SELENIUM IN CERTAIN FINNISH SEDIMENTS

TAPIO KOLJONEN

KOLJONEN, TAPIO 1974: Selenium in certain Finnish sediments. *Bull. Geol. Soc. Finland 46*, 15—21.

Almost 100 sediments, mostly Finnish, have been analyzed for selenium. Tentative values for the average selenium contents of the various groups are given. The distribution of the element in the sediments studied is interpreted as follows. During weathering of selenium-bearing sulphides, Eh-pH conditions favor liberation of elemental selenium, which is then adsorbed and concentrated in clays and organic colloids. Residual sediments contain mostly feldspar and quartz and are devoid of selenium; their specific content depends on the colloids and fine clayey fractions present. Cultivation appears to increase selenium content, this increase being particularly noticeable in peat soils, which originally contain very little selenium.

Tapio Koljonen, Department of Geology and Mineralogy, University of Helsinki, SF-00170 Helsinki 17, Finland.

Introduction

Previous studies on the sedimentary geochemistry of selenium have mostly been restricted to the abundance and occurrence of the element in volcanic soils and in soils where selenium is found in toxic concentrations. To the author's knowledge, little information is available on the distribution of selenium in the soils of Fennoscandia. For that reason, a number of analyses were carried out on various types of sediments, mainly from Finland. The behavior of selenium in soilforming processes and its correlation to the underlying bedrock will be dealt with in detail on a later occasion.

Sampling and analytical procedure

Soil specimens were collected mostly from the middle and southern parts of Finland and analyzed as described by the author (1973a). In this procedure, the organic part is dissolved in nitric and perchloric acids, after which mineral part is decomposed by fusing the soil with a mixture of $NaOH—Na_2O_2$. The flux and solution are then combined, and the selenium is distilled as $SeBr_2$. Thus selenium is quantitatively separated from the bulk of a sample and analyzed colorimetrically without the interference of other elements. Some results of this method are presented in Table 1 and calculated to the oven dry (110°C) weight.

In the following, the selenium contents found in various sediments are briefly reviewed and compared with the known behavior of selenium in sediments.

Unsorted sediments, tills

Selenium contents in tills are set out in Fig. 1 and Table 1, Nos. 1—10.

The tills investigated are of fine grain size (< 1 mm) and the selenium content is between the maximum and minimum values found in sorted sediments. The average content has probably decreased since the time of initial deposition of the glacial material, owing to the fact that selenium is concentrated in melanocratic rocks (Koljonen 1973b), which disintegrate more easily than do leucocratic rocks. The dissolved selenium may then migrate into hydrolysates, oxidates (Goldschmidt and Strock 1935, 138; Koljonen 1965), or organic sediments.

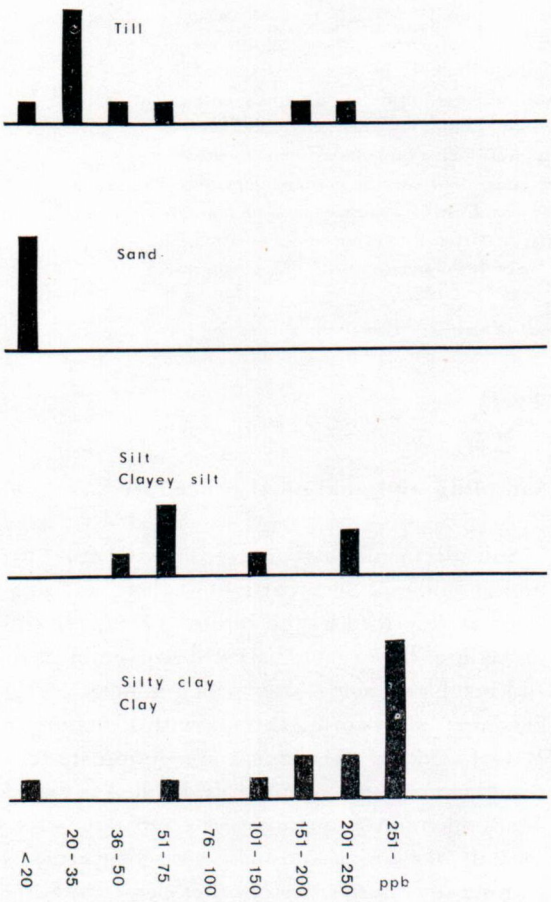

Fig. 1. Review of the selenium contents in unsorted and sorted sediments (■ one sample).

Sorted sediments

The distribution of selenium in sorted sediments is represented in Fig. 1 and Table 1, Nos. 11—36. The following specimens have been included in the figure:

Sand	Nos.	11—15
Silt, Clayey silt	»	16—22
Silty clay, Clay	»	23—36

Although the number of samples is rather small, the histograms (Fig. 1) reveal a clear trend in the distribution of selenium among the different groups of sediments. In sands, which contain predominantly quartz and feldspars, the selenium concentration is < 10 ppb, below the lower limit of the analytical method used. Through mechanical disintegration and weathering the mafic minerals and sulphides (*cf.* Baker 1973) are usually concentrated in the most fine-grained fractions and these fractions contain the greatest percentage of selenium (Koljonen 1973b; c). The most resistant silicate minerals are greatly depleted in selenium.

In solution, selenium is easily oxidized into its elemental form, which is electrically charged. Under strongly oxidizing conditions it may be converted to selenite (*cf.* Delahay *et al.* 1952), which easily migrates in solution.

Fig. 1 shows that clays are greatly enriched with selenium. A remarkable feature is that, under weathering conditions, selenium does not easily migrate far in the humid, relatively cold climate and mostly acid milieu that prevail in Finland. Rather it is removed from solution and adsorbed into sediments.

Mineral soils containing humus

The mineral parts of topsoils are formed chiefly from tills and to a lesser degree from sorted sediments. Only in coastal areas and in inland areas near lakes and rivers are soils apt to contain appreciable amounts of clay. Such soils are commonly under cultivation and tend to contain more clay than those found in forest areas. Moreover, their organic part is more humified than that of topsoils found under the coniferous forests that prevail in Finland. The forest topsoil contains more unhumified litter and little polymerized organic acid and tends to be more acidic than cultivated soils, with the possible exception of peat soils.

The terms used in this study for classification of soils containing organic matter are:

Topsoil, raw humus: the uppermost part of the soil under coniferous forest, containing soil particles and humified remains of vegetation.

Topsoil, forest mull humus: the soil under herbaceous forest, containing humified matter and soil particles.

Mull humus: soil containing much highly polymerized humic acid along with plant remains. Commonly its clay content is higher than that of other soils. This soil is or has been under cultivation.

Being a plant nutrient, selenium is accumulated by organisms. Its behavior in organic life has been treated extensively in the literature and the most comprehensive reviews have been published by Trelease and Beath (1949) and Rosenfeld and Beath (1964).

The occurrence of selenium in soils containing organic matter is given in Fig. 2 and Table 1, Nos. 37—64.

Selenium seems to be enriched in areas which are cultivated or have been used as pasture. On the average, such soils contain more clay than do forest soils and therefore, by adsorption, can more successfully prevent the migration of selenium. Probably part of the selenium present is introduced through synthetic fertilizers and manure.

The organic soils (Table 1, Nos. 37—42, 44) under coniferous forests are enriched with selenium. Presumably, when freed from organic detritus, selenium is in elemental form in an acid milieu and therefore migrates with difficulty. Under herbaceous forests, where soils (Table 1, Nos. 43, 45) are not as acid as under coniferous forests, selenium, being in a more oxidized form, may migrate more easily and therefore be depleted. The mobility of selenium has been studied in a basic milieu, especially in areas where limestone prevails. Supposedly, because calcium selenite is easily soluble (Leutwein 1972, 34-L-1), such soils may contain selenium in concentrations toxic for livestock (Walsh *et al.* 1951; Fleming and Walsh 1957).

Organic sediments

Organic sediments may be divided into two types:

Peats: sediments mostly formed of humified bryophyte and carex.

Gyttjas and dys: sediments formed on lake bottoms and related environments and which contain more or less humified organic remains along with soil particles.

Selenium contents for the investigated organic sediments are presented in Fig. 2 and Table 1, Nos. 65—78.

Only little selenium is found in uncultivated peat soils (Table 1, Nos. 68—73). Probably peats formed on lake shores (Table 1, No. 66) where vegetation also flourishes obtain their trace elements from the circulating water. Such an area is often submerged as a result of spring and autumn floods and, during this time, the detritus sediments deposited on the vegetation further increase their nutrient content. Under normal conditions, peats, which do not receive selenium from the surrounding area, are very much depleted: only by cultivation is their content of selenium increased.

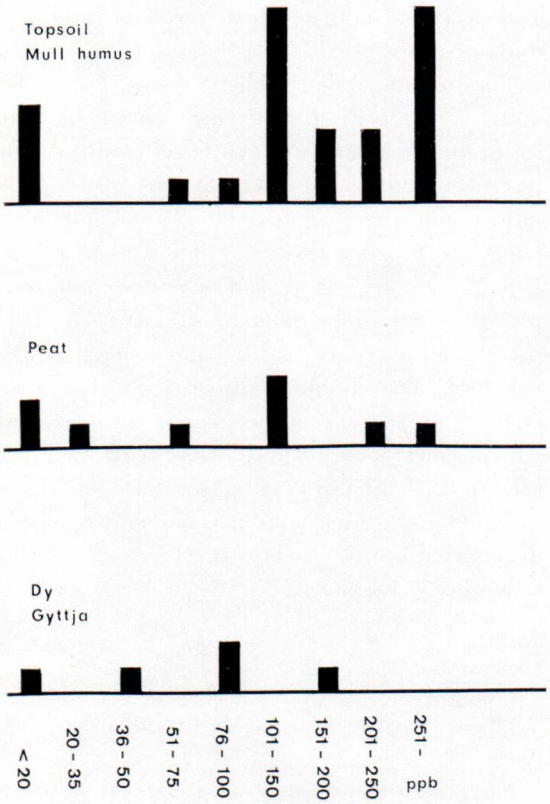

Fig. 2. Review of the selenium contents in soils containing organic matter (■ one sample).

The lake sediments analyzed are of two types: Table 1, Nos. 74—76 are sediments from common polyhumic, dystrophic lakes and ponds, whereas Nos. 77 and 78 are bottom sediments from oligotrophic, calcareous environments. The selenium content in the first type is approximately average for sediments. In lakes and ponds, soluble organic compounds, especially fulvic acid and its complex compounds containing cations, are oxidized near the surface. Forming charged humus colloids, they then precipitate and settle on the bottom (*cf.* Carlson 1973), probably accumulating selenium in the process.

The dys and gyttjas contain some selenium (Table 1, Nos. 74—75), even when the surrounding rocks are nearly devoid of it (Se < 10 ppb). It is therefore probable that part of the selenium present has migrated in in the form of organic compounds and become concentrated through time. Selenium, during its biocycle, appears to be incorporated into proteins and aminoacids (Byers and Knight 1935; Oldfield 1972, 174), which, because they contain nitrogen are more resistant to disintegration than most other organic compounds. Thus the C/N ratio decreases as lake sediments disintegrate. Since selenium enrichment has also been observed in lacustrine sediments, mudstone, bituminous shales, and coals (*cf.* Beath and Gilbert 1936; Beath *et al.* 1946; Chentzov 1963; Davidson and Gulbrandsen 1957; Gibson and Selvig 1944; Keys and White 1956; Meixner 1954; Fleming and Walsh 1957; Searight *et al.* 1946), it seems highly probable that selenium, like sulphur, is enriched into organic residues, which are resistant against weathering.

The gyttjas (Table 1, Nos. 77—78), formed in a calcareous environment, have a low selenium content. In those areas selenium tends to form soluble compounds (Walsh *et al.* 1951), probably inorganic selenites, that easily migrate out of the system. The sedimentation of humus is small, because the organic acids are neutralized and the organic remains are oxidized and disintegrated. Colloids, which could adsorb and collect selenium, are not formed, and selenium is therefore dissolved into circulating waters until it is removed.

Calcareous detritus sediments

Samples Nos. 79—82, Table 1, are from the seashore and contain the carbonate remains of the more or less weathered skeletons of recent molluscs as well as some soil particles. The selenium content is less than that commonly found in clayey sediments and nearer to that found in unsorted sediments. The smallest amount is found in No. 82, which is composed of weathered shell with little or no soil.

TABLE 1

Selenium content of the sediments.

No.	Sediment and locality	Selenium content, ppb
	Unsorted sediments	
1	Clayey till. Helsinki, Herttoniemi, Finland	230
2	Till. Helsinki, Herttoniemi, Finland	180
3	Till. Petäjävesi, Puttola, Finland	68
4	Till. Hämeenkyrö, Komi, Majajärvi, Finland	37
5	Till. Petäjävesi, Puttola, Finland	33
6	Till. Petäjävesi, Maunula, Finland	26
7	Till. Petäjävesi, Puttola, Finland	23
8	Till. Petäjävesi, Maunula, Finland	23
9	Till. Helsinki, Herttoniemi, Finland	21
10	Till. Petäjävesi, Puttola, Finland	n.d.
	Sorted sediments	
11	Sand, from the ancient sea shore of the Gulf of Finland. Helsinki, Laajasalo, Yliskylä, Finland	n.d.
12	Sand, glacial outwash. Hämeenkyrö, Komi, Finland	n.d.
13	Sand, glacial outwash. Hämeenkyrö, Komi, Finland	n.d.
14	Sand, glacial outwash. Petäjävesi, Piesala, Finland	n.d.
15	Clayey sand, from the sea shore of the Gulf of Bothnia. Korsnäs, Finland	n.d.
16	Silt. Petäjävesi, Puttola, Finland	240
17	Silt. Petäjävesi, Puttola, Finland	110
18	Silt, from the sea shore of the Gulf of Bothnia. Korsnäs, Finland	68
19	Silt, cultivated. Helsinki, Viikki, Latokartano, Finland	68
20	Silt, from the sea shore of the Gulf of Bothnia. Korsnäs, Finland	42
21	Clayey silt. Helsinki, Herttoniemi, Finland	220
22	Clayey silt. Hämeenkyrö, Komi, Mattila, Finland	66
23	Silty clay. Kaavi, Luikonlahti, Lake Retusjärvi, Finland	180
24	Silty clay. Kaavi, Luikonlahti, Finland	170
25	Silty clay. Hämeenkyrö, Komi, Mattila, Finland	59
26	Clay. Rome, Narni, Italy	600
27	Clay. Kuhmoinen, Patavesi, Finland	500
28	Clay. Kuhmoinen, Patavesi, Finland	490
29	Clay. Prov. Rome, Monterotondo, Salarese, Italy	400
30	Clay, Litorina. Eura, Karhala, Finland	390
31	Clay, containing a little humus. Helsinki, Viikki, Finland	330
32	Clay. Huittinen, Finland	260
33	Clay, Yoldia. Inkeri, Mga-river, USSR	230
34	Clay. Prov. Rome, Monterotondo, Salarese, Italy	210
35	Clay. Petäjävesi, Puttola, Finland	140
36	Clay, Ancylus. Oulu, Finland	n.d.
	Mineral soils containing humus	
37	Topsoil, raw humus. Kuhmoinen, Patavesi, Finland	280
38	Topsoil, raw humus. Helsinki, Herttoniemi, Finland	260
39	Topsoil, raw humus. Hämeenkyrö, Komi, Majajärvi, Finland	130
40	Topsoil, raw humus. Helsinki, Herttoniemi, Finland	130
41	Topsoil, raw humus. Petäjävesi, Puttola, Finland	120
42	Topsoil, raw humus. Petäjävesi, Maunula, Finland	95
43	Topsoil, forest mull humus. Petäjävesi, Puttola, Konttila, Finland	16
44	Topsoil, raw humus. Hämeenkyrö, Komi, Mattila, Finland	n.d.
45	Topsoil, forest mull humus. Helsinki, Laajasalo, Tahvonlahti, Finland	n.d.
46	Mull humus. Helsinki, Viikki, Latokartano, Finland	510
47	Mull humus. Petäjävesi, Puttola, Finland	470
48	Mull humus, cultivated. Kuhmoinen, Patavesi, Finland	320
49	Mull humus, cultivated. Helsinki, Viikki, Latokartano, Finland	320
50	Mull humus, cultivated. Hämeenkyrö, Komi, Finland	290
51	Mull humus, cultivated. Helsinki, Viikki, Latokartano, Finland	260
52	Mull humus, cultivated. Petäjävesi, Puttola, Konttila, Finland	230
53	Mull humus, cultivated. Petäjävesi, Vanha-Puttola, Finland	230
54	Mull humus, meadow. Hämeenkyrö, Komi, Konkola, Finland	210
55	Mull humus, cultivated. Petäjävesi, Puttola, Finland	200
56	Mull humus, cultivated. Viljakkala, Komi, Mattila, Finland	170
57	Mull humus. Petäjävesi, Puttola, Maunula, Finland	160
58	Mull humus, cultivated. Petäjävesi, Puttola, Maunula, Finland	150
59	Mull humus, cultivated. Petäjävesi, Puttola, Finland	130
60	Mull humus, cultivated. Hämeenkyrö, Komi, Finland	120
61	Mull humus, meadow. Hämeenkyrö, Komi, Mattila, Finland	110
62	Mull humus, cultivated. Petäjävesi, Puttola, Finland	110
63	Mull humus, cultivated. Petäjävesi, Puttola, Finland	59
64	Mull humus, meadow. Hämeenkyrö, Komi, Mattila, Finland	n.d.
65	Peat, Sphagnum, cultivated. Petäjävesi, Puttola, Finland	350
66	Peat, Equisetum and Menyanthes. Petäjävesi, Puttola, Finland	250
67	Peat, Sphagnum, cultivated. Petäjävesi, Puttola, Ruukinsuo, Finland	150
68	Peat, Sphagnum. Petäjävesi, Puttola, Ruukinsuo, Finland	140
69	Peat, Sphagnum. Hämeenkyrö, Komi, Mattila, Finland	115
70	Peat, Sphagnum. Petäjävesi, Puttola, Maunula, Finland	54
71	Peat, Sphagnum. Petäjävesi, Puttola, Ruukinsuo, Finland	24
72	Peat, Sphagnum. Petäjävesi, Puttola, Pappavainaansuo, Finland	n.d.
73	Peat, Sphagnum. Petäjävesi, Puttola, Finland	n.d.
74	Dy. Hämeenkyrö, Komi, Marjamaa, Finland	84
75	Dy. Hämeenkyrö, Komi, Mattila, Finland	81
76	Gyttja. Petäjävesi, Lake Kirrinjärvi, Finland	160
77	Gyttja, contains phlogopite. Siilinjärvi, Lake Särkilampi, Finland (Puustinen 1971, 23—28)	44
78	Calcareous gyttja. Stockholm, Sweden	n.d.
79	Calcareous detritus sediment. Åland, Finland	450
80	Calcareous detritus sediment, Mytilidae. Vänesborg, Älvsborg län, Sweden	230
81	Calcareous detritus sediment, Postglacial, Mytilidae. Kantalahti, Kujärska, East-Karelia, USSR	110
82	Shell, weathered oyster, Pelecypoda, from the ancient shore of the Arctic Ocean. Persamo, USSR (Gaarder and Bjerkan 1934)	20
	Miscellaneous sediments	
83	Kaolinite. Monte Kaolino, Bavaria, West Germany	180
84	Bauxite. Meleyes Banya, Gant, Hungary	170

Kaolinite and bauxite

Only one sample of each was analyzed (Table 1, Nos. 83—84). These soils contain mostly aluminium hydroxides along with some water and silica and are more weathered than the other soils investigated. The fact that they contain selenium s interesting. It may be tentatively proposed that aluminium hydroxide, like iron hydroxide, can bind selenium chemically and prevent its dissolution.

The present results are in accordance with the laboratory investigations of Jones and Belling (1967, 737). In their findings, 25—62 % of dissolved sodium selenate was adsorbed by lateritic soils.

Conclusions

Tentative averages for the selenium contents of sediments in Finland, representing only orders of magnitude, are:

	Se, ppb
Till	64
Sand	< 10
Silt	90
Clayey silt, Silty clay	140
Clay	320
Organic mineral soils	180
Peat	120
Mud, Gyttja	75
Calcareous detritus sediments	200

These averages illustrate the differentiation of selenium during exogenic processes.

In magmatic and metamorphic processes, selenium substitutes for sulphur in sulphides. In exogenic processes, however, selenium usually oxidizes to elemental form or to selenite (*cf.* Dyachkova and Khodakovskiy 1968), whereas sulphur oxidizes to sulphate. The behavior of the two elements is thus different. Because the selenium content of the underlying bedrock is low (Koljonen 1973b; c; d), the selenium contents of Finnish soils are probably lower than average (*cf.* Leutwein 1972, 34-K-1-3). Moreover, selenium in elemental form tends to become fixed in colloids or, as iron selenite, forms soluble compounds only with some difficulty. Consequently, its deficiency as a nutrient is likely over large areas of Finland (*cf.* Lakin 1972). Even such deficiency diseases as nutritional muscular degeneration (NMD) in ruminants (Oksanen 1965, 191; Oksanen and Sandholm 1970) may be caused by the low selenium contents in soils.

Acknowledgments — The author wishes to thank Professor Th. G. Sahama for his helpful comments and advice on many points. Dr. Kathleen Ahonen assisted with the English-language text.

REFERENCES

BAKER, W. E. (1973) The role of humic acids from Tasmanian podzolic soils in mineral degradation and metal mobilization. Geochim. Cosmochim. Acta 37, 269—281.

BEATH, O. A. and GILBERT, C. S. (1936) Selenium-bearing vegetation during late Cretaceous time. Science 84, No. 2187, 484—485.

BEATH, O. A., HAGNER, A. F. and GILBERT, C. S. (1946) Some rocks and soils of high selenium content. Wyo. Geol. Surv. Bull. 36.

BYERS, H. G. and KNIGHT, H. G. (1935) Selenium in soils. Ind. Eng. Chem., Ind. Ed., 27, 902—904.

CARLSON, L. (1973) Tärkeimpien mineraalien ja pääalkuaineiden vertikaalinen jakauma neljän dystrofisen järven pohjasedimenteissä Lounais-Suomessa. Unpubl. thesis, Arch. Dep. Geol. Miner., Univ. Helsinki.

CHENTSOV, I. G. (1963) Selenium in Paleogene deposits of Central Asia. Miner. Abstr. 15, 189—190.

DAVIDSON, D. F. and GULBRANDSEN, R. A. (1957) Selenium in the Phosphoria formation in Idaho, Wyoming, Utah, and Montana. Bull. Geol. Soc. Am. 68, 1714.

DELAHAY, P., POURBAIX, P. and VAN RYSSELBERGHE, P. (1952) Diagrammes d'équilibre potentiel pH de quelques éléments. C. R. Réunion du Comité Thermodynamique Cinét. Electrochim. Milano.

DYACHKOVA, J. B. and KHODAKOVSKIY J. L. (1968) Thermodynamic equilibria in the systems S—H_2O, Se—H_2O and Te—H_2O in the 25—300° temperature range and their geochemical interpretations. Geokhimiya 5, 1108.

FLEMING, G. A. and WALSH, T. (1957) Selenium occurrence in certain Irish soils and its toxic effects on animals. R. Ir. Acad. Proc. 58, Sec. B, 151—166.

GAARDER, T. and BJERKAN, P. (1934) Østers og østersrkultur i Norge. A. s. John Griegs Bogtrykkeri, Bergen.

GIBSON, F. H. and SELVIG, W. A. (1944) Rare and uncommon chemical elements in coal. U.S. Bur. Mines, Tech. Pap. 669.

GOLDSCHMIDT, V. M. and STROCK, L. W. (1935) Zur Geochemie des Selens, II. Nachr. Ges. Wiss. Gött., Math.-Phys. Kl., 4, 123—142.

JONES, G. B. and BELLING, G. B. (1967) The movement of copper, molybdenum, and selenium in soils as indicated by radioactive isotopes. Aust. J. Agric. Res. 18, 733—740.

KEYS, W. S. and WHITE, R. L. (1956) Investigation of the Temple Mountain collapse and associated features, San Rafael Swell, Emery County, Utah, in Contributions to the geology of uranium and thorium by the United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, 1955. U.S. Geol. Surv., Prof. Pap. 300, 285—298.

KOLJONEN, T. (1965) Seleenin esiintymisestä suomalaisissa kivissä. Unpubl. manuscr., Arch. Dep. Geol. Miner., Univ. Helsinki.

— (1973a) Determination of selenium in rocks, soils, and plants. Suomen Kemistil. 46 B, 133—138.

— (1973b) Selenium in certain igneous rocks. Bull. Geol. Soc. Finl. 45, 9—22.

— (1973c) Selenium in certain metamorphic rocks. Bull. Geol. Soc. Finl. 45, 107—117.

— (1973d) Selenium in certain sedimentary rocks. Bull. Geol. Soc. Finl. 45, 118—123.

LAKIN, H. W. (1972) Selenium accumulation in soils and its absorption by plants and animals. Geol. Soc. Am. Bull. 83, 181—190.

LEUTWEIN, F. (1972) Selenium. Biochemistry, 34—L—1—2. Handbook of Geochemistry II—3 (Ed. Wedepohl, K. H.).

MEIXNER, H. (1954) Neue Mineralfunde in der österreichischen Ostalpen XIII. Carinthia II 64, 18—29.

OKSANEN, H. (1965) Studies on nutritional muscular degeneration (NMD) in ruminants. Acta Vet. Scand., Suppl. 2.

— and SANDHOLM, M. (1970) The selenium content of Finnish forage crops. J. Sci. Agric. Soc. Finl. 42, 250—253.

OLDFIELD, J. E. (1972) Selenium deficiency in soils and its effect on animal health. Bull. Geol. Soc. Am. 83, 173—180.

PUUSTINEN, KAUKO (1971) Geology of the Siilinjärvi carbonatite complex, eastern Finland. Bull. Comm. géol. Finl. 249.

ROSENFELD, IRENE and BEATH, O. A. (1964) Selenium; geobotany, biochemistry, toxicity, and nutrition. Academic Press, New York—London.

SEARIGHT, W. V., MOXON, A. L., HILLMOE, R. J. and WHITEHEAD, E. L. (1946) Occurrence of selenium in Pleistocene deposits and their derivatives in South Dakota. Soil Sci. 61, 455—463.

TRELEASE, S. F. and BEATH, O. A. (1949) Selenium, its geological occurrence and its biological effects in relation to botany, chemistry, agriculture, nutrition, and medicine. Publ. auth., New York.

WALSH, T., FLEMING, G. A., O'CONNOR, R. and SWEENEY, A. (1951) Selenium toxicity associated with an Irish soil series. Nature 168.

WEDEPOHL, K. H. (1972) Handbook of Geochemistry II—3. Springer—Verlag, Berlin—Haidelberg—New York.

Manuscript received, July 3, 1973.