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Origin and distribution of selenium in the upper Cretaceous Niobrara and Pierre formations, northeastern North Dakota

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ORIGIN AND DISTRIBUTION OF SELENIUM IN THE UPPER CRETACEOUS NIOBRARA AND PIERRE FORMATIONS, NORTHEASTERN NORTH DAKOTA

by
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Bachelor of Science, University of Wisconsin 1957

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for the degree of

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This Thesis submitted by Robert M. Novak in partial fulfillment of the requirements for the Degree of Master of Arts from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

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Title ORIGIN AND DISTRIBUTION OF SELENIUM IN THE UPPER CRETACEOUS NIOBRARA AND PIERRE FORMATIONS, NORTHEASTERN NORTH DAKOTA

Department GEOLOGY

Degree MASTER OF ARTS

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Date April 16, 1971

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ABSTRACT

High concentrations of selenium, often as much as 28 ppm, have been found in the bentonitic zones near the contact of the Niobrara and Pierre Formations of Cretaceous age in northeastern North Dakota. A 64-foot section in the Pembina Hills area reveals that the highest selenium content occurs in shale and marlstone beds adjacent to the bentonite beds which, themselves, contain comparatively little selenium. Higher concentrations of selenium were found in the brown shale than in the black, with a small variation in color making a big difference in selenium content.

The selenium content of the shale and marlstone drops off considerably with increasing distance from the bentonitic zone in the vertical section. This suggests that the selenium had a volcanic source and accompanied the volcanic ash that formed the bentonite beds.

Soils formed from rock in the bentonitic zone above and below the Pierre-Niobrara contact can be presumed to be seleniferous and capable of producing toxic vegetation. These soils present a potential danger of selenium poisoning to livestock and to humans who inhabit the area.

INTRODUCTION

Purpose of Study

The Pembina Hills area was chosen for this study because its great relief results in unusually good exposures of a formation elsewhere known to contain selenium.

The purposes of this study are: (1) to delineate areas of known high selenium concentrations in North Dakota, (2) to delineate areas of potentially high selenium concentrations in North Dakota, (3) to determine the source of selenium and explain the origin of high concentrations in nature, and (4) to identify seleniferous formations and soils which are capable of producing vegetation that is a potential hazard to livestock and humans living in these areas.

Previous Investigations

Selenium poisoning of animals in the western part of the United States has been reported as early as 1857 (Rosenfeld and Beath, 1964, p. 2). It was then known as "alkali disease," because people thought it was caused by alkali or mineral salt. Farmers in affected areas early learned to associate the disease with certain restricted tracts of land. Many of them believed that the disease was caused by something in the vegetation.

In 1931 H. G. Knight suggested that selenium might be the toxic agent in plants that were poisonous to livestock (Beath, 1936, p. 104).

In 1933, Robinson published a report of his analysis of the selenium content of toxic wheat from South Dakota, and the connection between selenium and livestock poisoning was established (Beath and others, 1941, pp. 887-900). This led to a series of investigations of the selenium content of various types of vegetation, and finally to the selenium content of soils and formations on which these plants grew.

Work on the occurrence of selenium in certain geological formations was started in 1934 by Beath and his co-workers (Beath and others, 1934, pp. 1-84). Beath's work was substantiated by Williams, Lakin, and Byers, who have made many analyses of the selenium content of plants, soils, and geological formations in western United States and Canada (Byers, 1935, 1936; Byers and others, 1938; Williams and others, 1940, 1941; Lakin and Byers, 1941, 1948).

Description of the Study Area

The study area is located in the Pembina Hills in western Cavalier County, North Dakota (Fig. 1). It is rugged hill country, which is rapidly being eroded by the Pembina River and its tributaries. Bedding is horizontal, or nearly so, except where slumping occurs. A part of the Niobrara Formation and 100 feet or more of the Pierre Shale is exposed along many of the drainages leading to the Pembina River. Numerous bentonite beds occur in this area.

Other descriptions of the stratigraphy of the Pembina Hills have been given by Laird (1951, pp. 1-3) and Gill and Cobban (1965, pp. A1-A20).

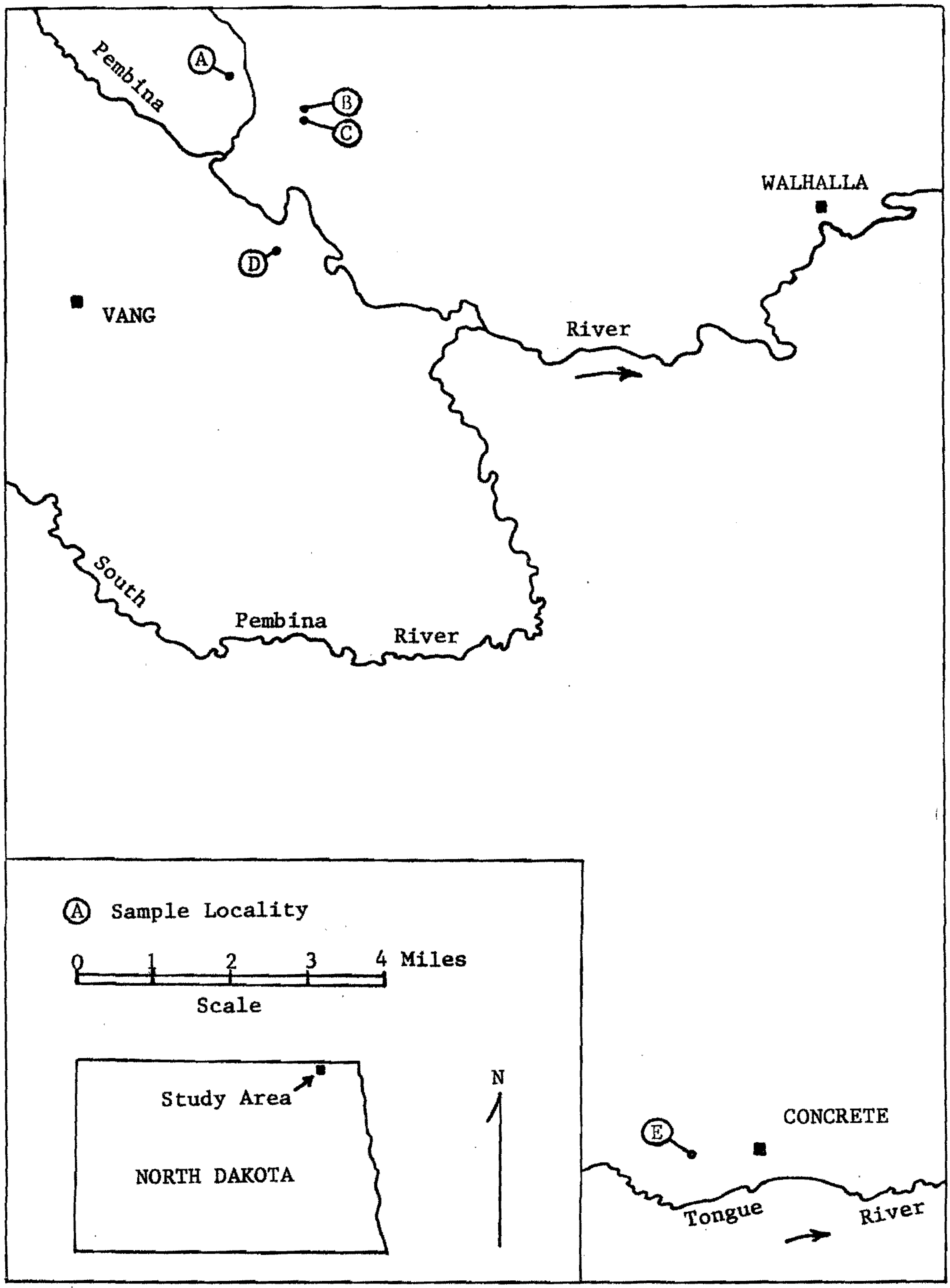


Fig. 1.--Map of study area

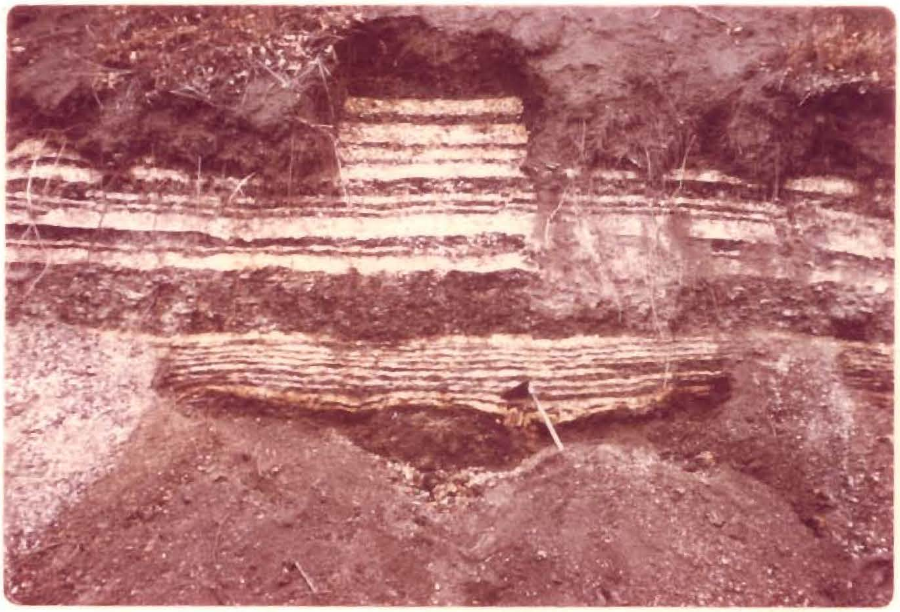
Field Work

Field work, consisting of measurement, description, and sampling of five stratigraphic sections was conducted in the fall of 1970. Thickness of individual units was measured by steel tape and hand level. Samples were taken from each bed in a vertical line up the section, and all samples were taken from the center of the beds, unless otherwise stated.

Fig. 2--Bentonite beds at the base of the Pierre Shale at location A. Bed 1 through Bed 34 are exposed here (Fig. 4). The Pierre-Niobrara contact lies a few inches below the shovel handle. These same beds appear near the center of the section exposed in Fig. 3.

Fig. 3--A fresh exposure of lower Pierre-upper Niobrara lithology at location A. The bentonite beds marking the basal Pierre can be seen near the center of the picture. At least 24 separate bentonite beds are exposed in the Pierre Shale from the center to the top of the picture.

Just above the road in front of the car is bentonite Bed 16 in the Niobrara Formation. It is about 24 feet below the base of the Pierre Shale.



THE GEOCHEMICAL OCCURRENCE OF SELENIUM

Abundance and General Geochemical Character

The chemistry of selenium is closely related to sulfur, with which it is commonly associated in nature. Selenium is far less abundant than sulfur in the earth's crust with an estimated concentration of 0.05 ppm. In chondrite meteorites its concentration is much higher, 8.5 ppm (Ahrens, 1965, p. 97). The accuracy of the figure for selenium content in the earth's crust is poor, because selenium is strongly enriched in sulfide-ore bodies, the mass of which cannot be accurately determined.

Selenium occurs in the native state and also in about 25 minerals, but none of these is considered a commercial source. The commercial source of selenium at present is the anode mud or slime produced in the electrolytic refining of blister copper.

There are three allotropic forms of selenium: (1) Metallic hexagonal, crystalline-stable form, lustrous gray to black in color; (2) Red selenium, monoclinic crystals; (3) Amorphous selenium, black, amorphous red, or colloidal.

Selenium may substitute for sulfur in the lattices of sulfides. The radii of S^{2-} (1.74 angstroms) and of Se^{2-} (1.91 angstroms) are close enough to make this possible (Goldschmidt, 1954, p. 532).

Selenium in Igneous Rocks

Average selenium content of igneous rocks is about 0.09 ppm (Sargent, 1955, p. 2). In magmatic rocks probably all the selenium is in the sulfide minerals (Goldschmidt, 1954, p. 532).

The average S:Se ratio in early magmatic sulfides is 2,000:1 to 20,000:1 and in high-temperature hydrothermal sulfides the ratio is 400:1 to 20,000:1. Hydrothermal rocks and minerals found at intermediate and low temperatures had a S:Se ratio of 70,000:1 to 250,000:1 (Rankama and Sahama, 1950, p. 746). The values of the S:Se ratio show that selenium is more abundant in hydrothermal sulfides formed at high temperatures.

Replacement of sulfur by selenium in sulfide minerals occurs more readily at elevated temperatures than at low ones. In hydrothermal rocks selenium forms a number of selenides containing silver, copper, mercury, bismuth, lead, and other elements. These minerals are relatively rare geochemically and their selenium content may run as high as 48 percent (Goldschmidt, 1954, pp. 533-534).

So far, the selenium content of the various classes of igneous rocks is unknown (Rankama and Sahama, 1950, p. 747).

Selenium in Sea Water and Sedimentary Rocks

Stratigraphic Distribution

A large area of North America west of the Mississippi from Mexico up into Canada is underlain by seleniferous rocks. Selenium is present in every formation from the Carboniferous to Recent. Rocks of the Cretaceous Period have been found to be the most seleniferous (Goldschmidt, 1954, p. 535). This was a period of intense volcanic activity in the western United States. It has been postulated by Byers and others (1938, pp. 60-61) that the selenium found in the formations of the western United States had a volcanic origin.

The Cycle of Selenium and Sulfur

The geochemical cycles of selenium and sulfur leading to their presence in sedimentary rocks differ widely from each other. The S:Se ratios in some geochemically important materials analyzed by Goldschmidt and others (1954, pp. 532-539) are listed in Table 1.

TABLE 1

S:Se RATIOS IN SOME GEOCHEMICAL MATERIALS

Material	S:Se
Igneous rocks	6,000:1
Magmatic sulfides	10,000:1
Argillaceous sediments	4,000:1
Oxidates	250:1 to 10,000:1
Sedimentary iron sulfides	100,000:1
Limestones	14,000:1
Evaporites	>500,000:1
Sea water	232,000:1
Nitrate sediments	8,000:1

The table shows that in sea water selenium, compared with sulfur, is much less abundant than in igneous rocks. It is evident that selenium is removed from the sea to a very much greater extent than sulfur is. The S:Se ratio of the argillaceous sediments shows that the selenium is enriched. In the oxidate sediments the degree of enrichment is still higher. This is caused by the fact that freshly precipitated hydroxides of Fe^{3+} and Mn^{4+} are able to absorb selenium from aqueous solutions. The selenium thus is removed from sea water.

A part of the selenium is removed during the precipitation of the carbonate sediments, but the evaporites are nearly entirely free of selenium, although they contain much sulfur. This shows that sulfur and selenium become separated from each other during the exogenic cycle. The sulfur deposits formed in this cycle contain no selenium at all (Texas and Louisiana). Goldschmidt (1954, p. 535) suggests that the absence of selenium is due to the relatively low oxidation potential under which ordinary weathering takes place, and that while the potential was sufficient to transform sulfide to sulfate, it was not high enough to oxidize selenides to a higher state than selenites.

Deep-sea Cores

An extensive series of selenium determinations on recent sediments has been carried out by Byers and his colleagues. In a set of cores from the Atlantic the selenium content in the surface of the sediments was 0.2 to 0.6 ppm. The content of selenium increased with depth in the core, in one case rising to 2 ppm at 200 cm. when the sulfur content was highest (Williams and others, 1940, p. 54). In sediments from the Gulf of California, Lakin and Byers (1941, p. 9) found 0.1 to 5 ppm of selenium.

Shale and Carbonaceous Material

Shales usually contain more selenium than associated limestones and other sedimentary rocks (Beath and Gilbert, 1936, p. 484; Beath, 1943, p. 201; Byers, 1935, p. 7). Shales formed during the Cretaceous Period have been found to be the most highly seleniferous. Based on samples taken over a wide area in the western interior of the United States, the selenium content of a typical sample of Pierre Shale was found to average about 2 ppm (Rader and Grimaldi, 1961, p. A-26; Tourtelot, 1962, p. 68).

Selenium content of some European and Japanese shales range between 0.24 and 1.2 ppm (Goldschmidt, 1954, p. 535).

High concentrations of selenium occur in the carbonaceous laminae of some shales. These may represent the selenium compounds accumulated by plants that gave rise to the carbonaceous deposits (Rosenfeld and Beath, 1964, p. 29). Lignitic material, however, has been found to be less seleniferous than associated carbonaceous shale or carbon laminae (Rosenfeld and Beath, 1964, p. 29). Beath (1943, p. 702) mentioned a carbonaceous vanadium-uranium ore sample which contained 2,630 ppm selenium.

Limestone, Sandstone, and Bentonite

The selenium content of limestones collected by Beath from various formations in the western United States ranged from <0.1 to 14 ppm. Sandstones carried selenium in highly varying amounts ranging up to 112 ppm. Highest concentrations occurred in ferruginous sandstones and sandstones that were in contact with carbonaceous shale (Rosenfeld and Beath, 1964, pp. 31-32).

Bentonite beds occurring in shales are commonly non-seleniferous unless they contain ferric oxide, which readily absorbs selenium (Goldschmidt, 1954, p. 536). Byers (1935, p. 8 and 1936, p. 6) found bentonite in the Pierre Shale of Nebraska to contain 9 to 76 ppm selenium. He did not indicate the degree of purity of this bentonite.

Selenium in Soils

Selenium in soils may be present as selenates, elemental selenium, pyritic selenium, ferric selenites, and organic selenium compounds of unknown composition (Rosenfeld and Beath, 1964, p. 41). The largest part of the selenium content of soils is probably in the form of the basic iron selenite, $Fe_2(OH)_4SeO_3$, with the ratio of Se:Fe being variable, suggesting an absorption reaction of the compound (Goldschmidt, 1954, pp. 537-538).

Only a small part of the selenium in soils is water soluble. In an examination of a large number of samples, Byers (1936, p. 71) found that only a small proportion contained more than 1 ppm water soluble selenium. It was shown that most of this soluble selenium consisted of selenate. The low oxidation potential under which ordinary weathering takes place is usually not high enough to oxidize selenides to a higher state than selenites (Goldschmidt, 1954, p. 535).

Selenium in Plants

Certain plants, which are limited to seleniferous soils, are capable of accumulating large amounts of selenium. These plants, called "selenium indicators" by Beath, commonly contain 1,000 to 3,000 ppm selenium. A few plants may carry as high as 1 percent or more of selenium. These high selenium contents impart an offensive odor to the plants and make them highly toxic to animals. In one instance in Wyoming, 340 mature sheep died within 24 hours after consuming Astragalus bisulcatus Hook. (Rosenfeld and Beath, 1964, p. 143).

The amount of selenium in soil required to produce poisonous effects is small. Williams and others (1940, p. 30) collected a sample of Astragalus pectinatus Hook. which had a selenium content of 5,170 ppm. The soil on which this plant was growing contained only 0.5 ppm of selenium.

There are many other plants which are capable of absorbing considerable quantities of selenium, but which are not restricted to seleniferous soils (Rosenfeld and Beath, 1964, p. 81). Even grains and grasses may accumulate selenium in amounts high enough to be fatal to animals feeding on them. A build-up of seleniferous plant decay contributes considerable amounts of soluble organic and inorganic selenium compounds to the soil (Rosenfeld and Beath, 1964, p. 41). However, in areas of high or moderate rainfall, part of these soluble selenium compounds may be removed from the soil by leaching (Byers, 1936, pp. 17-18).

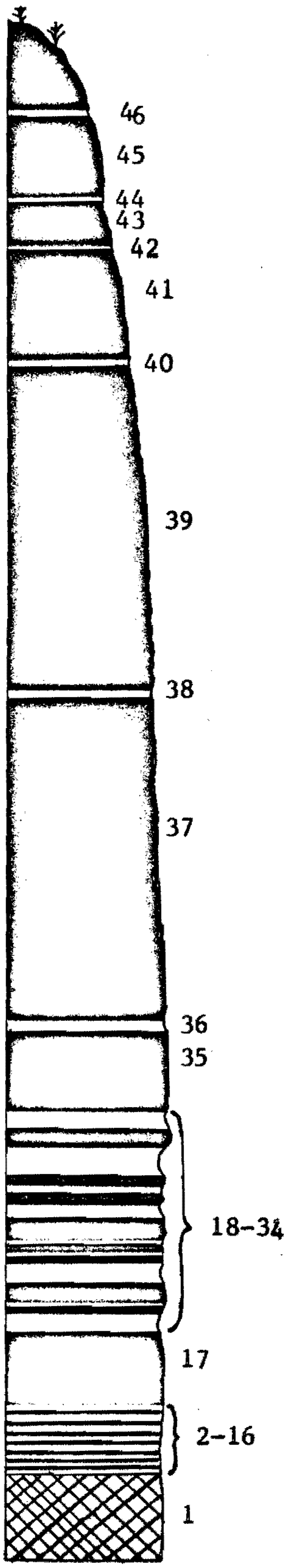
DESCRIPTIONS OF SAMPLE LOCATIONS AND SELENIUM CONTENT OF BEDS

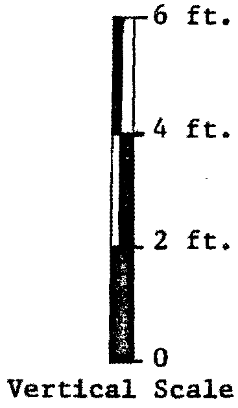
Location A

A large fresh roadcut on the side of a very steep slope at the site has exposed over 35 feet of the lower Pierre and parts of about 30 feet of the upper Niobrara Formations. At least 24 separate beds of bentonite are exposed in the lower part of the Pierre Formation here (Figs. 2 and 3). This section is located on the west side of the road in the SE ¼ NE ¼ sec. 13, T. 163 N., R. 58 W., Cavalier County, eight miles west-northwest of Walhalla, North Dakota.

Pierre Formation (lower part)

Beds from a 38-foot section (Fig. 4) were measured and sampled beginning with the limonitic layer at the base, which marks the boundary between the Pierre Shale and Niobrara marlstone. Forty-eight samples were taken from this section and analyzed for selenium content (Table 2). Selenium content of the bentonite beds averages considerably lower than that of the shale. Selenium content of the shale beds varies considerably, with the lighter-colored brown beds averaging higher than the darker, more organic-rich beds. It was found that a small difference in color made a great difference in selenium content.





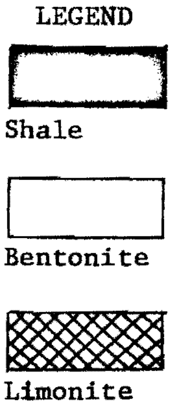


Fig. 4--Stratigraphic section of bentonitic zone at base of Pierre Shale Formation, location A. Numbers identify beds. The base of the limonitic bed marks the Pierre-Niobrara contact. Parts of this section appear in Figs. 2 and 3.

TABLE 2

SELENIUM CONTENT OF BEDS IN THE LOWER PART OF THE PIERRE SHALE FORMATION AT LOCATION A (FIG. 3)

Bed No.	Description of Sample	Thickness in Inches	Selenium in ppm
	Oak leaves from small oak growing on soil formed from beds 18 to 28		none
	Humus, sample taken from under above-mentioned oak		3
	Dark shale, sample taken 15 ft. above bed 40		1
	Dark shale, sample taken 6 ft. above bed 40		8
41	Dark shale, sample taken 1 ft. above bed 40		6
40	Bentonite, gray with much brown iron oxide	2	
	Yellow jarosite in shale just below bed 40	2	3
39	Shale, sample taken 3 ft. below bed 40, dark brown	72	28
38	Bentonite, very light tan, no yellow	2	2
37	Shale, sample taken from center of bed, dark brown	72	20
	Sample taken 1 ft. above bed 36		17
	Sample taken immediately above bed 36		22
36	Bentonite, cream-colored	3	2
35	Shale, dark, slightly brownish	18	23
34	Bentonite, cream-colored	4	2
33	Shale, very dark brownish-black	3	2
32	Bentonite, cream-colored	7	1.5
31	Shale, very dark brownish-black	2	4
30	Bentonite, cream-colored	3	1.5
29	Shale, very dark brownish-black	2	6
28	Bentonite, cream-colored	4	1.5
27	Shale, dark, slightly brownish	5	23
26	Bentonite, cream-colored	2	2
25	Shale, dark brownish-black	1.5	21
	Jarosite, yellow		3
24	Bentonite, cream-colored	1	2
23	Shale, dark brownish-black	1.5	24
22	Bentonite, cream-colored	5	1
21	Shale, very dark brownish-black	4	4
20	Bentonite, cream-colored	1	1
19	Shale, dark brownish-black	1	16
18	Bentonite, very light gray	5	2
17	Shale, medium dark brown	16	29
16	Bentonite, very light brown	1	12
15	Shale, medium dark brownish-black	1	19
14	Bentonite, light brown, very little yellow	1	5

TABLE 2--Continued

Bed No.	Description of Sample	Thickness in Inches	Selenium in ppm
13	Shale, medium dark brownish-black	1	20
12	Bentonite, light brown, very little yellow	1	3
11	Shale, medium dark brownish-black	1	5
10	Bentonite, light brown, very little yellow	1	2
9	Shale, medium dark brownish-black	1	14
8	Bentonite, very light gray, very little yellow	1	2
7	Shale, medium dark brownish-black	1	8
6	Bentonite, very light gray, very little yellow	1	4
5	Shale, medium dark brownish-black	1	12
4	Bentonite, very light gray, very little yellow	1	4
3	Shale, medium dark brownish-black	1	8
2	Bentonite, creamy-tan	1	11
1	Limonite and gypsum, dark brown, hard	20	14

Two samples of jarosite taken from this section contained small amounts of selenium. The jarosite occurs in seams along bedding, joint, and fracture surfaces in the shale and is more abundant in the upper part of this section (Fig. 5).

Niobrara Formation (upper part)

A 26-foot section of Niobrara just below the Pierre Formation was sampled at various intervals (Table 3). This is a light gray, brittle, massive cliff-forming marlstone, which was once used as a raw material for the manufacture of cement in this area (Carlson, 1964, p. 1). Of particular interest in the analysis of this section is the high selenium content of the marlstone immediately beneath the 6-inch bentonite bed.

Fig. 5.--Jarosite in Pierre Shale just below Bed 40 at location A. The selenium content of all jarosite samples taken averaged much lower than the selenium content of adjacent shale.

Fig. 6.--Bentonite beds in the upper Niobrara Formation at location B. Beds 1-8 are exposed here. Note dark bed just above hammer. This dark shale had a selenium content more than 4 times that of the light-colored marlstone just above it.

TABLE 3

SELENIUM CONTENT OF BEDS IN THE UPPER PART OF THE NIOBRARA FORMATION AT LOCATION A

Bed No.	Description of Sample	Selenium in ppm
	Limonite concretion 1 foot below limonite layer at junction of Pierre and Niobrara Formations	28
	Marlstone, 16 feet below limonite layer	8
	Marlstone, 22 feet below limonite layer, and 2 feet above 6-inch bentonite bed	6
16	Bentonite, light gray, 6 inches thick	2
	Marlstone, just below bentonite bed	28
	Marlstone, 2 feet below bentonite bed	6

Location B

This is a section of upper Niobrara exposed in an old roadcut on the northeast side of the road in the SE ¼ sec. 18, T. 163 N., R. 57 W., Cavalier County, seven miles west-northwest of Walhalla, North Dakota (Figs. 6 and 7). This section is about one mile southeast of location A. Bentonite bed 16, which is described here, is in the same stratigraphic position in the section as the 6-inch bentonite bed described at location A. It lies 24 feet below the base of the Pierre Formation. This was determined by hand-leveling down from the bentonite beds of the lower Pierre, which crop out across the road a short distance away.

A 10-foot section of this Niobrara outcrop was measured and sampled. Samples were taken from the weathered surface of the nearly vertical exposure. A 4-inch layer of soil, which overlies bentonite bed 16, was also sampled along with plant material growing in this soil.

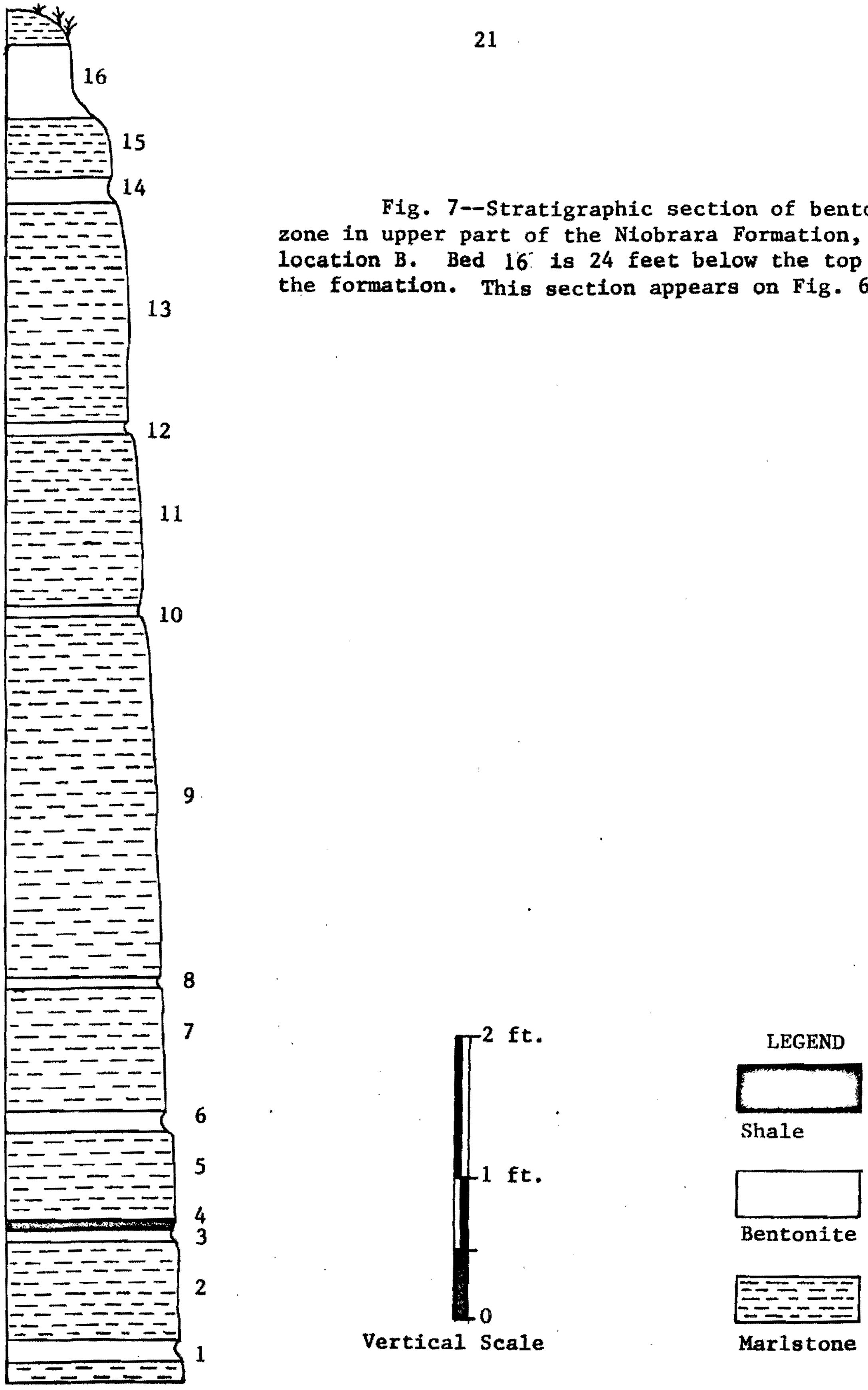


Fig. 7--Stratigraphic section of bentonitic zone in upper part of the Niobrara Formation, location B. Bed 16 is 24 feet below the top of the formation. This section appears on Fig. 6.

The bentonite beds in this section have a higher average selenium content than that of the marlstone. They also contain a high percentage of dark brown iron oxide, which is capable of absorbing selenium. Of special interest in this section is the high selenium content of the dark shale in bed 4 compared to the selenium content of the marlstone just above it. This shale bed is not calcareous.

A higher ferric iron content of this dark bed compared to the marlstone above it may account for its higher selenium content. Another reason may be a high selenium content of the Cretaceous plant materials in the bed. There has been some evidence obtained in the past which suggests that selenium-absorbing plants existed during Cretaceous time (Beath and Gilbert, 1936, pp. 484-485).

TABLE 4

SELENIUM CONTENT OF BEDS IN THE UPPER PART OF NIOBRARA FORMATION AT LOCATION B

Bed No.	Description of Sample	Thickness in Inches	Selenium in ppm
	Aster-like plant growing in top soil.		None
	Soil at surface, 4 inches from top of bentonite bed 16. Gray, calcareous		10
	Soil 2 inches below surface and 2 inches from bentonite bed 16		10
	Soil 4 inches below surface and immediately above bentonite bed 16		9
16	Bentonite, weathered, light gray with much dark brown iron oxide	6	8
15	Marlstone, calcareous, light gray	5	14
14	Bentonite, light gray with some yellow and dark brown	2	11
13	Marlstone, similar to unit 15	18	7
12	Bentonite, light gray and red brown	1	8
11	Marlstone, similar to unit 15	14	4
10	Bentonite, similar to unit 12	1	12

TABLE 4--Continued

Bed No.	Description of Sample	Thickness in Inches	Selenium in ppm
9	Marlstone, similar to unit 15	30	7
8	Bentonite, similar to unit 12	1	13
7	Marlstone, similar to unit 15	10	9
6	Bentonite, similar to unit 12	2	12
5	Marlstone, similar to unit 15	8	3
4	Shale, brownish-black, non-calcareous	1	13
3	Bentonite, similar to unit 12	1	10
2	Marlstone, similar to unit 15	8	8
1	Bentonite, similar to unit 12	2	11

Location C

This section of lower Pierre was measured and sampled in an old roadcut on the southwest side of the road in SE ¼ sec. 18, T. 163 N., R. 57 W., Cavalier County, seven miles west-northwest of Walhalla, North Dakota. It is located a few hundred feet southeast of location B and about one mile southeast of location A. The outcrop here is covered with much talus shale, and the bentonite beds are not visible until exposed by digging through the talus. Samples taken from this location were very dry, brittle, weathered, and faded compared to samples taken from identical beds at site A. Numbers of the beds here correspond to the same beds at location A.

Table 5 shows that the selenium content of the shale at this exposure averages considerably less than that from the shale at location A. However, the selenium content of the bentonite beds is slightly higher than at location A with the highest readings coming from the yellowest beds. Bed 38 attracted special attention because, unlike the other bentonite beds, it was not gray or white, but a rich, dark yellow throughout.

TABLE 5

SELENIUM CONTENT OF BEDS IN THE LOWER PART OF THE PIERRE SHALE AT LOCATION C

Bed No.	Description of Sample	Thickness in Inches	Selenium in ppm
	Humus taken one foot above bed 38 and one inch below the surface.	4	2
	Twigs from small birch tree rooted into bed 22		None
38	Bentonite, uniformly very dark yellow	1	28
37	Shale	72	
36	Bentonite	2	
35	Shale	18	
34	Bentonite	5	
33	Shale	3	
32	Bentonite	7	
31	Shale, very dark, brownish-black	2	8
30	Bentonite, very light gray	3	1.5
29	Shale, very dark, brownish-black	2	9
28	Bentonite, very light gray	3	2
27	Shale, very dark brown	3	16
26	Bentonite, very light gray	1	2
25	Shale, very dark brown	1.5	12
24	Bentonite, very light gray. Some yellow	5	4
23	Shale, dark brown	1.5	10
22	Bentonite, very light gray	1	2
21	Shale, very dark brownish-black	4	6
20	Bentonite, very light gray. Some yellow	1	5
19	Shale, very dark brown	1	15

Location D

This section of lower Pierre was measured and sampled on a roadcut on the south side of the road in the center of sec. 30, T. 163 N., R. 57 W., Cavalier County, seven miles west of Walhalla, North

Dakota. This is about two miles south of location A. Numbers of the beds here correspond with the same beds at location A.

This outcrop has a more horizontal profile than the one at location A which is almost vertical. It also shows considerable erosional effects from small rills, which have cut many small channels normal to the bedding to give a striking black and white display of the shale and bentonite. The selenium content of the shale here (Table 6) averages lower than the same beds at location A.

TABLE 6

SELENIUM CONTENT OF BEDS IN THE LOWER PART OF THE PIERRE SHALE AT LOCATION D

Bed No.	Description of Sample	Thickness in Inches	Selenium in ppm
	Astragalus canadensis, over bed 37		None
37	Shale, grayish-brown	72	17
36	Bentonite, cream-colored	3	2
35	Shale, medium dark brownish-black. Color is between that of beds 37 and 33.	18	11
34	Bentonite, cream-colored	7	2
33	Shale, dark brownish-black	2	4
32	Bentonite, cream-colored	4	2
31	Shale, much darker than 37	3	3
30	Bentonite, cream-colored	3	1.5
29	Shale, dark brownish-black	2	6
28	Bentonite, cream-colored	2	1.5
27	Shale, medium dark brownish-black	2	7
	Jarosite, yellow		2
26	Bentonite, cream-colored	4	2

Selenium content varies with colors in the shale very markedly here, with the higher concentrations occurring in the lighter colored shale beds.

A sample of the plant Astragalus canadensis L. growing over bed 37 was analyzed, but contained no selenium. This result was as expected since this species is not a selenium accumulator (Rosenfeld and Beath, 1964, p. 85).

Location E

This is a small exposed section under an overhanging bank located in the second deep gully south of an abandoned old log cabin in NE ¼ sec. 25, T. 161 N., R. 57 W., Cavalier County, North Dakota. It is one mile west of the former town of Concrete and 15 miles south-southeast of location A. The numbers of the beds here correspond to the same beds at location A.

Thickness of individual beds here vary somewhat compared to the same beds at location A. This may be explained by a difference in the amount of sediments received at the time of formation or it may be the result of slumping, which would deform the beds. The exposure here is quite fresh, since any amount of surface weathering is rapidly eroded by stream action in this steep gully.

Table 7 shows that average selenium content of the shale here is slightly lower than at location A. Samples contaminated with jarosite show the lowest readings.

TABLE 7

SELENIUM CONTENT OF BEDS IN THE LOWER PART OF THE PIERRE SHALE AT LOCATION E

Bed No.	Description of Sample	Thickness in Inches	Selenium in ppm
32	Bentonite, cream-colored	2	2
31	Shale, dark, mixed with jarosite	2	4
	Jarosite, yellow		2
30	Bentonite, cream-colored	4	1
29	Shale, medium dark, mixed with jarosite	1	7
	Jarosite, yellow		3
28	Bentonite, cream-colored	2	2
27	Shale, medium dark, mixed with jarosite	1	5
26	Bentonite, cream-colored	2	2
25	Shale, dark, brownish-black	2	15
24	Bentonite, cream-colored	1	1
23	Shale, dark, brownish-black	3	12
22	Bentonite, cream-colored	4	1.5
21	Shale, dark, brownish-black	3	11
20	Bentonite, cream-colored	1	3
19	Shale, dark, brownish-black	1	14
18	Bentonite, cream-colored	5	2

THE ORIGIN OF SELENIUM IN THE PEMBINA HILLS

Selenium in Volcanic Gas

The bentonite in the Pembina Hills area is believed to be the altered product of volcanic ash which emanated from volcanoes in western Montana during late Cretaceous time (Gill and Cobban, 1965, p. A7).

Since the selenium content of the Pierre and Niobrara Formations is highest in the vicinity of the bentonite beds, it would seem logical to assume that the volcanic emanations were somehow responsible for the selenium being there. One might also suspect that the selenium was originally present in the volcanic ash in a soluble form and then migrated to the adjacent shale beds where it was precipitated. This does not seem to be the case.

Samples of volcanic ash and lavas from modern-day volcanoes have been found to be almost free of selenium (Byers and others, 1936, p. 822; Lakin and Byers, 1948, p. 21; Davidson and Powers, 1959, pp. 69-81). This is not surprising considering the high temperature of ejection and the relatively high solidifying temperature of the volcanic material.

In an investigation of the selenium content of Hawaiian soils, Byers and others (1938, pp. 51-55) found that selenium did not occur in sufficient quantities in parent materials to account for its presence in the soil. Selenium content of parent lava was less than 2 ppm whereas soil samples contained as high as 26 ppm.

Samples of sulfur taken from the rim of the Kilauea Crater on the Island of Hawaii had a selenium content of 0.14 and 0.22 percent (Byers and others, 1936, p. 822). A sample of volcanic gas taken from the same crater contained 0.005 milligrams of selenium in 600 cc of gas.

More recently, Murata (1966, p. C5) mentioned selenium concentrations in samples of gas and sulfur which he took from the Kilauea Crater in 1959. The elemental sulfur present as a sediment in a sample of steam condensate was found to contain 2.9 percent selenium, and another sulfur sample taken from the pumice cone contained 1.1 percent selenium.

Because of the presence of a relatively high percentage of selenium in the volcanic sulfur and volcanic gas, Byers and others (1936, p. 823) concluded that this gas was the major source of the selenium found in Hawaiian soils.

The Hawaiian Islands present wide variations in the amount of annual rainfall, and an attempt was made by Byers and others (1938, pp. 51-55) to correlate the selenium content of the soil with the amount of rainfall. One would ordinarily expect the selenium content of soils to be high in areas of low rainfall and low in areas of greater rainfall due to leaching. However, they found just the opposite to be true.

Soil samples taken from a hillside on the island of Maui clearly reveal this relationship. At 2,500 feet elevation, soil samples contained an average of about 11 ppm selenium. The annual rainfall at this elevation is over 100 inches. Samples taken at 450 feet elevation on the same hillside had an average selenium content of 1.4

ppm. At that elevation, the annual rainfall is only 20 inches. The soils which developed under the higher rainfall are more laterized than those developed under lower rainfall, therefore, it would appear that the soils obtained their selenium not from the parent lava but through rainfall since the lavas themselves contain little or no selenium (Byers and others, 1936, p. 822).

The question arises as to why selenium remains in these soils since it is known that heavy rainfall will leach elements from ordinary soil. The Hawaiian soils tested were very ferruginous. Any selenium which originated from volcanic emanations and which fell on such a soil would readily be absorbed by the ferric oxide in the soil and transformed from the soluble to the highly insoluble form of a basic ferric selenite. Therefore, loss of selenium by leaching would be at a minimum (Byers and others, 1938, p. 54).

Since volcanic activity was intense during late Cretaceous time, Byers and others (1936, p. 823) suggest that the shales formed during that period derived their selenium from dust and gaseous material of volcanic origin, which was carried down by rain into the Cretaceous seas. The abundance of selenium in the bentonitic zones of the upper Niobrara and lower Pierre Formations in northeastern North Dakota supports this hypothesis. The volcanic ash, which produced the bentonite was accompanied by the selenium-bearing dust and gaseous material.

Although it is known that some volcanoes are sources of selenium, one should not conclude that they all are. In the area around Mexico City where extensive volcanic activity has produced vast deposits of volcanic ash, no selenium has been found (Byers, 1937, pp. 1200-1202).

Variations in Selenium Content with Thickness of Beds as an Indication of Its Origin

Selenium content of a lithologic unit may vary with its thickness. A study of the Mobridge Member of the Pierre Formation in South Dakota by Moxon and others (1938, pp. 801-802) revealed a selenium content which ranged between 0 and 103 ppm. They found the concentration of selenium to be high where the Mobridge was thin, and low in localities where this member was much thicker. This suggests that the rate of deposition of the sediments containing the selenium may be an important factor in selenium distribution. Moxon offers no explanation for this uneven distribution of selenium.

Bentonite beds occur in the Mobridge Member (Searight, 1937, p. 46). Their presence suggests that the sediments, from which the shale was formed, were receiving selenium from volcanic emanations at the time of their deposition. The selenium coming in contact with the shale would be dispersed vertically to a greater degree in areas where shale beds were thicker. This would account for the lower concentrations of selenium in the thicker parts of the beds.

If the source of the selenium were in the sediments from which the shale was formed, one would not expect such variations to occur. But if the source were in the volcanic materials, with greater dispersal of the selenium in the thicker parts of the shale beds later on, then it is easy to see why such variations would exist.

THE SIGNIFICANCE OF SELENIUM IN NORTH DAKOTA

The Extent of the Seleniferous Zone

The line of contact between the Pierre Shale and Niobrara Formations runs almost due north-south across the eastern part of North Dakota and bentonite occurs all along this line. Although it is best exposed in the Pembina Hills, the bentonitic Pierre-Niobrara contact zone also crops out at a few other places along the line (Fig. 8).

All soils formed from Cretaceous rock in the bentonitic zone on both sides of the Pierre-Niobrara contact can be presumed to be seleniferous and capable of producing toxic vegetation. These soils present a potential danger of selenium poisoning to livestock and to humans who inhabit this area.

Selenium Poisoning in Animals

Selenium is among the few elements known to be absorbed by plants in sufficient amounts to create toxic hazards to animals. Most of the highly seleniferous indicator plants are unpalatable to livestock. Some of these plants possess an offensive, garlicky odor and are usually avoided by animals for that reason. The danger of selenium poisoning to livestock is greatest during dry seasons or in overly-grazed areas. Such conditions force the animals to feed on seleniferous plants which they would not ordinarily consume if enough other forage were available (Rosenfeld and Beath, 1964, p. 141).

In addition to weeds, selenium may also accumulate in crops in amounts hazardous to livestock. Corn, wheat, barley, oats, grasses, and hay containing 10 to 30 ppm selenium are known to cause chronic selenium poisoning (Rosenfeld and Beath, 1964, p. 155).

No treatment is known for counteracting the toxic effects of large amounts of selenium. Death usually occurs before the disease can be diagnosed. In one case 285 g. of the seleniferous weed, Astragalus bisulcatus was fed to a sheep. The animal died within 30 minutes (Rosenfeld and Beath, 1964, p. 143).

Selenium poisoning of livestock can best be prevented by denying them access to seleniferous plants. Deaths of any livestock in seleniferous areas should be investigated for the possibility of selenium poisoning. If it does occur, the distribution of selenium indicator plants and the selenium content of forage plants growing in the area should be checked. In many cases it may be possible to fence off affected areas. Over-grazing should always be avoided.

Selenium Poisoning in Humans

Selenium presents a public health hazard because of possible human injury caused by consumption of grains, vegetables, eggs, and dairy products from affected areas. Any food containing as much as 5 ppm of selenium is potentially dangerous. One-tenth this concentration is hazardous in milk or water (Rosenfeld and Beath, 1964, p. 279).

Samples of wheat and other grains taken from seleniferous areas in South Dakota had selenium contents as high as 30 ppm (Rosenfeld and

Beath, 1964, p. 105). Selenium in wheat and grain is of special interest because of their extensive use in bread and breakfast foods.

Maximum selenium content in ppm of some garden vegetables tested were: 20 in corn, 17 in onions, 11 in asparagus, 6 in rutabagas, and 4.5 in cabbage. Maximum readings in other foods were: 1.3 in milk, 9.1 in eggs, 8.0 in meat, and 1.0 in bread (Rosenfeld and Beath, 1964, p. 279).

Symptoms of diseases which are believed to be the direct result of abnormally high selenium content in the diet are: bad teeth, icteroid discoloration of the skin, dermatitis, arthritis, gastrointestinal disorders, and pathological nails (Rosenfeld and Beath, 1964, p. 283).

Although an excess of selenium in the diet produces toxic effects, a deficiency of this element will also do so. Trace amounts of selenium is necessary in diets to produce growth and prevent various diseases in both animals and humans (Rosenfeld and Beath, 1964, pp. 233-267).

Fig. 8.--A map marking an area of high selenium concentration in North Dakota.

The north-south line represents the contact of the Pierre Shale and Niobrara Formations of Cretaceous age. Much of this area is covered by glacial till. The black dots represent locations where the Pierre-Niobrara contact is exposed. The shaded area represents the zone of possible high selenium content in the Pierre and Niobrara. All soils formed from Cretaceous rocks in this zone can be presumed to be seleniferous.

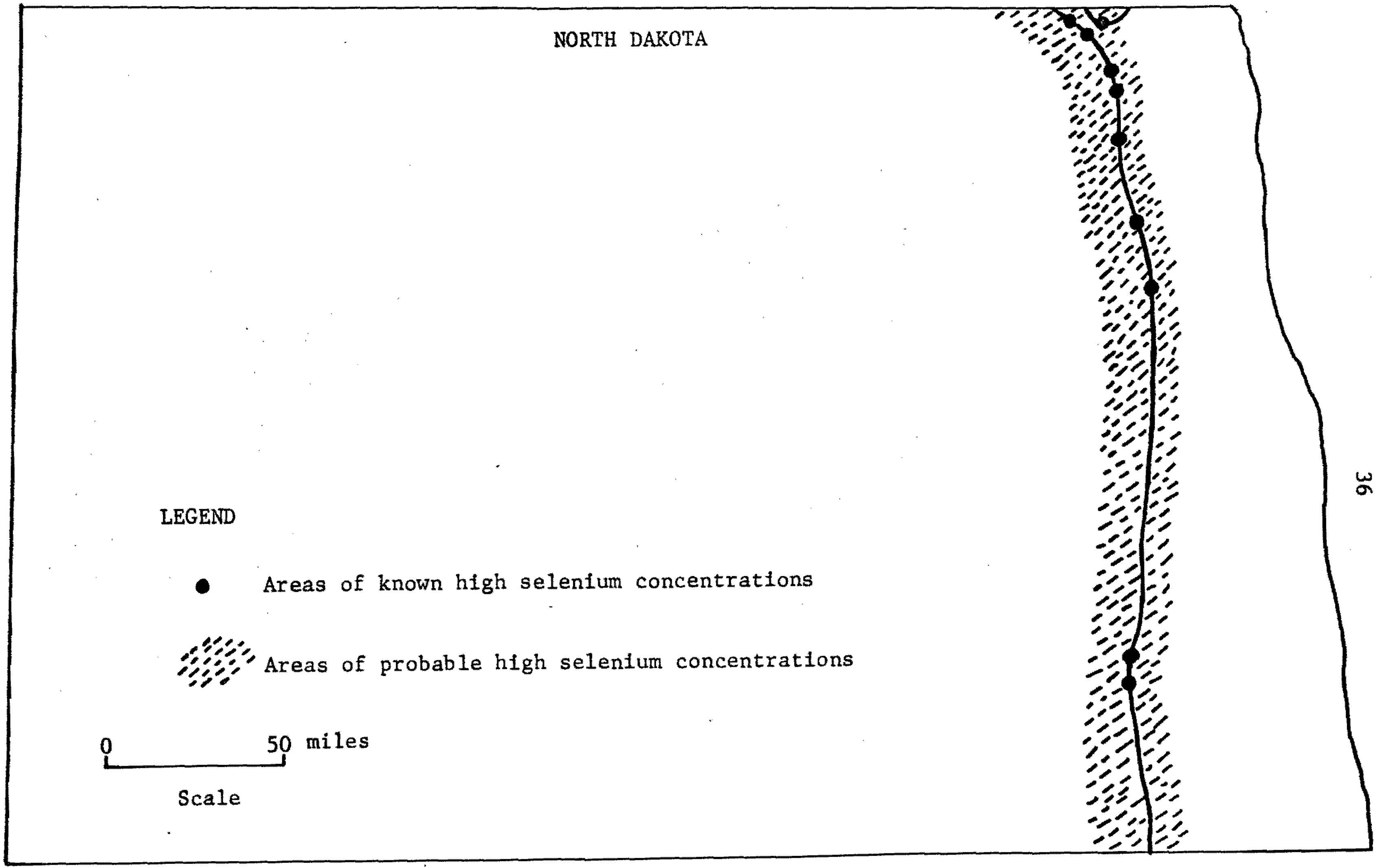


Fig. 8--A map marking an area of high selenium concentration in North Dakota.

CONCLUSIONS

1. High concentrations of selenium exist in the bentonitic zones of the lower Pierre and upper Niobrara Formations.

2. In general, selenium content of the shale beds is higher than that of adjacent bentonite beds. Highest concentrations of selenium in the bentonite occur in beds which contain yellow or red-brown impurities. The very light-colored uncontaminated beds are the least seleniferous.

3. The lighter colored, or browner shale has a higher selenium content than the black, organic-rich shale with a small difference in color making a big difference in the amount of selenium present. The lighter color may be caused by a lower content of carbonaceous material than that of the darker shale. It could also mean that the lighter shale was formed in a more oxidizing environment than the darker shale. This would increase ferric iron content, which would, in turn, facillitate selenium absorption and account for the higher selenium content.

4. Concentration of selenium in dark shale beds or laminae is greater than that of adjacent marlstone.

5. Selenium content of jarosite is much lower than that of adjacent shale and about equal to that of the average bentonite.

6. Selenium content of a bed in a formation will vary in different parts of the same bed.

7. All soils formed from Cretaceous rock in the bentonitic zone above and below the Pierre-Niobrara contact can be presumed to be seleniferous and capable of producing toxic vegetation. These soils present a potential danger of selenium poisoning to livestock and to humans who inhabit the area.

APPENDIX

APPENDIX A

Laboratory Procedure Used for the Determination of Selenium

The general method followed in the quantitative analysis of selenium is taken primarily from that outlined by Rader and Grimaldi (1961). It was still used by personnel working in U. S. G. S. analytical laboratories at the time of this writing (Riley, written communications, December, 1970). This general procedure was supplemented by information from Robinson and others (1934, p. 274) and Rosenfeld and Beath (1964, p. 312).

Principles

The selenium is distilled as the tetrabromide from a sulfuric acid solution of the sample that has been freed of organic matter by oxidation with nitric acid in the presence of mercury as a catalyst. The selenium must be in, or converted into, the hexavalent condition before distillation in order to insure its distillation with the acid. This is done by the use of bromine. The excess bromine distills at a low temperature and the hydrobromic acid then reduces the selenium to the quadrivalent state in which it distills along with the hydrobromic acid.

Only germanium and arsenic accompany the selenium under the conditions outlined for distillation. These elements do not interfere when selenium in the distillate is precipitated in the elemental form with sulfur dioxide from strong acid solutions. The reduced selenium from the distillate is redissolved and reprecipitated in order to purify and concentrate it in a total volume of 2 ml of solution. The intensity of the color imparted to the solution by the suspension of elemental selenium is compared visually against known standards treated in the same manner.

Apparatus and Reagents

1. Pyrex glass still, standard taper joints, 250-ml capacity, supplied with a condenser.
2. Color comparison light source: An oblong box, 9 cm wide by 19 cm long by 9 cm deep, with a slit for light passage, 0.1 by 10 cm, positioned in the top face of the box directly over a 25 watt tungsten filament tubular lamp.
3. Vacuum pump with hose connected to side of 125 ml vacuum flask fitted with a rubber stopper through which the stem of a small funnel is inserted from above.
4. Splintered glass-bottom crucible with rubber gasket positioned over funnel.
5. Tall-form, flat-bottom glass vials with plastic screw crown: Capacity of 10 ml is preferable, but other tubes can be used.
6. A wire or metal rack designed to hold a series of vials partly immersed in a shallow pan containing water.
7. Sulfur dioxide: Compressed gas in cylinder with bleeder valve.

8. Sulfuric, nitric, red-fuming nitric, and 48% hydrobromic acids, all reagent grade.
9. Catalyst-acid: Five percent W/V mercuric oxide in concentrated nitric acid.
10. Bromine-hydrobromic acid mixture: Add 2 ml of bromine to 100 ml of 9 N hydrobromic acid.
11. Hydroxylamine hydrochloride, small crystals.
12. Standard selenium stock solution, 1 ml = 1 mg Se: Weigh 0.2811 g of selenium dioxide, transfer to a 200 ml volumetric flask with about 50 ml water, add 25 ml 2% bromine-hydrobromic acid solution, and dissolve the compound without heating. Dilute to volume with water. Alternatively, dissolve 0.2000 g selenium metal in 25 ml bromine-hydrobomic acid solution, dilute to 200 ml with water, and standardize the solution gravimetrically.

Procedure

1. The sample should be air-dried and ground fine enough to pass through a 100-mesh sieve. Weigh 2.0 g sample and transfer to a 125 ml Erlenmeyer flask.
2. Add 5 ml nitric acid containing 5% mercuric oxide; cover the flask and keep it cool until any vigorous reaction subsides.
3. Add 5 ml nitric acid and 10 ml sulfuric acid, cover, and carefully digest on the hot plate until there is no danger of frothing over. Frothing will occur for samples high in organic matter.
4. Add increments of red-fuming nitric acid, 1 ml at a time, until all organic matter is destroyed. The solution must be cooled each

time before adding the acid to avoid sudden violent fuming. The number of times this must be done will depend on (a) the percentage of organic matter in the sample, (b) the size of the particles in contact with the acid, and (c) the amount of time that the particles are in contact with the hot acid. Temperature must be controlled very carefully, since excess heat will only fume off the nitric acid more rapidly, which will decrease the time the acid has to react with the organic matter. This in turn will necessitate cooling, adding of more acid, and re-heating. Some samples will require this cycle to be repeated 5 or 6 times before all organic matter is destroyed. This is a very time-consuming procedure and may require several hours to complete. The solutions should be raised to the incipient fuming point of sulfuric acid after each fuming of nitric acid. All organic matter must be fully digested to insure complete recovery of the selenium from the material tested. When this occurs, the digest will change from black to a pale yellow. It is necessary to oxidize the organic material sufficiently and to expel the excess HNO_3, otherwise the Br_2, subsequently added, will be reduced. When all excess HNO_3 is driven off, there will be a change from brown fumes to white fumes. It is very important to generate thick white fumes for a few minutes, but prolonged fuming of the SO_3 should be avoided, because it will cause a loss of Se.

5. Cool the solution and transfer the sludge to the distilling flask. Rinse the flask with exactly 5 ml of water, adding the rinses

to the still. This addition of water is necessary to prevent decomposition of hydrobromic acid by the sulfuric acid. Rinse the flask three times with 5 ml bromine-hydrobromic acid solution (total 15 ml) and pour the solution into the distilling flask.

6. Connect the flask to the condenser and check all connections to be sure they are tight. Place a receiver tube containing 2 to 3 ml water under the condenser with the tip of the condenser submerged and the tube supported in a beaker of ice water.
7. Start the distillation slowly with a small flame. Heat the flask at a point above the sulfate sludge in order to minimize bumping. The flame must be moved as the distillation proceeds, so that solution is over the flame at all times, otherwise the flask may break. One or two grams of bromine should distill over in the beginning indicating an excess of the reagent. If insufficient bromine has been added to produce this quantity, the distillation is stopped and cooled and more $HBr-Br_2$ is added. A somewhat greater excess of bromine does no harm, but too great an excess should be avoided because of the formation of too much sulfuric acid later. Distill over and collect about 18 to 20 ml of distillate. Stop the distillation when incipient fuming of sulfuric acid appears in the flask, indicating that all hydrobromic acid and water have distilled over. Make a second or even a third distillation with intervening additions of hydrobromic acid and bromine to make certain all selenium is removed from the sludge.

8. Disconnect the distilling flask and rinse the condenser into the receiver tube with 2 to 3 ml of water. Arrange the tubes containing the distillates in a rack immersed in ice water. Pass a slow stream of sulfur dioxide to each solution from a delivery tube into the solution because of possible loss of selenium by sweeping out as the tetrabromide. Stir the distillates and continue gassing until the bromine is reduced to a colorless solution.

9. Add about 10 mg of hydroxylamine hydrochloride to each solution, stopper the tubes, and warm on the steam bath for 20 minutes at 80°C. An estimate of the selenium content can be made at this time as a guide for the selection of the concentration range for the standards (step 11). Allow the solution to stand overnight at room temperature. This is especially necessary if little or no selenium can be seen in the solutions. If the selenium precipitate stands too long, it may partially redissolve.

10. Filter the solution with suction through the splintered glass filter and wash with water. Reject the filtrate if clear, otherwise refilter through the same filter.

11. The precipitate is redissolved by passing 1 ml bromine-hydrobromic acid solution through the filter. The solution is collected in a flat-bottomed vial placed inside the filtrator flask at the end of the funnel. The filter is washed with 1 ml of water to make the total volume 2 ml of solution. At this time, prepare a series of graded standards containing as much as 15 ppm of

selenium, each in a total volume of 2 ml of solution at the same acidity as the samples.

12. Gas the sample and standard solutions, as before, with sulfur dioxide and add 1 to 2 crystals of hydroxylamine hydrochloride to each. Stopper and warm the vials for 20 minutes at 80°C. Compare the color intensity of the sample against the standards by arranging the vials on the slit of light on top of the comparator box.
13. Calculate the percentage of selenium in the sample. It is difficult to match solutions containing more than 15 ppm of selenium. Treat samples containing more than 15 ppm of selenium as in steps 11 through 13, except that the selenium on the filter is dissolved and made to 10 or 25-ml volume with bromine-hydrobromic acid solution, the final volume depending on the selenium content.

Precision of Selenium Determinations

To determine the accuracy of this method of selenium analysis, checks were run on six samples which had high selenium concentrations. One of these six samples was analyzed three different times. Results of the checks revealed an accuracy of ± 10 percent.

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