

# SELENIUM IN CERTAIN SEDIMENTARY ROCKS

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The selenium contents of some sedimentary rocks were studied and tentative averages are presented.

The distribution pattern of selenium in sedimentary rocks can be summarized as follows:

The highest contents are found in clayey sediments (excluding possibly oxides). Carbonaceous matter clearly has an increasing effect on the amount of selenium present. In slates the geochemistry of selenium partly coincides with that of uranium and vanadium. The organic carbonate sediments contain less selenium than would be expected, that found being primarily bound by organisms. The organic matter and selenium are probably oxidized by the high calcium content, the selenium migrating out of the sedimentary rock with percolating waters.

The rocks formed from sands and evaporites are nearly devoid of selenium.

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## Introduction

This paper, concerning low metamorphic sedimentary rocks, is part of a study of the distribution and geochemical behaviour of selenium in Finnish rocks (Koljonen 1973a; b).

The occurrence of selenium in sedimentary rocks is comparatively well studied in many seleniferous areas where this element is met in toxic concentrations (Beath, Draize, Eppson, Gilbert and McCreary 1934; Beath, Gilbert and Eppson 1937; Beath, Hagner and Gilbert 1946; Fleming and Walsh 1957; Walsh, Fleming, O'Conner and Sweeney 1951; Williams and

Byers 1936; Williams, Lakin and Byers 1941). The behaviour of selenium in sedimentary rocks is covered by a considerable amount of literature, the most comprehensive reviews having been published by Trelease and Beath (1949), and Rosenfeld and Beath (1964).

The information dealing with the abundance of selenium in common sedimentary rocks outside the seleniferous area is scanty. Minami (1936) published some determinations of Japanese and European slates and Sindeeva (1964) made three analyses of the shales of Estonian SSR. For comparison with the data presented in this paper, their values are reproduced here (Table 1).

TABLE 1

The selenium analyses presented by Minami (1936) and Sindeeva (1964).

Slate, Paleozoic, European	Se	1 300 ppb	Minami
» , » , »		1 200 » »	
» , » , »		1 100 » »	
» , Mesozoic, Japanese		380 » »	
» , » , »		240 » »	
Dictyonema shale, Silurian, Estonian SSR		9 000 » Sindeeva	
Dictyonema shale, Silurian, Estonian SSR		740 » »	
Dictyonema shale, Silurian, Estonian SSR		300 » »	

According to Goldschmidt and Strock (1935) the selenium content of an average of 32 German limestones is less than 100 ppb. For comparison, some averages presented in previous literature are reviewed. However, as stated by Turekian and Wedepohl (1961) the values are significant only in order of magnitude.

TABLE 2

The average selenium contents presented by Green (1959), Turekian and Wedepohl (1961) and Vinogradov (1962).

Shale	Se	600 ppb	Green
Slate		600 »	Turekian and Wedepohl
Sandstone		50 »	» » »
Carbonate	?—100	»	Green
Carbonate	80	»	Turekian and Wedepohl
Slate and Clay	600	»	Vinogradov

Finland is part of an old Precambrian shield and only a few occurrences of younger sedimentary rocks are known. Therefore, for comparison, a part of the samples were taken from outside Fennoscandia.

In the following, the selenium contents of various sedimentary rock groups are briefly reviewed and compared with the known behaviour of selenium in sedimentary rocks.

### Sandstones

Table 3, Nos. 1—2. The samples analysed have originally been sands containing quartz and feldspars and only sparsely clayey material. Selenium tends to follow feric minerals and

sulphides (Koljonen 1973, 12—13). These minerals are most easily disintegrated by mechanical and chemical weathering.

The detected selenium content is low, normally under 10 ppb, this being under the lower analytical limit of the method used.

### Shales

Table 3, Nos. 3—6. The studied samples are metamorphosed sediments which originally contained much clay and probably organic residue, but little quartz and feldspars. During exogenic processes selenium is easily oxidized to an elemental form and is adsorbed into clays. It is, therefore, considerably enriched into sedimentary rocks of clayey origin. This phenomenon has been observed in the seleniferous areas of sedimentary rock in which the content of selenium is higher in the shales than in the adjacent layers of sandstones or limestones (Byers 1937; Fleming and Walsh 1957). When the carbon content is high, as in the studied bituminous shale which contains uranium (Table 3, No. 4), the selenium content is also high (Table 3, No. 3, contains about 200 ppm U). Selenium tends to follow uranium and in places vanadium in exogenic processes. This phenomenon has been observed in many sedimentary rocks especially in the USA (Beath and Gilbert 1936; Beath, Hagner and Gilbert 1946; Cannon 1952, 1953, 1954, 1956, 1957; Cannon and Kleinhampf 1956; Cannon and Starrett 1956; Coleman 1956; Coleman and Delevaux 1957; Granger, Santos Dean and Moore 1961; Grutt 1956; Keys and White 1956; Love 1954; Miesch and Connor 1956; Vine and Prichard 1954).

### Limestones

Table 3, Nos. 7—12. The selenium content is low in limestones. This is in accordance with the known chemical behaviour of selenium, according to which selenium easily migrates if

TABLE 3  
Selenium contents of the sedimentary rocks

No.	Rock and locality	Selenium content ppb
1	Sandstone. Eura, Kiperjärvi, Finland (Sederholm 1903; and 1913, 112—114; Laitakari 1925, 1—43; Simonen and Kouvo 1955, 57—58) .....	< 10
2	Sandstone. Harjavalta, Lammastenkoski, Finland (Sederholm 1903; and 1913, 112—114; Laitakari 1925, 1—43) .....	< 10
3	Shale (carbonaceous, uranium ore). Billingen, Sweden (Magnusson, Lundqvist and Granlund 1957, 205—206) .....	1 220
4	Shale (bituminous). Kohtla, Virumaa, Estonia SSR .....	410
5	Siltstone. Muhos, Monta, Finland (Brenner 1941; Lokka 1950; Tynni and Siivola 1966) .....	230
6	Shale. Hungary .....	140
7	Limestone (fossiliferous). Jomala, Finland (Asklund and Kulling 1926, 509—511; Kulling 1926, 503—509 Metzger 1922, 1—8; and 1927, 1—20) .....	70
8	Limestone (mollusca). Estonia SSR .....	30
9	Limestone (the baltic limestone, fossiliferous). Mariehamn, Ytternäs, Sökskär, Finland (Asklund and Kulling 1926, 509—511; Kulling 1926, 503—509; Metzger 1922, 1—8; and 1927, 1—20) .....	30
10	Limestone (fossiliferous). Jomala, Ytterby, Finland (Asklund and Kulling 1926, 509—511; Kulling 1926, 502—509; Metzger 1922, 1—8; and 1927, 1—20) .....	30
11	Limestone (coral). Kalinin, USSR .....	20
12	Limestone (fossiliferous). Sala, Västmanland, Sweden .....	< 10
13	Halite (NaCl). Lehrte, W. Germany (Goldschmidt and Hefter 1933) .....	< 10

oxidized. The sediments containing carbonates are neutral or only slightly acidic. The organic compounds, which may have enriched selenium, are disintegrated and oxidized. Selenium is freed in the oxidized form and migrates with solutions. Beath, Gilbert and Eppson (1937) and Chenzov (1961) have observed that in some places selenium occurs in carbonaceous beds, but not in carbonate beds in the same formation.

### Evaporate

One sample, halite (Table 3, No. 13), is analysed. The result is in accordance with that obtained by Goldschmidt and Hefter (1933, 250—252). The content of selenium in evaporates is very low and far below the average in common sedimentary rocks.

### Summary

The average selenium contents in sedimentary rocks are presented only in order of magnitude representing contents typical to the investigated rocks and areas.

The results in this study are well in accordance with the previous studies presented in Table 1 and Table 2.

Tentative averages calculated from Table 3.

Sandstone	Se < 10 ppb
Shale	500 »
Carbonate . . . . .	30 »

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