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### SELENIUM CONTENT OF SOIL-FORMING ROCKS

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#### Abstract

Low amounts of selenium occur in granites, rhyolites, rhyolitic pumices, limestones, and schists. High amounts occur in andesites (particularly ashes), Upper Cretaceous argillites, and basalts. The selenium content of soil-forming rocks averages 0.42 p.p.m. Se; this value is strongly influenced by the large areas covered by sedimentary rocks having a clay component and it is higher than an average based upon igneous rocks. Weathering processes at the soil surface result in a retention of selenium and prevent a recycling of the element via the marine environment.

Tuffaceous greywackes of the Kawhia and Southland regions have selenium values that are above average for greywacke. Re-sorting of greywacke by river systems results in bouldery and sandy alluvia that are low in selenium, silt loam alluvium and loess that are average in selenium, and clay loam alluvium that is above average in selenium.

#### INTRODUCTION

Interest in the element selenium in animal health studies has shifted from the toxic effects investigated in the 1930s towards deficiencies in the 1960s. The toxic effects, initially noted with horses in south-western U.S.A., were associated with selenium accumulator plants having up to 1% Se and commonly 0.1% Se; deficiency becomes apparent in New Zealand, initially in young sheep, with pasture at 0.000003% Se (0.03 p.p.m.). Rock analyses reported below were undertaken to provide data on the selenium content of soil-forming rocks as a prelude to analysing soil profiles. The rocks represent the pedological D horizon; in some profiles there is a link through the subsoil weathering processes to the parent material of the soil (pedological C horizon) but in many soils the parent material is derived from composite rocks.

The geochemistry of selenium is well known (Goldschmidt, 1954); the close ionic radius similarity of sulphur  $(S^{2-}, 1.74 \text{ \AA})$  and selenium  $(Se^{2-}, 1.91 \text{ \AA})$  allows for easy substitution of selenium into sulphides, and the element has very strong chalcophile characteristics. This co-partnership with sulphur is broken by the weathering cycle as sulphur is more readily oxidised than selenium.

 $S \rightarrow H_2SO_3$  requires -0.47 V while  $Se \rightarrow H_2SeO_3$  requires -0.74 V; and  $H_2SO_3 \rightarrow H_2SO_4$  requires -0.17 V while  $H_2SeO_3 \rightarrow H_2SeO_4$  requires -1.15 V. Both stages of oxidation of sulphur can proceed readily, but selenium usually does not go beyond selenite  $SeO_3^{2-}$  in soils, although **No**. 1

selenates can occur in rocks. Reduction of selenite to selenium can also easily take place.

The marine environment can be one in which sulphate enrichment takes place but this is not so for selenium. Selenium is trapped by exogenetic processes and is held at the earth's surface by the products of mineral weathering. In particular, colloidal ferric hydroxide has a negative charge and will absorb anions; it was suggested by Byers *et al.* (1938) that selenium formed  $Fe_2(OH)_4SeO_3$ , with variable amounts of ferric iron.

Goldschmidt (1954) derived the mean composition of selenium in the lithosphere from its sulphur content (520 p.p.m. S) and an average Se : S ratio of 6000, which was obtained from the mean of ratio 7000 in magmatic sulphides and 4000 in shales. This gave a value of selenium in the lithosphere as 0.09 p.p.m. Vinogradov (1959) gave the Russian crystalline rocks as having  $1 \times 10^{-6}\%$  Se (i.e., 0.01 p.p.m.), but this value was considered too low by Sindeeva (1964), who gave the Clarke Index for selenium, based upon acidic, basic, and ultrabasic rocks, as  $1.4 \times 10^{-5}$  (equivalent to 0.14 p.p.m. Se). Selenium contents of New Zealand topsoils (Watkinson, 1962) were mostly in the range of 0.1 to 2 p.p.m.

The average selenium value based upon a summation of the results for granitic areas in New Zealand is 0.15 p.p.m. However, for soil formation we are concerned with the greater importance of sediments and volcanic ashes in the outer crust. The mean selenium content of soil-forming rocks, pedological D horizon, corrected for areas, has been estimated in this paper as 0.42 p.p.m. Analyses of soil profiles indicate that the main enrichment of selenium takes place in the B horizon where clay accumulation occurs. These B horizons have an average selenium content of 1.4 p.p.m. The pedological A horizon, where the biosphere has had its maximum impress is not in general a zone that is as greatly enriched with selenium as the B horizon. The A horizon has an average selenium content of 0.60 p.p.m.

#### OUTLINE OF ANALYTICAL METHOD

Between 0.02 and 0.1 g of ground material is digested with 1 ml of mixed acids (9 parts  $H_3PO_4 + 1$  part HNO<sub>3</sub>) in a 50 ml conical flask fitted with a 6 in. air condenser. This is heated on an asbestos covered hot plate at 120°C for 10 minutes, then transferred to the metal part of the hot plate at 200°c for a few minutes to complete the digestion. After cooling the condenser is washed into the flask with saturated ammonium oxalate solution (20 ml), the flask boiled briskly for 5 minutes, cooled and the contents filtered under vacuum through glass filter papers. After washing with water the combined filtrate is transferred to a separating funnel and brought to 20°C. All following procedures are carried out in a dark room. 5 ml of reagent (0.1% 2, 3 diaminonaphthalene in 0.1N HCl, extracted twice with cyclohexane) are added. After one hour the piazselenol is extracted with 5 ml of cyclohexane, washed with 0.1N HCl and the fluorescence is excited at 366 m<sub> $\mu$ </sub> and measured at 550 m<sub> $\mu$ </sub> in an EEL Fluorimeter. Mineral material high in organic matter requires extra nitric acid in the digestion. Plant material is burnt in oxygen using the oxygen flask technique.

The digestion procedure is based upon methods developed for sulphur in soils by Mr A. J. Metson and Mr T. W. Collie, Soil Bureau. The fluorescence technique is a simplification of the procedure described by Parker and Harvey (1962).

Analytical cross reference—by the above method the National Bureau of Standards plastic clay No. 98 contains 1.37 p.p.m. Se.

#### VOLCANIC ROCKS

More than half the surface of the North Island has had its soils modified by volcanic ashes; their influence outside the main ash beds depends upon the distance and direction of the sources plus the stability of the underlying land surface. The volcanic ashes can differ widely in their micro-element composition, but there are patterns of association related to the geochemical processes of the volcanism. The pumices tending towards a rhyolitic composition are low in most micro-elements, but the andesitic and basaltic ashes are usually rich in these elements. The amount of selenium in a volcanic rock tends to follow the amount of copper present; there is about a tenfold difference in both these elements between the rhyolitic and the andesitic ashes. The pumice showers have been described and mapped by Baumgart (1954) and Healy *et al.* (1964).

#### Rhyolitic Pumiceous Ashes

Soils derived from rhyolitic pumices are mainly classified as yellow-brown pumice soils and they cover about a quarter of the North Island. The selenium content of pumices forming the present-day soils (Taupo and Kaharoa showers) and some buried soils are given in Table 1. These values

Shower	Grade	Site	Se (p.p.m.
Kaharoa	Lapilli	Tarawera	0.11
Taupo	Lapilli	Taupo	0.17
Taupo	Lapilli	Waiotapu	0.14
Taupo	Sand	Waiotapu	0.14
Putty ash	Ash	Taupo	0.21
Hatepe	Lapilli	Taupo	0.21
Waimahia	Lapilli	Taupo	0.11
Rotokawau	Sand	Tikitere	0.10
Rotorua	Sand	Mamaku	0.20
Sea-borne	Lapilli	Wellington	0.21
Lake-borne	Lapilli	Taupo	0.24

TABLE 1-Selenium Content of Rhyolitic Pumiceous Ashes

for selenium are low, about half the average value for the common sedimentary rock greywacke, but they are about the same as the granites.

Selenium deficiency in sheep, as a component of ill-thrift, occurs on highly improved pastures growing on Taupo silty sand (topsoil selenium 0.17 p.p.m.) derived from Taupo pumice. The early sites for deficiency were above the water-sorted pumice deposited in the temporary lakes formed by debris-blocked rivers.

Where the 1886 eruptions have ejected hydrothermally altered breccia in the Rotomahana and Waiotapu regions (Lloyd, 1959; Cross, 1963) the selenium content of the soils developed on these materials is more variable than that of pumice (Table 2). The largest eruption from Lake Rotomahana deposited hydrothermally altered lake-bottom mud. The deposit has a lower selenium content than pumice. Where the pumice has been altered to a kaolin by hot spring activity in an area at Wairakei the selenium content approaches ten times that of unaltered pumice. The small eruptions of the Waiotapu region, which include the underlying siltstone in their deposits, are variable in their selenium contents.

#### Andesitic Ashes and Rocks

Andesitic ashes cover about a quarter of the surface of the North Island; they weather to form the parent material for most of the yellow-brown loams with allophane clays as the product of weathering (Fieldes, 1955). The selenium contents of the andesitic ashes of the central region are given in Table 3; they are about ten times higher than the values for the rhyolitic pumices. There are also yellow-brown loams formed on ash showers deposited to the north of the central volcanic zone; they are mapped in the General Soil Survey of the North Island (Taylor *et al.*, 1954). These showers form soils (Table 4) with high amounts of selenium similar to andesitic ashes of the central region.

#### Basaltic Ashes and Rocks

Soils derived from basaltic rocks cover only a small area of the North Island (approximately a hundredth of the surface). They comprise recent soils from Rangitoto and Tarawera eruptions, red loams from scoria, and brown loams from the basalt flows. The selenium contents of basaltic materials are given in Table 5; the ejected rocks tend to have higher amounts of selenium than the flow rocks. The average selenium value is below that for the andesitic rocks.

#### Other Igneous Rocks

The effusive rocks discussed above have a greater chance of becoming soil formers than many of the intrusive rocks; soils from these latter rocks are in places modified by factors such as loess. A selection of igneous rocks is given in Table 6.

Soil Name	Texture	Composition of Ejecta	Site S	e (p.p.m.)
Rotomahana	Sandy loam	Rhyolitic lake mud	Waimungu	0.09
Ngapouri	Silt loam	Ash plus altered silt- stone	Waiotapu	0.12
Ngahewa	Stony silt loam	Ash plus rhyolite	Waiotapu	0.35
Opal Lake	Silt loam	Ash plus rhyolite	Waiotapu	0.14
Okaro	Silt loam	Ash plus rhyolite and altered siltstone	Waiotapu	0.33
_	Clay (kaolin)	Hydrothermally altered pumice	Wairakei	1.08

TABLE 2-Selenium Content of Hydrothermal Eruptions

TABLE 3-Selenium Content of Andesitic Ashes and Rocks

Shower	Grade	Site	Se (p.p.m.)
Ngauruhoe	Sand	Desert Road	1.25
Burrell	Pumice lapilli	Stratford Mountain House	0.60
Stratford	Sand	Waipuku	1.68
Egmont	Ash	Whareroa	0.75
Lahar	Boulder	Egmont	0.47
Tongariro	Ash	Ohakune	2.64
	Rock	White Island	0.92

TABLE 4-Selenium Content of Soils from Andesitic Ashes

Soil Name	Texture	Site	Se (p.p.m.)
Whakatane	Gravelly sandy loam	Whakatane	1.32
Waihi	Sandy loam	Katikati	0.77
Tirau	Silt loam	Tirau	1.05
Mairoa	Silt loam	Ohaupo	1.46
Hamilton	Clay loam	Te Rapa	1.10

The granites are very low in selenium; one selected Stewart Island sodic granite analysed at 0.01 p.p.m. The granites give mainly steepland yellowbrown earth soils, often podzolised with very low selenium contents.

The rhyolite from Whangarei has a lower value for selenium than most of the rhyolitic pumices; however, unlike the pumice the soil from the rhyolite is a strongly weathered halloysite clay enriched in selenium. The phonolite from Dunedin is not a main soil-forming rock as it is blanketed with loess. The highest value for selenium in this group of rocks is in the norite which is also conspicuous for its high copper content. The ultrabasic rock dunite and the serpentines are all low in selenium.

#### SEDIMENTARY ROCKS

The sedimentary rocks have been separated into three groups; the first is covered by the term "greywackes", the second by "argillites", and the third includes calcareous rocks and mudstones. The greywackes in the South Island are eroded to form steepland soil complexes with a loess component, and in the North Island many stable sites have accumulated volcanic

Shower	Grade	Site	Se (p.p.m.)
Tarawera	Lapilli	Tarawera	1.50
Rangitoto	Scoria	Rangitoto	0.52
Rangitoto	Sand	Motutapu	0.69
	Scoria	Whangarei	0.24
	Flow	Kiripaka	0.17
	Flow	Auckland Is.	0.47

TABLE 5-Selenium Content of Basaltic Ashes and Rocks

TABLE 6-Selenium Content of Some Igneous Rocks

Rock	Site	Se (p.p.m.)
Granite	Takaka	0.13
Granite	Westport	0.17
Granite	Stewart Is.	0.22
Granite	Snares	0.38
Rhyolite	Whangarei	0.09
Phonolite	Dunedin	0.27
Norite	Longwood	1.08
Dolerite	Whangarei	0.78
Dunite	Wairau	0.28
Serpentine	North Cape	0.15
Serpentine	Mossburn	0.23

ash. The calcareous rocks and Tertiary mudstones tend to form more fertile soils with less development of B horizons, for the same depth of soil, when compared with greywackes.

#### Greywackes

The greywacke group (Table 7) includes a range of rock fabrics from sandstone to siltstone. Some samples are from individual beds, others as in the case of the age-undifferentiated rocks, are composite samples. The selenium contents of the greywackes are all higher than the values associated with rhyolites. The analyses fall into two groups, those with levels about 0.20 to 0.35 p.p.m. Se and those, including Jurassic and Triassic basic greywackes, that have about 0.60 to 0.70 p.p.m. Se. The maximum level of selenium occurs in an Upper Jurassic greywacke (siltstone, fine sandy siltstone, with white tuffaceous horizons) from Ruakiwi, near Hamilton.

The greywacke from Taita has been subsampled to show the selenium content of three fractions. The composite rock is a pedological  $C_2$  horizon composed of iron-stained sandstone with argillite beds; the average selenium content is 0.33 p.p.m. The sandstone component contains 0.31 p.p.m., the argillite component 0.33 p.p.m., and the less frequent iron-enriched zones contain 0.55 p.p.m. A reddish greywacke, also from Taita, had possibly been through a multicyclic weathering process that enriched the level of selenium to 1.00 p.p.m. This rock produces a soil having extremely high levels of selenium (3.20 p.p.m.) in the kaolin-rich B horizon.

Age	Series	Site	Se (p.p.m.)
Cretaceous	Clarence	Kekerengu	0.35
Cretaceous	Taitai	Ruatoria	0.29
Cretaceous	Taitai	Opotiki	0.31
Jurassic	Wakarara Group	Dannevirke	0.23
Jurassic	Ruahine Group	Palmerston North	0.17
Jurassic (upper)	Kawhia (Heterian)	Ruakiwi	0.72
Jurassic (lower)	Herangi (Ururoan)	Waingaro	0.64
Jurassic (lower)	Herangi (Aratauran)	Hokonui Hills	0.57
Triassic (upper)	Balfour (Otapirian)	Hokonui Hills	0.50
Triassic		Nugget Point	0.67
Triassic (upper)	Balfour (Otamitan)	Papakura	0.29
Triassic	Torlesse Group	Porters Pass	0.26
Permian	Waipapa Group	Whangarei	0.44
Permian	Maitai	D'Urville Is.	0.22
Carboniferous	Pelorus	Picton	0.49
Precambrian	Waiuta	Reefton	0.24
Precambrian	Greenland	N. Greymouth	0.21
Uncertain		Maramarua	0.32
		Wellington	0.24
**		Taita	0.33
23		Waimakariri	0.33

#### TABLE 7-Selenium Content of Greywackes

#### Argillites

Abnormally high amounts of selenium occur in the very slightly calcareous upper Cretaceous argillites. Those from Kekerengu had 2.90 p.p.m., Gisborne 1.16 p.p.m., and Kaikohe 0.98 p.p.m. A chocolate shale from Waipawa contained 2.50 p.p.m. and a Cretaceous shale from Kekerengu had 1.66 p.p.m. However, a silicified Cretaceous claystone from Kaikohe had 0.25 p.p.m. and a siliceous Cretaceous shale from east of the Ninety Mile Beach, Northland, had only 0.09 p.p.m. These siliceous materials are the parent rocks of many Northland podzols.

#### Calcareous Rocks and Mudstones

The pure limestones (Table 8) have selenium contents that are below the average value for greywacke. The presence of impurity generally leads to an increase in the selenium levels. Mudstones (Tertiary siltstones) have a variable amount of selenium, but they tend to have more than the limestones.

#### METAMORPHIC ROCKS

The schist rocks (Table 9) form the parent rocks for soils over a large area as they contribute to much of the loess in the southern part of the South Island for developing soils of the brown-grey, yellow-grey, and yellow-brown earth groups. The gneiss is more resistant to weathering and is the parent rock of many steepland podzolised yellow-brown earths. The schists have selenium levels that are slightly below those normally associated with greywacke.

#### **RE-SORTED MATERIAL**

Many of the rocks that contribute to soil formation have been through stages of resorting. In the South Island the upper slopes of the greywacke mountains fracture under frost action producing shingle slides from which the boulders are transported in the rivers and subjected to abrasive action. The sandy and silty fractions are deposited as alluvium, but some of the fine sand and silt is blown as loess from the partly dried wide river beds. If we take the average greywacke as having 0.35 p.p.m. of selenium then the river boulders and river sands (Table 10) are lower than this value. The alluvial silt loams and loess (both present at Barrhill and in the past at Timaru) have selenium contents that are just below the average value for greywacke rock. Loess from the basic greywacke in Southland has about twice the selenium content of the loess from normal greywacke; this is a direct reflection of differences in the rock. The river systems of the South Island usually deposit the clay-rich alluvium near the sea-coast; the selenium contents of these clay loams are 50% higher than the average value for greywacke rock. The river systems of the South Island therefore tend to separate greywacke rock into size fractions : a large sandy fraction as alluvium low in selenium, a silt loam fraction as alluvium and loess both average in selenium, and a small clay loam fraction as alluvium enriched in selenium.

Rock	Site	Se (p.p.m.)
Limestone	Arapohue	0.21
Limestone	Te Kuiti	0.20
Shell limestone	Wairarapa	0.14
Shelly sand	Napier, from lagoon	0.21
Sandy marl	Waihao Downs	0-24
Calcified siltstone	Raglan	0.66
Mudstone	Gisborne	0.32
Siltstone (shelly)	Taihape	0.20
Siltstone	Wairarapa	0.58
Banded sandstone	Puhoi	0.59

TABLE 8-Selenium Content of Calcareous Rocks and Mudstones, Etc.

TABLE 9-Selenium Content of Metamorphic Rocks

Rock	Site	Se (p.p.m)
Schist (Chlorite 3)	Alexandra	0.19
Schist (Chlorite 4)	Alexandra	0.22
Schist (Chlorite 3)	Picton	0.33
Schist (Biotite)	Ahaura River	0.14
Gneiss (Hornblende)	Thompson Sound	0.20
Gneiss	Homer Tunnel	0.40
Rodingite	Nelson	0.15

#### TABLE 10-Selenium Content of Resorted Greywacke Rocks

Greywacke Deposit	Site	Se (p.p.m.)
Moraine	Windwhistle	0.15
Moraine (weathered)	Racecourse Hill	0.29
Boulders	Waimakariri River	0.11
Boulders	Rakaia River	0.21
Boulders	Waitaki River	0-12
Sands	Waimakariri River	0.19
Silts	Waimakariri River	0.25
Loess	Barrhill	0.30
Loess	Timaru	0.30
Loess (basic greywacke)	Morton Mains	0.63
Sands (aolian coastal)	Foxton	0.14

No. 1

The coastal sands are a windblown return of material from the river transport system. These sands are not enriched in selenium by their period in the marine environment and they form a group of soils, yellow-brown sands, in which selenium deficiency can readily be induced by intensive farming. Shell fragments are very low in selenium and sea-borne rhyolitic pumice lapilli have 0.13 p.p.m., which is a value similar to that of subaerial rhyolitic pumice. These are both aspects of the very low level of selenium in sea water (less than 0.001 p.p.m. Se; Sindeeva, 1964). However, many of the older coastal dune systems have weathered to produce better soils and in the North Island contain more basic minerals derived from volcanic ash or intermediate to basic igneous rocks. These soils have levels of selenium that are in excess of those derived solely from greywacke. These dunes, high in selenium, include those forming the Patea soils, Koputaroa soils, and Red Hill soils. The dunes low in selenium belong to the Foxton grey soils and the related younger dunes in regions free of andesitic ash.

#### CONCLUSIONS

The average amounts of selenium in the parent rocks of soils in New Zealand have been listed in Table 11. High values are found in andesites (especially ashes), upper Cretaceous argillites, and basalts (particularly ashes). Very low values of selenium occur in granites and rhyolitic pumices; other low values are in limestones, ultrabasic rocks, and schists.

In the process of re-sorting greywacke rocks by the river systems, large areas of stony and sandy alluvium are produced having low amounts of selenium; areas of silty alluvium and large areas of silty loess have average amounts of selenium; and the small areas of clay loam alluvium are enriched in selenium. Recycling of sands through the marine environment has not added selenium to the aeolian coastal sands. Soil weathering produces a

Rock Group	Se (p.p.m.)	Rock Group	Se (p.p.m.)
Rhyolitic pumice	0.16	Gneiss	0.25
Andesitic ash, andesite	1.19	Granite	0.15
Basalt ash, flow	0.61		
Ultrabasic	0.20	Sediments from:	
Greywacke	0.36	Greywacke, mudstone	0.35
Mudstone	0.33	Gneiss	0.25
Argillite	1.80	Granite	0.15
Limestone	0.20	Volcanic ash	1.00
Schist	0-22	Peat	0.20
Average corrected for areas		0.42	

TABLE 11-Average Selenium Content of Soil Parent Rocks

retention of selenium at the earth's surface; this reaches a maximum effect in the pedological B horizon, and this retention suppresses the supply of the element to sea waters.

The average selenium content of New Zealand's soil-forming rocks, taking areas occupied on the surface, is 0.42 p.p.m. Se. This value is higher than the world lithosphere value of 0.14 p.p.m. based upon calculations for values of acid plus basic rocks. These calculations ignore the enrichment of selenium in andesitic ashes which cover large areas of the land surface and they also ignore the enrichment in argillaceous sediments. This average value is also higher than the mean of 0.09 p.p.m.. Se based upon S/Se ratios.

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