cf.* Wiik 1953) responsible for the asbestos formations were genetically related to those that caused the deposition of the ores.

Fe, Zn, Cu, Pb, and S ores in the Vihanti Ore Zone (Nos. 33—47).

More Se than the average for Precambrian rocks is found in rocks near the ore body. The S/Se ratio is in the magnitude of 15 000—20 000, which is higher than in the Outokumpu Ore District. This higher ratio is also observed in the analyses (Nos. 33—38) of rocks from Rouhunkoski (1968). Se content for the ore production year 1955 (No. 33) seems to be higher and the S/Se ratio lower than in country rock, but the Se found in sulfides indicates a higher S/Se ratio (about 10 000—25 000, Nos. 34—38) for the ore as a whole.

## The sulfide ores in the Svecofennian zone

Fe, Cu, and S ore of Karsikumpu (Fig. 1, Table 1, Nos. 48—51).

Se contents are high and the S/Se ratio resembles that found in the Outokumpu Ore District.

Fe, Cu, W, As, Ag, (B), and S ore of Ylöjärvi (Nos. 52—58).

Analyses presented are those of Clark (1965) Although he analysed minerals, it seems that the Se concentration is highest and the S/Se ratio the lowest of all the samples investigated in this study. Arsenic and boron are the typical elements in this catathermal-pneumatolytic ore and Se is known to follow As in minerals. The high Se content indicates enrichment along with the other mobile elements under magmatic conditions.

Pb (and REE) and S deposit of Korsnäs (Nos. 56—58).

The deposit represents a different type from the others investigated. It is small and formed in a fracture, and contains much calcite, low temperature minerals, and secondary clay minerals (*cf.* Sahama 1965; Sahama & Lehtinen 1967). No general description to the geology of the mineralization is available.

Probably because of the low deposition temperature Se content is low and the S/Se ratio high in the specimens analysed. Also the Se-rich halo surrounding the ore body is more poorly formed than those around the other sulfide deposits investigated.

Sulfide schist, Valåsen, Sweden (Nos. 59—64).

This small and poor sulfide mineralization belongs to the western part of the Svecofennian supracrustal rocks. It represents typical, highly metamorphic Precambrian schists, which are composed mostly of quartz, feldspars, and micas, sometimes contain poor pyrite or pyrrhotite dissemination, and are rusty when the outcrop is weathered.

The samples are taken from an area some tens of square meters in size. Se content is low and the S/Se ratio is high, being of the magnitude common in sedimentary sulfides.

## Sulfide schists from Finland

Specimens (Fig. 1, Table 1, Nos. 65—69) are from various parts of the Svecokarelian schist belt (*cf.* also the analyses of argillaceous and calcareous carbonaceous schists of Peltola, 1960).

Se contents are higher and the S/Se ratio is lower in carbonaceous schists than in quartz-feldspar schist or in gneisses. In general it seems that the Se content relative to S decreases when

TABLE 1

Se content and the S/Se ratio in some ores, rocks, and minerals.
[1] type of rock in area; [2] taken from the surface; [3] taken from a mine; ~ content is estimated

| No. | Rock type | S % | Se ppm | S: Se |
|---|---|---|---|---|
| | THE SULFIDE ORES IN THE KARELIAN ZONE | | | |
| | *Outokumpu Ore District* | | | |
| | Outokumpu (Peltola 1960, Tables X—XI): | | | |
| 1 | Carbonaceous schist, average content of 17 specimens | 5.35 | 20.0 | 2 700 |
| 2 | Outokumpu ore, average composition | 25.3 | 47.0 | 5 400 |
| | Luikonlahti: | | | |
| 3 | Carbonaceous schist [1] | 4.83 | 21.5 | 2 200 |
| 4 | Pegmatite. A small tongue from granite (No. 22). 20 m from compact ore [3] | 0.03 | 0.12 | 2 500 |
| 5 | Quartzite. A few meters from compact ore [3] | 1.36 | 4.5 | 3 000 |
| 6 | Feldspar-rich boudinaged vein in ore [3] | 0.05 | 0.14 | 3 600 |
| 7 | Quartzite [1] | 9.75 | 14.7 | 6 600 |
| 8 | Serpentine rock [1] | 0.42 | 0.59 | 7 100 |
| 9 | Granite, »Maarianvaara type» [1] | 0.10 | 0.13 | 7 700 |
| 10 | Serpentine rock. About 30 meters from compact ore [2] | 0.32 | 0.41 | 7 800 |
| 11 | Amphibole-spinel-olivine rock [1] | 1.58 | 1.90 | 8 300 |
| 12 | Skarn. 20 m from compact ore [3] | 2.14 | 2.45 | 8 700 |
| 13 | Skarn. 3 m from compact ore [3] | 1.36 | 1.46 | 9 300 |
| 14 | Diopside skarn [1] | 3.39 | 3.42 | 10 000 |
| 15 | Limestone [1] | 1.77 | 1.32 | 13 400 |
| 16 | Skarn, sulfide-poor type [1] | 0.11 | 0.07 | 15 700 |
| 17 | Mica gneiss [1] | 0.08 | 0.05 | 16 000 |
| 18 | Serpentine rock [2] | 0.80 | 0.45 | 17 800 |
| 19 | Tremolite skarn [1] | 4.86 | 2.70 | 18 000 |
| 20 | Granite. About 100 m from compact ore [2] | 0.42 | 0.21 | 20 000 |
| 21 | Serpentine rock [2] | 0.67 | 0.32 | 21 000 |
| 22 | Granite. 7-m broad dyke, 20 m from compact ore [3] | 0.94 | 0.38 | 25 000 |
| 23 | Serpentine rock. 1 m from a vein (No. 6), near serpentine rock (No. 25) [3] | 4.69 | 1.60 | 29 000 |
| 24 | Pegmatite [3] | 0.85 | 0.24 | 35 000 |
| 25 | Serpentine rock. Altered biotite-rich contact with a vein (No. 6) [3] | 0.55 | 0.04 | 140 000 |
| | Paakkila: | | | |
| 26 | Carbonaeous schist [1] | 0.13 | 1.7 | 750 |
| 27 | Anthophyllite asbestos rock. 10 m from the contact with granite (No. 32) [3] | 0.42 | 1.20 | 3 500 |
| 28 | Anthophyllite asbestos rock. From the central part of a lens [3] | 1.58 | 2.80 | 5 600 |
| 29 | Tremolite rock [3] | 3.55 | 4.95 | 7 100 |
| 30 | Anthophyllite asbestos with plagioclase. From the central part of a lens [3] | 0.18 | 0.24 | 7 500 |
| 31 | Biotite rock. From the contact with granite (No. 32) [3] | 0.60 | 0.05 | 110 000 |
| 32 | Granite. 10-m broad dyke in anthophyllite asbestos rock [3] | < 0.04 | 0.03 | |
| | *Vihanti Ore Zone* | | | |
| | Lampinsaari: | | | |
| 33 | Zinc ore. Production in 1955 (Rouhunkoski 1968, TABLE 4, No. 1) | 9.79 | 40 | 2 400 |
| 34 | Black schist, sulfide concentrate (Rouhunkoski 1968) | ~30 | 29 | ~ 10 000 |
| 35 | Cordierite gneiss, sulfide concentrate (Rouhunkoski 1968) | ~30 | 18 | ~ 17 000 |
| 36 | Mica schist, sulfide concentrate (Rouhunkoski 1968) | ~30 | 14 | ~ 21 400 |
| 37 | Zinc ore (Rouhunkoski 1966, TABLE 10) | ~30 | 13 | ~ 23 000 |
| 38 | Pyrite ore (Rouhunkoski 1966, TABLE 10) | ~40 | 14 | ~ 29 000 |
| 39 | Tremolite skarn [3] | 9.30 | 11.5 | 8 100 |
| 40 | Mica schist [3] | 3.70 | 4.1 | 9 000 |

| No. | Rock type | S % | Se ppm | S: Se |
|---|---|---|---|---|
| 41 | Cordierite gneiss [3] | 2.29 | 2.2 | 10 400 |
| 42 | Microcline granite, porphyritic [3] | 0.52 | 0.31 | 17 000 |
| 43 | Plagioclase porphyry [1] | 0.32 | 0.17 | 19 000 |
| 44 | Amphibolite [3] | 3.17 | 1.50 | 21 000 |
| 45 | Graywacke [1] | 5.41 | 2.40 | 23 000 |
| 46 | Dolomite [1] | 2.42 | 0.72 | 33 000 |
| 47 | Diopside skarn [1] | 1.42 | 0.24 | 58 000 |
| | THE SULFIDE ORES IN THE SVECOFENNIAN ZONE | | | |
| | Karsikumpu: | | | |
| 48 | Garnet skarn [3] | 0.14 | 0.38 | 3 700 |
| 49 | Mica rock [3] | 0.15 | 0.32 | 4 700 |
| 50 | Diorite [3] | 0.81 | 0.44 | 18 000 |
| 51 | Granite [3] | $<$ 0.03 | 0.10 | |
| | Ylöjärvi (Clark 1965, TABLES 1, 41, 42): | | | |
| 52 | Arsenopyrite, average of 10 specimens | ~19.7 | 230 | ~ 900 |
| 53 | Chalcopyrite, average of 2 specimens | ~35.0 | 125 | ~ 1 900 |
| 54 | Pyrrhotite, average of 3 specimens | ~36.5 | 150 | ~ 2 800 |
| 55 | Pyrite | ~53.5 | 190 | ~ 2 800 |
| | Korsnäs: | | | |
| 56 | Mica gneiss, mylonitic and much altered by ground waters. 3 m from compact PbS ore [2] | 1.69 | 1.85 | 9 100 |
| 57 | Serpentine rock. 4 m from ore [2] | 0.71 | 0.15 | 47 000 |
| 58 | Diopside skarn. About 10 meters from ore [2] | 0.39 | 0.04 | 78 000 |
| | Sweden, Valåsen: | | | |
| 59 | Quartz-feldspar schist, much weathered [2] | 0.55 | 0.92 | 6 000 |
| 60 | Quartz-feldspar schist with poor pyrrhotite dissemination [2] | 0.23 | 0.23 | 10 000 |
| 61 | Quartz-feldspar schist with pyrrhotite dissemination [1] | 2.22 | 0.64 | 35 000 |
| 62 | Gneiss [2] | 0.07 | 0.13 | 52 000 |
| 63 | Gneiss [2] | $<$ 0.05 | 0.05 | |
| 64 | Granite [2] | $<$ 0.03 | 0.07 | |
| | SVECOKARELIAN SCHISTS FROM FINLAND | | | |
| 65 | Carbonaceous schist [1]. Lapua | 3.09 | 8.7 | 3 600 |
| 66 | Carbonaceous schist [1]. Sotkamo, Talvivaara | 13.18 | 37.0 | 3 600 |
| 67 | Carbonaceous schist [1]. Pyhäselkä, Mulo | 5.02 | 4.1 | 12 200 |
| 68 | Pyrite from carbonaceous schist [2]. Kuhmoinen, Patavesi | 20.0 | 11.0 | 18 000 |
| 69 | Sulfide-rich quartz-feldspar-mica schist [1]. Jäppilä | 1.23 | 0.57 | 22 000 |
| | MISCELLANEOUS MINERALS FROM FINLAND | | | |
| 70 | Pyrite, from a loose glacial boulder in Svecofennian schist belt. Jämsä, Vekkula | 49.5 | 24.0 | 21 000 |
| 71 | Pyrite cement in sandstone, from a loose glacial boulder. Pattijoki, Kopsankylä | 8.1 | 3.6 | 22 500 |
| 72 | Pyrite from migmatitic granite [2]. Helsinki, Kamppi | 47.8 | 13.0 | 37 000 |
| 73 | Pyrite, from a small pyrite ore [3]. Sotkamo, Tipasjärvi | 38.8 | 9.1 | 43 000 |
| 74 | Marcasite. Pyhäjärvi, Pyhäsalmi | 52.7 | 4.3 | 123 000 |
| 75 | Pyrite. Kurikka, Myllykylä | 48.0 | 3.8 | 130 000 |
| 76 | Pyrite. Kälviä, Hopeakallio | 46.6 | 2.2 | 211 000 |
| 77 | Galena [3]. Orijärvi mine in the Svecofennian zone. Kisko, Orijärvi (see Vorma 1960) | 13 | 465 | 280 |
| 78 | Löllingite [3]. Peräseinäjoki, Haapaluoma quarry | 0.3 | 0.004 | 750 000 |

carbon content diminishes and argillaceous or quartz-feldspar content increases.

## Miscellaneous minerals

In sulfides (Fig. 1, Table 1, Nos. 70—80) the Se content and the S/Se ratio vary greatly. Although analyses are few, it seems that outside schist belts selenium is depleted in sulfides found in gneisses and granites.

Sulfides which are economically the most interesting are particularly enriched in Se because during magmatic processes it is enriched with Cu, Ni, As, Ag, Au, etc. to the same deposit. The S/Se ratio could therefore be used as a geochemical indicator when ore bodies are prospected, *e.g.*, by means of glacial boulders, as commonly is done in Finland.

## Discussion

Selenium content is highest and the S/Se ratio lowest (in magnitude, 1 000—20 000) in carbonaceous schists, indicating enrichment with organic matter during sedimentation. Gradually the amount of Se decreases as the content of the argillaceous part increases in the sediment, and the S/Se ratio is then about 15 000—30 000. When the schist contains mostly quartz and feldspars, Se content is low and the S/Se ratio is about 30 000—100 000, typical of many sedimentary sulfides (*cf.* Goldschmidt & Strock 1935).

In country rock Se concentration is increased near sulfide mineralizations and it forms a halo around sulfidic ore bodies. The content is high in many Ca- and Mg-rich rocks and skarns, but it also seems that the S/Se ratio is high compared with other rocks in the surrounding area, which indicates increasing mobility of Se in basic milieu.

Near contacts with igneous rocks, Se content is decreased (Koljonen 1974 d) and the S/Se ratio is high (*cf.* Table 1, Nos. 25, 31) because Se is mobilized before S during the emplacement of magmatic rocks.

The most important sulfide ores in Finland are situated in the Svecokarelian schist belt. In these, Se content is highest in Cu-rich ores and decreases slighly in those rich in Zn. Under magmatic conditions Se migrates somewhat faster than S but, as a whole, the S/Se ratio changes only slightly when those elements, in reduced form, are mobilized. Therefore, it seems that the sulfides in Cu—Zn ores and possibly even pentlandite type Ni—Cu deposits which are rich in selenium have originated from the schists (*cf.* Koljonen 1975 b). The sulfides which originate from carbon-rich metasediments possibly contain more Cu and those which originate from argillaceous sediments with little carbon, more Zn.

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