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Department of
Experiment Station Chemistry

AGRICULTURAL EXPERIMENT STATION
South Dakota State College of Agriculture and Mechanic Arts
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Selenium in Rocks, Soils and Plants

By Alvin L. Moxon, Oscar E. Olson
and Walter V. Searight[1]

Introduction

The element selenium was discovered in 1817 by John Jacob Berzelius and Gotlieb Gahn at Gripsholm, Sweden. They were examining a sulfuric acid plant and found the element in some of the sediments. Of the known elements selenium ranks about fiftieth in order of abundance which makes it about as rare as silver.

Selenium belongs to the oxygen-sulfur family and in many of its properties it resembles sulfur. It occurs in many parts of the world, especially in association with sulfur deposits and in combination with elements such as iron, lead, and copper.

Selenium has been used for many years in the glass, rubber, and electrical industries but otherwise it has been of little commercial importance.

Little interest was shown in the physiological and toxicological properties[2] of selenium until the discovery that the natural occurrence of selenium in soils, its absorption by vegetation, and the ingestion of the vegetation by livestock is the cause of the so-called "Alkali Disease" (1).[3] Since that discovery considerable interest has been aroused and many articles concerning the toxicity of various selenium compounds have appeared.

The selenium which is found in the soils of the Great Plains has been derived from geological formations, especially those formations deposited during Cretaceous time. The sedimentary rocks which make up the Cretaceous formations are the most important selenium bearers. They were deposited in a shallow sea which covered the Great Plains area during the Mesozoic era. This shallow sea probably occupied an area from the Gulf of Mexico on the south to the Mackenzie river on the north and from somewhere in Minnesota and Iowa on the east to Utah and Idaho on the west.

The selenium which was laid down in these sedimentary formations has been carried through the soil-forming processes and is found in the soils of certain areas. Plants growing on these soils absorb the selenium which further finds its way into the tissues of animals that happen to feed upon the plants. The element has also been traced through the animals into the animal products such as milk and eggs.

The geological distribution of selenium received attention early in the investigations on the selenium problem. In 1934 Beath, and co-workers (2) reported the association of selenium-bearing plants with certain geological formations. In the same year Franke et al. (3) reported that the "Alkali Disease" of livestock in South Dakota was associated with soils derived from Pierre shale. Byers (4, 5, 6)

1. Assistant Professor of Geology, University of South Dakota. Employed by the Experiment Station during the summer of 1938 to assist with the geological part of this study.
2. Early in the twentieth century some interest was shown in the pharmacological action of selenium as a possible cure for cancer.
3. Numbers in parentheses indicate articles referred to in Bibliography on pages 92 to 94.

has investigated many geological materials for their selenium content and (5) has also reported on the selenium content of unnamed divisions of the Pierre formation.

The division of the Pierre based on lithology and microfauna (7) has afforded the possibility of determining the stratigraphic distribution of selenium in this formation and its members. Preliminary work in this laboratory (8) indicated that the selenium was more or less concentrated at two distinct stratigraphic positions in the Pierre formation. This information made the surface mapping of the outcrops of these seleniferous strata of great importance in delimiting toxic areas.

The outline of the selenium project approved by the office of Experiment Stations in 1937 provided for a study of the relation of geology to the selenium problem and in the summer of 1938 the main part of the work reported herein was accomplished. Since only six weeks time was available for the field work it was, of necessity, more or less general in character. The results, however, are quite conclusive and point the way for more detailed work in the most toxic areas. Farmers and ranchers could derive much benefit from detailed mapping and analyses of formation outcrops in the most toxic areas as will be discussed in a later section of this bulletin.

Composite samples of geological sections were taken in all cases, unless otherwise stated. The samples were ground and passed through a 0.5 mm. sieve. The method of collection of plant samples and their preparation for analysis used in this study are described by Moxon et al. (8). All samples were analyzed by the digestion-distillation method (1).

Rocks of South Dakota, With Particular Reference to Those Involved in the Selenium Problem

Rocks consist of all natural materials which are aggregates of minerals or of mineral matter. Thus defined, they include substance not considered to be rock by the layman. They may be loose materials such as clay, sand or gravel and, of course, include solid masses such as granite or limestone. Even soil is essentially rock modified by weathering and organic agencies.

Rocks are commonly classified according to the dominant geological processes to which they owe their origin. Those resulting from the solidification of lava, liquid rock, are known as igneous rocks. Rocks which are the result of disruption, transportation, and deposition of other rocks are sedimentary rocks. All those rocks which have been modified by great pressure and by heat, whatever their previous history, are metamorphic rocks. The rocks of South Dakota belong in all three of these general types.

Whatever the type of rocks and regardless of the process of formation, they are grouped in the order of their age into subdivisions, each formed in an era. A group includes all rocks which have originated in an era of geologic history. Those of South Dakota, from oldest to youngest are the Proterozoic, Paleozoic, Mesozoic, and Cenozoic groups. Each group is further divided into systems, and systems of rocks are further subdivided into lesser units. (Figures 1, 2).

System			Formation	Columnar Section	Selenium Content N	L	M	H	Thickness Feet	Character	Distribution
Cenozoic		Pleistocene			X					Glacial drift, ash, etc	Mostly east of Missouri
Cenozoic	Tertiary	Pliocene			X					Fine-grained sandstone	Southern, West River
Cenozoic	Tertiary	Miocene	Arikaree		X				650-1100	Light gray and white massive sandstone and clays	Pine Ridge, outliers on Slim Buttes and elsewhere
Cenozoic	Tertiary	Oligo-cene	Brule			X			350-650	Light colored clays, sandstone and volcanic ash	Big Badlands, Slim Buttes, Short Pine Hills, other outliers.
Cenozoic	Tertiary	Oligo-cene	Chadron			X			0-180	Sandy clay, sandstone	Badlands, Slim Buttes
Cenozoic	Tertiary	Eocene	Fort Union			X			300	Sandstone, clay, shale, coal	N. Harding, Perkins & Corson Counties
Mesozoic	Cretaceous	Upper	Lance			X			700 ±	Clays, shales, sandstones, coal beds	Wide distribution in N. western counties.
Mesozoic	Cretaceous	Upper	Fox Hills			X			25-350	Sandstone & shale, local coals.	Mostly N. western counties, wide outcrop
Mesozoic	Cretaceous	Upper	Pierre		X	X	X	X	400-1800±	Shale, chalkyshale & chalk, concretions at several positions. Bentonite beds in basal part and at various other positions within formation.	About one third of western South Dakota, wide distribution east of Missouri River under cover of glacial drift and recent deposits
Mesozoic	Cretaceous	Upper	Niobrara			X	X	X	165-270	Chalk, chalky shale. Numerous bentonites.	Band around Black Hills, Missouri trough.
Mesozoic	Cretaceous	Upper	Carlile			X			200-750	Shale, in part chalky, sandstones in upper and lower parts, bentonites.	Band around Black Hills, fraction to five miles wide, very restricted S. East
Mesozoic	Cretaceous	Upper	Greenhorn			X			20-350±	Limestone, chalk, dark shale, bentonite.	Hog back outside 'Dakota' hog back restricted S.E.
Mesozoic	Cretaceous	Upper	Graneros		X	X			80-800	Dark shale, siliceous shale (Mowry) in lower part, bentonite.	Band one to five miles wide around Black Hills, restricted S.E.
Mesozoic	Cretaceous	Upper	Dakota			X			25-200	Sandstone, white, buff, gray, some clay locally.	Outer hog back, Black Hills.
Mesozoic	Cretaceous	Lower	Fuson			X			25-188	Variecolored clays and shales, thin sandstones.	Restricted, outer hog back, Black Hills.
Mesozoic	Cretaceous	Lower	Minnewaste		X				0-25	Thin gray limestone	Local, S Black Hills
Mesozoic	Cretaceous	Lower	Lakota		X				70-485	Sandstone, some thin shale beds	Crest of outer hog-back, Black Hills
Mesozoic	Jurassic		Morrison			X			0-220	Clay, shale, sandstone	Within outer hogback, Black Hills
Mesozoic	Jurassic		Unkpapa		X				0-225	White & variegated 'calico' sandstone	Inner face of outer hogback, Black Hills
Mesozoic	Jurassic		Sundance		X				70-300	Sandstone, limestone & shale of various colors	Inner face of outer hogback, Black Hills
Mesozoic	Triassic		Spearfish			X			500-700	Brick red shale, sandy shale, sandstone, gypsum	Red Valley surrounding Black Hills
Paleozoic	Permian		Minnekahta		X				30-50	Pink to purplish gray limestone.	Inner hogback, Black Hills.
Paleozoic	Permian		Opeche			X			75-115	Maroon, brick red, sandy shale, shaly sandstone	Very restricted, Black Hills.
Paleozoic	Pennsyl-vanian		Minnelusa		X				400-600	Yellow, red, gray, shale sandstone, limestone, gypsum.	Restricted to the Black Hills
Paleozoic	Mississip-pian		Pahasapa		X				300-650	White & light gray, cavernous limestone.	Restricted to the Black Hills
Paleozoic	Mississip-pian		Englewood		X				30-60	Gray, pink, purple limestone.	Black Hills, very restricted.
Paleozoic	Ordovician		Whitewood			X			0-80	Buff & pink limestone.	N. Black Hills
Paleozoic	Cambrian		Deadwood		X				50-500	Sandstone, shale, conglomerate	Black Hills
Pre-Cambrian										Quartzite, diabase, slate, granite, E. S. Dak schists, slates, quartzite, granite, pegmatite, in Black Hills.	Core of Black Hills, quartzite, Sioux Falls to Mitchell granite northeast.

FIG. 1. Columnar section showing geological formations of South Dakota
Selenium Content Column
N = No selenium
L = Low selenium content
M = Medium selenium content
H = High selenium content

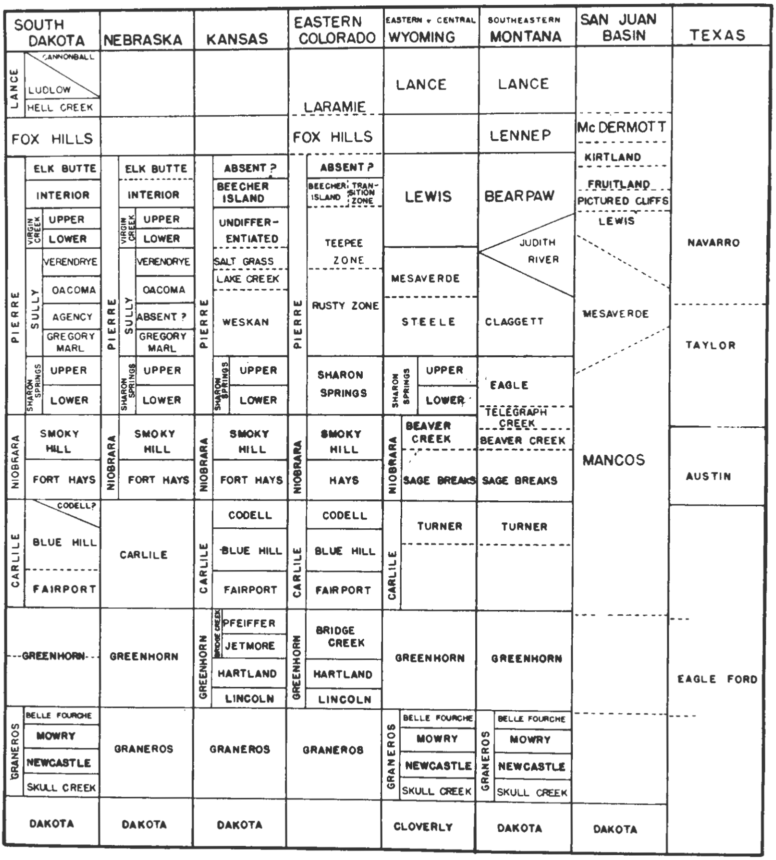

FIG. 2. Correlation chart of Upper Cretaceous formations of parts of the Great Plains area, showing probable equivalence of formations.

PRE-CAMBRIAN

The most ancient rocks of South Dakota are pre-Cambrian which are included with the Proterozoic group of rocks. They occur in the core of the Black Hills in Lawrence, Pennington, and Custer counties. Proterozoic rocks occur at the surface in southeastern counties from Sioux Falls westward nearly to Mitchell in Moody, Minnehaha, Lincoln, McCook, and Hanson counties. Over most of this area, however, they are covered by a veneer of glacial deposits. Another small area of pre-Cambrian rock outcrops in Grant county in the northeastern part of the state.

In the Black Hills the pre-Cambrian rocks consist predominantly of schists, slates, quartzites, and marble, and other more or less highly metamorphosed sedimentary rocks. Granite, an intrusive igneous rock, is also included in the Proterozoic rocks of the Black Hills. Although numerous rocks of much geologic interest occur in the Black Hills they will not be discussed further here and the interested reader is referred to the geological literature for further information. Some of the most important references to this literature are cited in the bibliography (9, 10, 11).

The Sioux formation represents the Proterozoic in eastern South Dakota. The rock consists almost entirely of pink quartzite, a metamorphosed sandstone. Red to black spotted slates similar to the catlinite or pipestone of Minnesota occur also. One body of igneous rock, associated with the quartzite, the Corson diabase, occurs near Corson in Minnehaha county. The outcrop in Grant county consists of red granite continuous with and part of the igneous Ortonville, Minnesota intrusion. Although the Proterozoic rocks of South Dakota have not been adequately investigated to determine their selenium content, no cases of selenium poisoning are known to be associated with them and no plants of selenium selecting habit have been observed on these rocks or on soils derived from them. They are, therefore, not given further discussion here although their possible relation to the selenium problem cannot be entirely discounted until the original source of selenium in later rocks of South Dakota is definitely known.

PALEOZOIC

In South Dakota, as in adjoining states, the Paleozoic rocks overlie the pre Cambrian. At the surface, however, they appear only in the Black Hills, where they form successive bands surrounding the pre-Cambrian. The oldest lie near to the pre-Cambrian whereas the youngest lie farthest from it. East of the Black Hills, Paleozoics have been identified, deeply buried under later beds, nearly to the Missouri river, and at Elk Point in Union county. Over the area underlain by the Sioux quartzite they are known to be absent. Possibly they occur under thick cover in some of the northeastern counties since they have been identified in southeastern North Dakota.

The systems of Paleozoic rocks in North America from the base up are the Cambrian, Ordovician, Silurian, Devonian, Mississippian, Pennsylvanian and Permian. All of these except the Silurian and Devonian are represented in South Dakota. Reference to the columnar section (Figure 1) indicates that these rocks are all of sedimentary origin. The Deadwood of Cambrian age, Minnelusa of Pennsylvanian age, and Opeche of Permian age are mostly sandstones which differ in color and texture. The Whitewood of the Ordovician system, the Pahasapa of the Mississippian system, and the Minnekahta of the Permian system are limestones. The thicknesses of the formations and brief descriptions are included with the columnar section (Figure 1). Each of these formations has limited distribution at the surface. The selenium content of these beds has not been thoroughly investigated. No cases of selenium poisoning are known to have occurred from vegetation grown on Paleozoic rocks of South Dakota. Since, however, selenium has been found in Permian rocks in Wyoming (12), in considerable amounts and since small amounts of selenium are known to occur in the Whitewood Pahasapa, and Opeche formations (Table 1) there is the possibility that selenium may occur in greater amounts than available analyses indicate in these and other Paleozoic formations.

MESOZOIC

Mesozoic beds occupy more of the surface of South Dakota than those of any other group except the glacial deposits of the Pleistocene. Their combined thickness is also greater than that of the rocks of any other era. They are commonly divided into three or four systems. The three part subdivision consists of the Triassic, Jurassic, and Cretaceous systems. In the four part division, a Lower Cretaceous system called Comanchean by some authors, and an upper system, the Upper Cretaceous are included. In the columnar section (Figure 1) four systems are recognized and subdivisions into formations are made accordingly.

Triassic

The Triassic rocks, Spearfish formation of South Dakota, occur at the surface in the Red Valley of the Black Hills. They are bounded toward the core of the mountains by the outwardly dipping Minnekahta limestone hogback which forms the inward wall of the Red Valley. Away from the Black Hills they are bounded by the assemblage of beds which makes up the escarpment of the outer or Dakota-Lakota hogback. The Spearfish thus lies at the bottom of the Red Valley and forms an outcrop varying in width between one and nearly eight miles. The widest outcrop in South Dakota is west of Spearfish in the northern Black Hills.

The rocks consist of conspicuously bright brick red beds of sandy shale and shaly sandstone. They are, for the most part, soft and nonresistent so that the beds are not continuously exposed because of alluvial cover. Beds of gypsum varying in color from snowy white to pink occur in the formation but are most abundant and of greatest thickness in the lower part. These gypsum beds reach thicknesses of twenty-five feet or more. The Spearfish doubtless underlies most of western South Dakota under thick cover. The red beds continue around the Black Hills into Wyoming where they are known as the Chugwater formation. In central Wyoming they are the Dinwoody, Chugwater and Jelm formations and the Alcova member. In western Wyoming the Triassic includes the Woodside formation overlain by the Thaynes limestone, sandy limestone and yellow sandstone, and the Ankareh shale which continues westward into Utah (12,13).

The Spearfish formation varies in thickness from approximately 500 feet to 700 feet (9). The Triassic thickens greatly to the westward in Wyoming. The Chugwater alone reaches a thickness of 1000 feet, and the total thickness of Triassic beds reaches 4000 feet in western Wyoming (13).

Jurassic

Jurassic beds in South Dakota include the Sundance and the Unkpapa sandstones. These rocks outcrop for the most part in the area surrounding the Red Valley near the base of the escarpment of the Dakota-Lakota hogback. The outcrop is relatively narrow, varying in width from a small fraction of a mile to a mile. Around the eastern Black Hills from near Spearfish to a few miles west of Minnekahta the outcrop is narrow. Northwest of Spearfish and northwest of Minnekahta toward Wyoming outcrops are wider.

The Sundance formation consists mostly of beds of sandstone, sandy shale, and shale. Limestone beds, commonly fossiliferous, and only a few feet in thickness are associated with shale in many places. The sandstone beds vary in thickness from a few feet up to 50 feet or more. They are commonly greenish gray and buff, although reddish buff and red sandstones are observed locally. A bed of sandstone similar to the Unkpapa sandstone lies at the base of the formation in several places near Sturgis and elsewhere. The shales are of considerable thickness reaching 150 feet. These beds are of dark gray color in many places and have a greenish gray cast. The total thickness of the Sundance is variable from 70 to 300 feet.

The Unkpapa sandstone lies above the Sundance in apparent conformity but it probably underlies the Morrison with unconformable relations. The formation consists of massive, uniformly very fine-grained, soft sandstone. In most places it is pure white although it is conspicuously yellow, red, brown, and maroon in certain locations. These conspicuous shades are notable features near Hot Springs and in Calico Canyon, near Buffalo Gap. Distributive faulting is a notable feature where the formation is highly colored. The thickest outcrops are in the eastern Black Hills where the sandstone reaches a thickness of 150 feet. In the northern Black Hills it thins greatly to a few feet of white and yellow sand of characteristic lithology.

MORRISON FORMATION. The Morrison formation is an assemblage of clay and shale beds of various colors including light and dark gray, red, buff, and brown to purplish gray. Thin sandstone beds, some cross-bedded, occur in this formation. Zones of calcareous concretions and limestone (9) up to 40 feet in thickness have been observed in certain places. Pyrite beds have also been noted in the upper part. The clays are in many cases mottled and structureless. Some of the sandstone beds, particularly near the top, contain root remains. Bones of dinosaurs have been collected from this formation both in South Dakota and elsewhere. The character and fossils indicate that the Morrison formation in South Dakota is of terrestrial and fresh water origin. It is assigned to the Jurassic by some authors (14,15) although it was formerly referred, in South Dakota, to the Lower Cretaceous (9).

LOWER CRETACEOUS

The Lower Cretaceous beds include the Lakota, Minnewaste, and Fuson formations. The Morrison was formerly included with the Lower Cretaceous but is discussed here with the Jurassic. The Fuson is mostly shale and clay, whereas the Lakota is dominantly sandstone.

LAKOTA SANDSTONE. The Lakota sandstone surrounds the Black Hills, where it commonly forms the crest of the outer or Lakota-Dakota hogback and the dip slope of the hogback away from the Hills. The outcrop is for the most part narrow, one mile or less, but it reaches a width of nine or more miles in certain areas.

The formation has not been recognized separately from the Dakota in eastern South Dakota. However, the Lakota has been recognized under cover as far southeast as Lincoln, Neb. (16).

The Lakota formation consists of fairly coarse-grained, massive, cross-bedded sandstone which weathers to a buff color. Here and there, dark shale reaching a thickness of 20 feet is interbedded with the sandstone. Concretions of iron oxide are of common occurrence. Petrified logs, in many cases of great size, are found in many places. The Lakota sandstone varies in thickness from 70 feet to 485 feet (9).

MINNEWASTE LIMESTONE. The Minnewaste is a thin bed of white limestone lying between the Lakota and the Fuson formation between Buffalo Gap and Fuson canyon, Custer county. It reaches a thickness of 12 to 18 feet (9).

FUSON FORMATION. The Fuson shale forms a narrow, mostly covered, outcrop on the outward slope of the Dakota-Lakota hogback of the Black Hills. It occurs under cover as far southeast of the Black Hills as Lincoln, Neb. (16).

The formation consists for the most part of light colored siliceous clays but is, in many places, mottled with buff, red, and dark purple gray. Carbonized plant and wood fragments are of common occurrence. Sandstone beds of yellow or buff color are interbedded with the clay in many outcrops. The clays are structureless for the most part. Thin beds of impure coal lying over beds of clay suggest that the Fuson is of terrestrial origin. The clays are similar to those commonly present beneath coal beds.

UPPER CRETACEOUS

DAKOTA FORMATION: The Dakota sandstone consists of a succession of beds dominantly of sand but it includes also some beds of shale, clay, and thin impure coal.

The Dakota is best known in the Black Hills region where it is commonly exposed in a narrow outcrop near the base of the outer hogback. The formation is covered elsewhere in South Dakota although it outcrops across the Sioux river in Iowa, northeast of Jefferson, S. D., and in Nebraska, south of Elk Point, S. D. It is widely distributed beneath the surface and with the Lakota it is a source for artesian water over wide areas in eastern South Dakota. It is believed to overlap and pinch out around the Sioux quartzite area.

Around the Black Hills the Dakota consists mostly of gray, buff and brown, more or less ferruginous sandstone. It is locally conglomeratic in the lower part and also contains beds of sandy shale and shale. The sandstone is in part uniform and massive, but in many places it consists of ledge-producing beds which are the result of case hardening of ferruginous slabby sandstone. Under the surface of southeastern South Dakota thin beds of coal with associated clays, shales, and both thin and massive, fine-grained, gray sandstone probably occur, since these beds outcrop along the Iowa and Nebraska sides of the Sioux and Missouri rivers. Variations in lithology from place to place, both in the western and eastern outcrops, indicate the lenticular and variable character of the formation. In places in the Black Hills region and in the outcrop area in Iowa and Nebraska the uppermost beds grade upward into the Graneros shale.

Where the Dakota lies on Fuson in the western outcrop area there is no evidence of unconformity with the underlying formation (9). In southeastern South Dakota, however, it is unconformable on older beds. It appears to pass upward into the Graneros without a stratigraphic break.

The Dakota varies greatly in thickness both in the area of outcrop and where it is penetrated by wells. In the Black Hills it varies from 20 feet to 200 feet in thickness. Variations in thickness of this formation under eastern South Dakota appear to be equally great.

The Dakota is commonly referred to Upper Cretaceous on the basis of plant fossils and is correlated with sandy beds of similar position in adjacent states. In the southern Black Hills, however, beds at this position (Fall River sandstone) contain Lower Cretaceous leaves (17), and near Sioux City Lower Cretaceous invertebrates have been collected from these beds (18).

Graneros Shale. The Graneros is the thick succession of shales outcropping between the Dakota and the Greenhorn formations around the Black Hills. The outcrop in that region forms a band from one to four miles in width. The formation is not known to outcrop elsewhere in South Dakota but it is near the surface in Union county and outcrops along the Sioux and the Missouri rivers both northeast and southeast of Elk Point, S. D.

The Graneros consists almost entirely of shale in the Black Hills area, but near the southeastern corner of South Dakota sandstone occurs. In Iowa and Nebraska near the South Dakota boundary interbedded sandstones are found in the lowermost beds and in beds 200 to 275 feet above the base.

The Graneros has been divided into four members immediately west of the Black Hills in Weston and Crook counties, Wyoming (19). These members have all been observed north, east, and south of the Black Hills in South Dakota. In ascending order the subdivisions of the Graneros are the Skull Creek shale member, Newcastle sandstone member, Mowry siliceous shale member, and Belle Fourche shale member.

The Skull Creek shale member consists of very dark gray to black fissile shale with lenticular ferruginous concretions. These beds have been observed south and east of the Black Hills and are identifiable in descriptions of the Black Hills region (9,20,21). This member was not measured during the field work of this study but is described as varying from 200 to 275 feet in thickness. West of the Black Hills, in Weston and Crook counties, Wyoming, the Skull Creek shale is 175-275 feet in thickness (19).

The Newcastle sandstone is composed of sandstone, sandy shale, and impure bentonite, and locally contains phosphatic nodules in the type locality (19). This sandstone appears to be the member described by Darton (9) as occurring at several locations in the eastern Black Hills at a position 200-275 feet above the base of the Graneros. The sandstone east of the Black Hills reaches a thickness of 25 feet and appears to pinch out completely in many places (9). West of the Black Hills the member varies between 0 and 75 feet in thickness.

The Mowry shale member is well known in the Black Hills region where it is a light colored and siliceous, dark when fresh, but weathering to hard, silvery, nearly white shale. It contains numerous thin beds of bentonite and in nearly every outcrop scales of fishes may be found. The Mowry member varies in thickness from 225 to 250 feet along the eastern side of the Black Hills (9) and is 125-225 feet thick west of the Black Hills in Wyoming (19).

The Belle Fourche shale member is composed of dark gray to nearly black shale. Limestone ledges and calcareous and sideritic concretions occur in it. The member also contains bentonite beds, the lowermost of which reaches a thickness of three feet. North of the Black Hills calcareous beds, previously mapped as Graneros, lying immediately under the Greenhorn limestone were found to contain *Inoceramus labiatus* and south of the Black Hills the uppermost shales contain foraminifera characteristic of the Greenhorn formation. These beds appear to be a part of the Greenhorn rather than the Graneros and are excluded from the Belle Fourche member of the Graneros in this report.

Although the Graneros does not outcrop in southeastern South Dakota, exposures in Iowa and Nebraska show the formation to be composed of dark shale which is interbedded with sandstone in the lower part.

The thickness of the formation varies from about 80 feet under southeastern South Dakota to approximately 800 or 900 feet in the Black Hills region, excluding beds referred to the Greenhorn in this report.

GREENHORN FORMATION. The Greenhorn formation consists of beds of chalk, shale, and limestone lying between the Graneros and Carlile. As treated in this report it includes calcareous shales in the Black Hills region previously included in the upper Graneros. Calcareous chalky beds containing fossil oysters in the Black Hills region appear to be Carlile rather than Greenhorn in age.

The Greenhorn of the Black Hills region forms a prominent, buff to yellow, low hogback extending south and east of the Black Hills. North of Sturgis the hogback becomes less apparent and the outcrop is less distinctly marked topographically. For the most part the outcrop around the Black Hills is narrow, but north of the Hills the width increases to a mile or more. The formation also outcrops in very small patches in Union county, South Dakota.

In the southern Black Hills the Greenhorn formation consists of calcareous shale, interbedded in the upper 30 to 35 feet with limestone beds which reach a thickness of six inches. In the upper 8 or 10 feet the thin beds of limestone and shale occur alternately in about equal proportions (Figure 3). Approximately 40 feet below the top these beds are underlain by dark, hard bituminous shale. The microfauna of this shale, previously referred to the Graneros, is Greenhorn in age. These beds are, therefore, included in the Greenhorn formation.

Several yellow bentonite beds one to four inches in thickness occur in the part of the formation lying above the dark shale member.

Concretions containing *Inoceramus labiatus,* a clam-like pelecypod characteristic of the Greenhorn of the Rocky Mountain region, occur a few feet above the dark shale member. This fossil occurs also in the limestone and is exceedingly abundant in the upper ledges.

North of the Black Hills the Greenhorn becomes predominantly calcareous, chalky shale with a few thin beds of limestone and concretionary limestone in the upper part. *Inoceramus labiatus* occurs throughout the Greenhorn north of the Black Hills. It is found more abundantly in the upper than in the lower part of the formation.

In southeastern South Dakota the formation is very similar to that exposed south and east of the Black Hills. It consists of alternating beds of calcareous shale, chalk, and limestone, the latter with abundant shells of *Inoceramus labiatus*. The Greenhorn appears to be conformable with the underlying Graneros and the overlying Carlile.

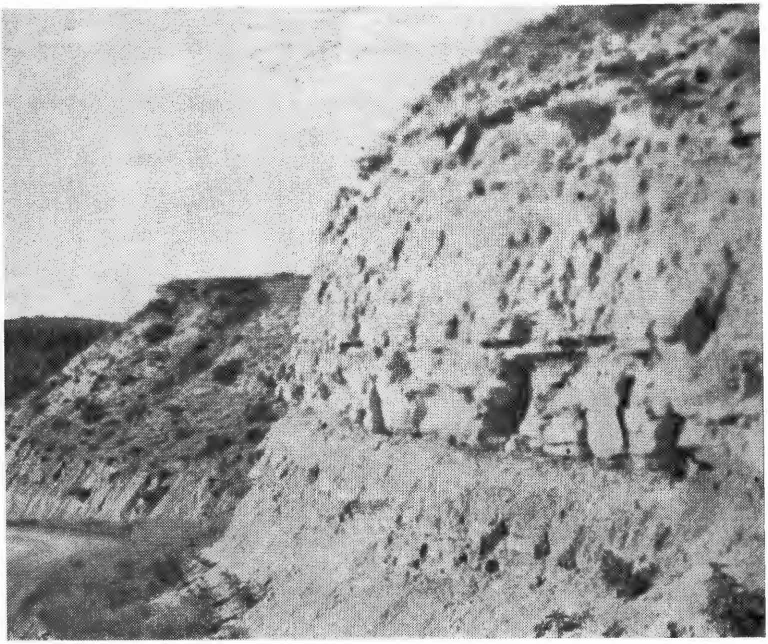

FIG. 3. Typical Greenhorn (upper) outcrop south of Edgemont, S. D. Thin beds of limestone and shale.

The thickness of the formation south and east of the Black Hills is not known. South of Edgemont it is more than 44 feet thick and north of Belle Fourche it appears to be more than 300 feet thick. In the Irish Creek well 336 feet of beds have been referred to the Greenhorn (8) and in State School Lands well No. 1 and Ole Tannberg well No. 1, 203 and 316 feet of Greenhorn have been identified (22).

The Greenhorn formation is correlated with the Greenhorn of Montana, Wyoming, Colorado, Nebraska, and Kansas (Figure 2). The limestone beds of the southern Black Hills and in southeastern South Dakota contain an abundance of *Inoceramus labiatus* and correspond closely to the Pfeifer and Jetmore members of Kansas. The dark shale below these limestone beds in Fall River county contains foraminifera found also in the Hartland shale member of Kansas. There is possibly a close correlation between the Greenhorn of the southern Black Hills and the Kansas facies. This formation probably should be correlated with the Mancos in the San Juan basin, New Mexico (23) and the Eagle Ford of Texas (24), both of which contain *Inoceramus labiatus,* and with similar beds in Mexico (25).

CARLILE. The Carlile formation is the succession of shale beds lying between the Greenhorn and the Niobrara formations. It outcrops in a band one to four miles wide around the Black Hills and is exposed where the glacial drift has been removed in eastern South Dakota along the James river and its tributaries, and in Clay and Union counties.

The formation consists of light to dark gray shale. North and northeast of the Black Hills from near Bear Butte to the Montana line, chalky beds with abundant oysters, including *Ostrea congesta* occur above the Greenhorn beds which contain *Inoceramus labiatus*. Similar beds in Kansas have long been included in the Fairport member of the Carlile and these beds are tentatively referred to the Carlile here. The upper beds in the Black Hills region are in part sandy and contain concretions and concretionary sandy ledges abounding in characteristic Carlile fossils, such as *Prionocyclus wyomingensis, Scaphites warreni, Prionotropsis woolgari, and Eutrephoceras elegantula*. In southeastern South Dakota, particularly in Union county and across the Sioux and the Missouri rivers, the Carlile consists of gray shale, in part very dark. The upper part contains calcareous, pyritic, and marcasitic concretions containing fossils which occur also in the Blue Hill shale member of the Carlile in Kansas. Along the James river and its tributaries fine sandstone comprises the upper part, lying below the Fort Hayes member of the Niobrara. These beds become less sandy southward toward Nebraska where they contain foraminifera believed to be characteristic of the Carlile. The uppermost beds of the Carlile are known as the Codell sandstone in Kansas. Since they represent similar and contemporaneous sedimentation in southeastern South Dakota the name Codell should probably be extended to this area. Bentonite occurs in the Carlile in the Black Hills region and at least one thin bed has been observed in southeastern South Dakota.

The Carlile is believed to lie conformably on the Greenhorn in South Dakota and elsewhere, and probably has the same stratigraphic relations with overlying beds. Unconformable relations within the formation have been suggested in eastern Wyoming (19). The thickness varies from 500 to 750 feet in the Black Hills region (9) and between 65 and 105 feet in southeastern South Dakota (26).

The lower chalky beds of the Carlile in the Black Hills region possibly represent the Fairport member of the Carlile of Kansas. The fossiliferous sandy beds of the upper Carlile in the Black Hills region probably correspond to the Turner sandy member of the Carlile of Wyoming and Montana (19), and to the Blue Hill shale of Kansas. The fossiliferous concretionary beds containing the characteristic upper Carlile fauna in southeastern South Dakota, Iowa, and northeastern Nebraska appear also to represent the Blue Hill member of the Carlile of Kansas.

NIOBRARA. The more or less calcareous and chalky beds of the Niobrara formation appear at many places in western, south central, and southeastern South Dakota. An outcrop, covered by later beds in many places, and varying in width from less than a mile to six miles or more, appears at the surface along White River and its tributaries on the Chadron anticline in southwestern Shannon county. The Niobrara outcrops along the Missouri river from Yankton to Fort Thompson, in patches along the James river and its tributaries, and on Turkey Ridge in Yankton and Clay counties. Smaller outcrops occur where drift cover has been removed from the formation elsewhere east of the Missouri river.

The formation east of the Missouri river consists of chalk and chalky shale. These beds are divisible on the basis of lithology and microfossils into two members: a lower member, the Fort Hays; and an upper member, the Smoky Hill (27).

FIG. 4. Ruins of Chapel at Fort Randall. Built from (upper) Smoky Hill, Niobrara Rock which contains 20 p.p.m. of selenium. Probably the first authentic account of the "Alkali Disease" or selenium poisoning was written in August, 1856, by Madison (1), an Army surgeon, stationed at Fort Randall.

The Fort Hays when fresh consists of beds of light to medium gray chalk and chalky shale which weather white to buff. Several thin bentonite beds occur in it. The Smoky Hill consists of beds which are dark gray to almost black chalk and chalky shale in the lower 100 to 130 feet. The uppermost beds are light to medium gray when fresh. The dark beds of the Smoky Hill on weathering become yellow to orange in color, whereas the uppermost beds weather to light gray and to snowy white. These upper white chalk beds are well exposed beneath the Pierre on Turkey Ridge in northwestern Clay county and northeastern Yankton county, west of Yankton, and opposite Chamberlain in eastern Lyman county. They are identifiable also by a characteristic microfauna which includes many species such as *Loxostoma applinae* Cushman, *Bolivina explicata (B. crenulata* of *Loetterle),* and *Shakoina trituberculata* (Morrow) in common with the Gregory zone of the Pierre (Figure 5). *Loxostoma applinae* is so characteristic east of the Missouri river that this zone might well be known as the *Loxostoma applinae* zone. Many thin beds of bentonite occur in the Smoky Hill member of the Niobrara.

In the outcrop area surrounding the Black Hills the Niobrara contains much more shale than in eastern outcrops. Near and at the base of the chalky shales of

FIG. 5* Some representative Cretaceous foraminifera of South Dakota, especially those of the Gregory marl, Sully member, Pierre formation. ×50.

1. *Bolivina explicata* Cushman and Hedberg. Gregory marl, Yankton. Occurs also in the (upper) Smoky Hill member of the Niobrara formation. *(Continued bottom opposite page.)*

* Acknowledgement is made to Miss Dorothy Ullery, senior student at the University of South Dakota for *camera lucida* drawings of these micro-fossils.

the formation, in many places, thin beds of chalk weather white and suggest the Fort Hays member. These beds are especially conspicuous in Sec. 33, T. 8 S., R. 1 W. along Highway 85 and north of the East Mule Creek oil field in Wyoming. Similar beds occur low in the Niobrara north and northeast of the Black Hills near the outcrop of the Carlile. These beds weather to a bright light yellow color. Possibly they represent the Fort Hays of eastern South Dakota. The uppermost beds of the Niobrara are also more chalky and tend, in some places at least, to weather white, thus resembling the upper white beds of eastern South Dakota.

Beds of most of the formation are medium to very dark shales which are more or less calcareous and chalky. Some are very dark and are speckled with crushed foraminifera. In certain locations, such as at Brennon, Pennington county, they weather to the characteristic buff to orange color of the Smoky Hill. North and northwest of Bear Butte, chalk is a less important constituent and zones of concretions, some septarian, occur in the beds which probably represent the Smoky Hill member.

In Shannon county, the upper Niobrara consists of calcareous medium gray shales containing limestone concretions. These beds are overlain by resistant ledges of hard chalk and shale, stained or weathered to brilliant yellow, and are 38 feet or more in thickness. These beds contain *Shakoina trituberculata,* a foraminifer believed to be characteristic of upper Niobrara (Figure 5).

The thickness of the Niobrara is commonly about 200 feet in eastern South Dakota. Possibly the easternmost outcrop is not more than 160 feet thick. Measurement of the thickness of this formation around the Black Hills is difficult due to incompleteness of exposures and discordance in dip. The thickness has been estimated at 150-225 feet (9). West of the Black Hills the thickness has been given as 375-525 feet (19). The Niobrara of South Dakota is correlated with the same formation of the adjacent areas (Figure 2).

PIERRE FORMATION. The Pierre formation is the thick succession of beds, consisting mostly of shales, lying between the calcareous Niobrara and the dominantly sandy beds of the Fox Hills formation. These beds occupy wide areas at the surface around the Black Hills and from the Black Hills to the Missouri river. In northwestern South Dakota the Pierre is covered by the Fox Hills for-

2. *Gaudryina pupoides.* d'Orbigny. Gregory marl. Yankton. Occurs at other positions in the Pierre formation and in the Fort Hays and (lower) Smoky Hill members of the Niobrara formation.
3. *Gaudryinella capitosa* var. *serrulata* Cushman. Gregory marl, Yankton.
4. *Marsonella oxycona* (Reuss). Gregory marl, Yankton.
5. *Shakoina trituberculata* (Morrow). Gregory marl, Yankton. Occurs also in the (upper) Smoky Hill member of the Niobrara formation.
6. *Gaudryinella* sp. Gregory marl, Yankton.
7. *Bolivina incrassata* Reuss. Gregory marl, Yankton. Occurs also at other positions in the Pierre formation.
8. *Eouvigerina achuleata* Cushman. Gregory marl, Yankton. Occurs also in the Fort Hays and Smoky Hill members of the Niobrara formation.
9. *Dentalina niobrarensis* Loetterle. Gregory marl, Yankton. Occurs also in the Fort Hays member of the Niobrara formation.
10. *Ventilabrella eggeri* Cushman. Gregory marl, Yankton. An ubiquitous Cretaceous form.
11. *Guembelina plummerae* Loetterle. Gregory marl, Yankton. Abundant also in the Smoky Hill member of the Niobrara formation.
12. *Planulina Taylorensis* (Carsey). Gregory marl, Yankton. Most common at this position but occurs also in the Smoky Hill member of the Niobrara formation.
13. *Loxostoma applinae* (Plummer). Gregory marl, Yankton. Common at this position but abundant in the (upper) Smoky Hill member of the Niobrara formation.
14. *Globigerinella aspera* (Ehrenberg). Gregory marl, Yankton. Ubiquitous in chalky facies of the Cretaceous formations.

mation and later beds and in the southern part of the state west of the Missouri river the formation is mostly covered by Tertiary beds. East of the Missouri river the Pierre is covered, except for limited outcrops, by glacial drift. Roughly a third of South Dakota west of the Missouri river has Pierre as the surface formation.

The Pierre formation of South Dakota is divided into five members on the basis of lithology and macroscopic and microscopic fossils. The original division with later revisions in classification and nomenclature is as follows:

Searight 1937 (7)	Searight 1938 (8)	This report
Elk Butte	Elk Butte	Elk Butte
Mobridge	Mobridge	Interior
Virgin Creek	Virgin Creek	Virgin Creek
upper	upper	upper
lower	lower	lower
Sully	Sully	Sully
Verendrye	Verendrye	Verendrye
Oacoma	Oacoma	Oacoma
Agency	Agency	Agency
	Gregory Marl	Gregory
Gregory	--------Unconformity------------	Unconformity-----
upper	Sharon Springs	Sharon Springs
lower		upper
		lower

Sharon Springs. The Sharon Springs member of the Pierre, as it is identified in South Dakota, consists of beds of very dark bituminous shale in the lower part, and dark, rusty-weathering beds above. These latter beds contain very large septarian concretions. The beds of the member in South Dakota are thus very similar to those of the type locality (28). In South Dakota all beds above the Niobrara formation and below the Gregory marl are included in the Sharon Springs member.

The Sharon Springs member outcrops in South Dakota along the Missouri river and its tributaries from Yankton to Fort Thompson. It is poorly exposed on Turkey Ridge, Yankton county. The member is exposed in Shannon county where it lies above the Niobrara formation and below White River beds and it outcrops around the Black Hills.

The Sharon Springs member is divisible in South Dakota, as in the type locality in Kansas, into a lower lithologic zone and an upper zone.

The lower Sharon Springs consists of dark nearly black beds of bituminous fissile shale which weather to dark brown. This part of the member weathers back less rapidly than the upper zone and forms relatively steep valley walls and escarpments of buttresslike appearance (Figure 6). Thin beds of bentonite occur along the Missouri river and eastward but around the Black Hills they reach thicknesses up to three feet. The thickest bentonite bed occurs near the top in the Black Hills region. North of Bear Butte in Meade county the lower zone thins out or becomes less fissile and more silty so that it is difficult to identify.

The upper Sharon Springs is somewhat similar to the lower zone but is much less fissile. Concretions, uncommon in the lower zone, are abundant in the upper zone (Figure 7). Most of these are small, ferruginous masses, but some are very

FIG. 6. Lower Sharon Springs outcrop south of Provo, S. D.

large, especially around the Black Hills, where they reach a diameter of several feet. These large concretions are septarian and weather yellow and cone-in-cone forms a crust around them. Only a few thin bentonite beds occur in this zone which weathers down to buff and brown silty clay soil.

Fossils are not common but those which have been found, mostly small vertebrated *Baculites,* apparently belong to the Eagle fauna of Montana and elsewhere. Mud Buttes, north of Belle Fourche in Butte county, exposes beds probably to be correlated with the upper Sharon Springs south of the Black Hills. Many *Baculites,* mostly *Baculites ovatus var haresi* (Reeside) occur in these beds.

The Sharon Springs member is thin in eastern South Dakota being only 7 feet thick at Yankton where only a part of the lower zone underlies the Sully. At Rosebud Bridge 45 feet of beds, probably most of the lower zone, are exposed under the Sully, and at the mouth of Bull Creek all of the lower zone and 110 feet of upper zone are exposed. The uneroded thickness of the Sharon Springs member at the mouth of White River and eastward was at least 155 feet. At Provo, Fall River county, the lower zone is about 95 feet thick, which is more than double the thickness along the Missouri river. The upper zone is at least this thick, around the southern Black Hills. The beds north of Belle Fourche, Butte county, assigned to the Sharon Springs member reach a thickness of possibly 200 to 250 feet.

The Sharon Springs of South Dakota is correlated with that of Kansas (28) and Colorado (29). The fauna of the member represents, in part at least, the Eagle member of Montana (30). Beds in southeastern Wyoming, Weston county, are an extension of the Sharon Springs.

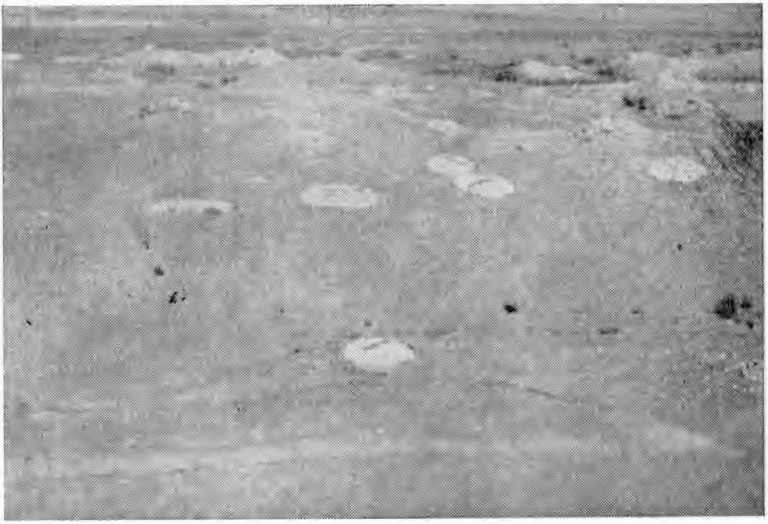

FIG. 7. Concretions in upper Sharon Springs.

Sully member. The Sully member of the Pierre formation in South Dakota includes the shale, chalky shale, and marl lying above the Sharon Springs member and below the bentonite bearing beds of the Virgin Creek member. The Gregory marl, originally included with the Gregory member (the Sharon Springs of this report), has been found to be related by its microfauna to the Sully member (31), and to be separated from the Sharon Springs member by an unconformity. From the base up, the Sully member is divisible into four lithologic subdivisions; the Gregory marl, the Agency shale, the Oacoma beds, and the Verendrye shale. These subdivisions have been described in considerable detail in previous publications (7,8,31).

Gregory marl: The Gregory consists of marl, shale, and chalky shale. Flat shale pebbles, mostly small but reaching one and one-half inches in diameter, occur in every outcrop investigated. These pebbles appear to be derived from material from the lower Sharon Springs member. A very thin bed of slabby sandstone occurs at the base of the marl from Rosebud Bridge to the Great Bend of the Missouri river. The microfauna grades upward into the Agency shale. The Gregory has not been identified around the Black Hills although the microfauna occurs in cuttings from Hunter No. 1 well north of Wall, Pennington county, and in the Irish Creek well in northern Ziebach county. Possibly the Gregory becomes less calcareous and grades lithologically into the Agency to the west.

Agency shale: The Agency shale, where it is most prominently developed, consists of shale which weathers to hard light silvery gray chips. It varies in thickness from a few feet in certain locations to 242 feet or more west of the type locality. The Agency has a microfauna consisting of an admixture of Gregory and Oacoma forms which is recognizable where the beds are very thin and cannot be identified by lithology.

Oacoma zone: The Oacoma zone is a thin succession of shale beds alternating with bentonite beds. South of the Great Bend this zone contains beds of sideritic and manganese-iron concretions. North of the Great Bend it thins, becomes increasingly siliceous, and contains but few concretions. The zone has been recognized by its microfauna from well cuttings in Meade, Ziebach, and Pennington counties. Typical outcrops occur as far west in South Dakota as Sec. 6, T. 4 N., R. 11 E., Meade county.

Verendrye shale: The Verendrye is somewhat similar to the underlying Oacoma. This zone weathers to broad red and brown bands strewn with flattened ferruginous concretions. The zone apparently thickens toward northwestern South Dakota. Teepee buttes formed from masses of cemented shells of the clam *Lucina occidentalis* in Meade and Butte counties are referred to this zone.

Virgin Creek. The Virgin Creek member is the body of dominantly dark shales which lies between the Verendrye and the calcareous beds of the Interior member.

The lower Virgin Creek differs conspicuously from the underlying and overlying beds because of its content of interbedded bentonites. These have been observed to outcrop from northern Nebraska, along the Missouri river and its tributaries northwest into Meade county. The bentonite beds are very thin in northern Nebraska but some thicken to two feet or more in Meade county along Elm Creek.

The upper Virgin Creek consists of dark gray shales which break down to gumbo clays. They commonly weather to shades of brown and buff in the upper part of the member. Bentonite beds are few in number. Concretions occur at various positions within the upper Virgin Creek. These limestone concretions contain the characteristic Sage Creek fauna of the upper Pierre and Bearpaw formations.

Near the top of the upper Virgin Creek along the Missouri river a chalky zone of interbedded chalk and shale has been observed. This zone is particularly significant in these studies since it is highly seleniferous and seleniferous vegetation has been observed growing upon it.

Interior. (8) The Interior member of the Pierre was first identified and named by Ward (32) from outcrops in the Big Badlands. The member was also separated from the remainder of the Pierre by Searight (7) in 1937. In eastern Colorado similar beds with a similar fauna were named Beecher Island by Elias (28). Studies of the macrofauna and microfauna, and tracing of beds in the field during this investigation satisfactorily establish the identity of the Interior and Mobridge. The name Interior has precedence over the term Mobridge and will be used throughout this bulletin. The name Interior probably should also be used for Beecher Island in Colorado if correlation is confirmed.

FIG. 8. Typical topography of the upper Virgin Creek member of the Pierre formation. (Type section) one mile south of Promise, S. D.

FIG. 9. Virgin Creek (lower) member of the Pierre formation same location as Fig. 8.

The Interior member of the Pierre includes beds of chalk, chalky shale, shale, and sandy shale and possibly beds of sandstone lying above the Virgin Creek member and below the Elk Butte shale in the type locality of the latter member.

The member varies considerably in lithologic facies from place to place. In northern Nebraska, particularly in Boyd county, beds mostly of chalk and chalky shale make up the succession. The member becomes more and more argillaceous northward, and is a chalky and calcareous mudstone containing numerous calcareous concretions near Mobridge. Westward from the Missouri river the member becomes sandy, particularly in the upper part, and concretions, in the sandy limestone occur. These beds grade upward into, and in many places are interbedded with sandstones which have been previously referred to the Fox Hills formation. In southwestern South Dakota (Fall River county) the member is not notably sandy but it contains masses of teepee butte-forming limestone which produces the teepee buttes near Smithwick. In northwestern South Dakota, from near Newell into Harding county toward the Glendive-Baker anticline, the Interior thins to a few feet of sandy, buff-weathering beds. These beds underlie sandstone which is commonly referred to the Fox Hills formation.

The Interior member varies greatly in thickness. It is 90 to 100 feet thick near Rosebud Bridge in Gregory and Charles Mix counties. Near Wicksville and north of Quinn, Pennington county, the member has not been measured but it appears to be 250 to 300 feet thick. Near Cottonwood, Jackson county, it is more than 195 feet thick.

The changes in facies of the Interior appear to be due to changes in position of the shoreline to the west and to differences in sedimentary environment. They are also associated with important variations in selenium content of these beds.

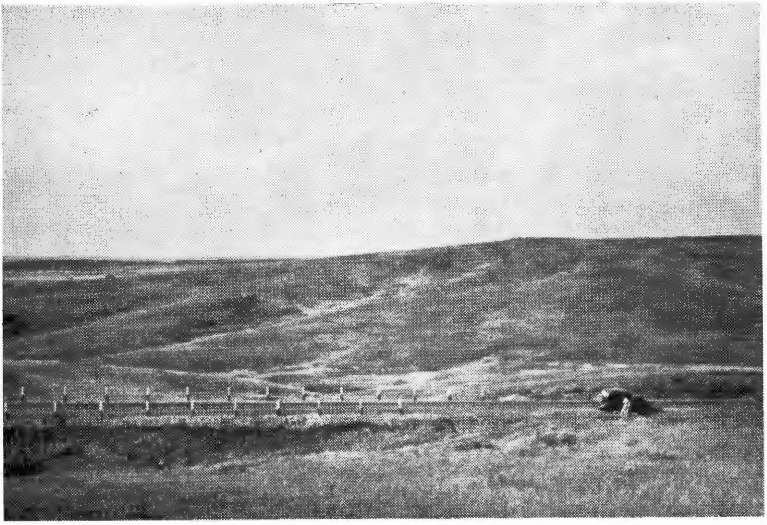

FIG. 10. Typical topography of the Interior member of the Pierre formation.

Elk Butte. The Elk Butte member of the Pierre consists of the dark shales lying above the calcareous beds of the Interior member in eastern Corson county. Beds lying along the Missouri river above the chalky Interior in Gregory and Charles Mix counties have been referred to the Elk Butte. Evidence indicates that these beds pinch out or grade into sandstone toward the west. For example the Elk Butte was not identified in the core of the Irish Creek well in northern Ziebach county. In Harding county, sandstone lies on beds believed to represent the Interior. In Harding and Butte counties, dark shale beds at the position of the Elk Butte have not been observed. Instead, buff weathering beds of Interior aspect grade upward into sandstone without intervening shale beds.

FOX HILLS FORMATION. The Fox Hills formation consists of those beds which are dominantly sandstone lying on the Pierre and below the Hell Creek member of the Lance formation. In eastern exposures the formation contains large calcareous concretions in which the characteristic marine fossil fauna of the Fox Hills is found. Although the Fox Hills formation lies on typical Pierre to the west, the Fox Hills fauna has not been observed in the sandstones of Harding, Butte, and Meade counties. The disappearance of the Elk Butte member and the thinning and increasingly sandy character of the Interior member in northwestern counties suggests that the sandstone there referred to the Fox Hills formation may be considerably older than the Fox Hills formation of the type locality.

LANCE FORMATION. The Lance formation consists of beds of sandstone, shale, clay and coal lying on the Fox Hills formation of northwestern South Dakota. A lower member, the Hell Creek, consisting of dull gray and dull brown gumbo clays and a few coal beds lies on the Fox Hills sandstone. The Hell Creek member is overlain in the northeastern part of the outcrop area by the yellow Cannonball sands containing marine fossils. To the southwest, however, no marine fossils have been found and the similar yellow sands and clays of the Ludlow member are coal bearing. The rather indefinite boundary between the marine Cannonball and the terrestrial Ludlow lies diagonally across Perkins county from northwest to southeast (33,34).

TERTIARY, EOCENE

FORT UNION FORMATION. The Fort Union formation consists dominantly of sandstones but also consists of beds of shale, sandy shale, and clay. The thickest coal beds of South Dakota occur in this formation. It occurs only in the northern parts of Harding and Perkins counties, mostly under the higher mesas, buttes, and hills. The Fort Union formation has been referred to the early Eocene series.

TERTIARY, OLIGOCENE SERIES

The Oligocene deposits consist of clays, sands, and conglomerates. They are widely distributed over the Big Badlands along White River. They occur also on the Slim Buttes, the Short Pine Hills of northwestern South Dakota, and on many other small outliers. They have been divided into the Chadron and Brule formations.

CHADRON FORMATION. The Chadron is made up of sandy clays and clays. The basal portion in many places in the Big Badlands, Slim Buttes and elsewhere is composed of coarse sands and conglomerates. In many places the lower beds above the sands and gravels are light gray when fresh but oxidize to a deep maroon red. In other places the clays are mostly light to medium gray in color. The thickness varies from 0 to 180 feet.

BRULE FORMATION. The Brule formation consists of light gray, white, and yellow sandy clays banded with pink, yellow, and various shades of red and brown. Here and there beds of sandstone occur. The Brule is conspicuously exposed in the Big Badlands, the Slim Buttes, and the Short Pine Hills. The thickness of the Brule varies from about 350 feet to 650 feet.

TERTIARY MIOCENE AND PLIOCENE SERIES

Miocene beds in South Dakota have been named the Arikaree, and Sheep Creek beds, and the Nebraska beds (35). They consist of sandstones, conglomerates, clays, and volcanic ash and occur mostly in the Big Badlands although they also occur elsewhere.

Pliocene beds of limited distribution are given local names from areas of outcrop.

The reader interested in more complete description of Miocene and Pliocene beds is referred to the bibliography (35).

PLEISTOCENE SERIES

The Pleistocene deposits of South Dakota consist of glacial deposits, sands, and gravels of fluvio-glacial origin, and alluvial deposits. These latter consist of sands, gravels, silts, and clays. Glacial deposits are restricted almost entirely to the east side of the Missouri river. West of the Missouri river Pleistocene alluvial deposits occur chiefly along drainage lines. Deposits of volcanic ash of Pleistocene age have been observed on both sides of the Missouri river.

Selenium in Geological Formations and Associated Vegetation

Selenium occurs in bedrocks underlying the Great Plains region and the element has been found in many of the bedrock layers of South Dakota. The primary occurrence in the Plains area is believed to be bedrock, that found in soils, plants, and animals having been derived from rock sources. An important part of the field and laboratory work on which this investigation was based was to determine the relative abundance of selenium in various formations.

Preliminary work on the occurrence of selenium in rocks of South Dakota was done in 1937 (1). Moxon and associates continued these studies and further data and conclusions were published in 1938 (8). From time to time other workers have reported on the seleniferous character of bedrock of the Great Plains and many of their reports pointed to the probability that selenium is concentrated in certain beds or groups of beds, some of which underlie South Dakota.

The geological field work of this investigation was chiefly concerned with the collection of geological materials known to be a source of selenium, and the mapping of the Pierre formation, especially the Sharon Springs and Interior members. Other beds, however, were investigated where suspicion was aroused by the presence of seleniferous vegetation.

PRE-CAMBRIAN ROCKS

The selenium content of the pre-Cambrian rocks of the Black Hills and elsewhere has been investigated only casually. However, some pre-Cambrian rocks of the Black Hills are selenium free, whereas, others contain selenium in considerable amounts. Thus, schists such as those collected near Keystone (Table I) contained no selenium. On the other hand, a sample of the Homestake ore body, Lead, South Dakota, from one of the deeper levels contained 17.5 p.p.m. of selenium. No seleniferous vegetation is known to occur on either the igneous or metamorphic rocks of this age. These rocks are believed to contain insufficient selenium to render any areas occupied by them dangerously toxic.

TABLE 1. Selenium in Pre-Cambrian and Paleozoic Rocks

Rock	*Location*	*Selenium Content p.p.m.*
Garnet schist	Keystone, S. D.	0.0
Mica schist	Keystone, S. D.	0.0
Homestake ore body	Homestake Mine, Lead, S .D.	17.5
Whitewood limestone	East of Deadwood on S. D. Highway No. 24	0.8
Pahasapa limestone	Rapid Canyon	0.25
Opeche	Hot Brook Canyon, Hot Springs, S. D.	Trace

PALEOZOIC ROCKS

Selenium occurs in Paleozoic rocks of South Dakota, but, so far as is known, only in small amounts. Although data are inadequate to indicate the amounts of selenium present in Paleozoic rocks, no soils derived from them are known to support seleniferous vegetation. A sample of the Ordovician (Whitewood limestone) collected near Deadwood contained 0.8 p.p.m. of selenium. The Pahasapa limestone (Mississippian) of Rapid Canyon contained 0.25 p.p.m. of selenium (Table 1). The Opeche at Hot Springs, S. D., also contains some of the element. An *Aster multiflorus* plant collected on the Opeche formation at this location contained 7.0 p.p.m. of selenium, while in 10 grams of a ten foot composite of material in which the plant grew only a trace of selenium was detected. Its average selenium content is therefore low.

Although these results indicate that Paleozoic rocks are not likely to produce toxic soils or vegetation they are significant inasmuch as they indicate that selenium is not qualitatively characteristic of the rocks of any particular era or system. Apparently, selenium is of common occurrence in small amounts in sedimentary rocks. Sources also appear to have been present in early Paleozoic time as well as in Mesozoic and Cenozoic time. The possibility of exposed areas of pre-Cambrian rocks on ancient land masses thus suggest themselves as sources for selenium, at least during Paleozoic time. Possibly they may have been a source for selenium in the later Mesozoic rocks.

MESOZOIC ROCKS

Cumulative data concerning selenium occurrence points significantly to rocks of Mesozoic age as the most important source of seleniferous soils and vegetation in the Great Plains area. Previous studies at this and other laboratories indicate important variations in the selenium content of the Mesozoic beds of the Great Plains. It is likely that the average selenium content of sediments, of both marine and non-marine origin, is commonly low. This is indicated by a few analyses of Paleozoic rocks, a great number from Mesozoic rocks and a number from Tertiary beds and recent deposits, particularly marine bottom sediments from the Gulf of Mexico.

Because of the importance of Mesozoic rocks in the selenium problem, their selenium content will be discussed in some detail.

TRIASSIC

In South Dakota the Triassic is represented by the red beds and gypsum of the Spearfish formation. The analyses of Triassic beds in Wyoming (12) indicate that some of these beds contain selenium. Available analyses of this formation are given in Table 1. Gypsum from the Spearfish formation at Hot Springs, Fall River county, contained 1.0 p.p.m. of selenium. Possibly other beds of the Spearfish contain more or less selenium. However, no seleniferous vegetation has been found growing on the Spearfish in South Dakota, and the formation is not considered a source of toxic soils in this state.

JURASSIC

The Jurassic is represented in South Dakota by the marine Sundance and by the Morrison which is mostly, if not entirely, non-marine in the Black Hills region. Investigation of the Sundance as to its selenium content is incomplete. Seleniferous soils are not known to be weathered from it, and highly seleniferous vegetation has not been found growing on it. Although available analyses indicate that it contains no selenium (13) it is probable that selenium in small amounts may occur in the formation.

The Morrison formation contains some selenium (Table 2). The formation also contains some of the element in Wyoming (13). The outcrop in South Dakota is so small that selenium poisoning probably never occurs on it. No toxic vegetation has been found growing on it in this state.

LOWER CRETACEOUS

LAKOTA SANDSTONE. An investigation of the selenium content of this formation has not been made by this laboratory. It is the opinion of the authors, however, that very little of the element will be found in its outcrops. Originally, selenium was probably present in it only in small amounts but, being composed of sand, conditions for subsequent leaching are most favorable. It is possible that the shaly, less pervious beds of the Lakota formation contain some selenium. No seleniferous vegetation has been found growing on it, nor on soils derived from it.

FUSON FORMATION. The Fuson formation has been found to contain small amounts of selenium. Investigations concerning the selenium content of the formation in South Dakota have been limited, however. Analyses of composite samples taken at Sturgis, South Dakota, show a selenium content ranging from 0.0 to 1.5 p.p.m., the average for the whole section being 0.13 p.p.m. (Table 2). The restricted area of outcrop in South Dakota, the low selenium content where samplings have been made, and the absence of toxic vegetation indicate that the Fuson does not produce toxic areas.

TABLE 2. Selenium Content of Rocks of Triassic to Late Cretaceous Age

Rock	*Location*	*Selenium Content p.p.m.*
Spearfish (Gypsum)	Hot Springs, S. D.	1.0
Morrison shale 0-10′ (composite)	"Slip-off Hill" Sturgis, S. D.	0.0
Morrison shale 0-10′ concretion	"Slip-off Hill" Sturgis, S. D.	4.8
Morrison shale 10-16′ (composite)	"Slip-off Hill" Sturgis, S. D.	3.0
Fuson shale 0-10′ (composite)	"Slip-off Hill" Sturgis, S. D.	0.0
Fuson shale 10-15′ (composite)	"Slip-off Hill" Sturgis, S. D.	1.5
Fuson shale (black) 15-16′ (composite)	"Slip-off Hill" Sturgis, S. D.	1.3
Fuson shale 15-30′ (composite)	"Slip-off Hill" Sturgis, S. D.	1.3

UPPER CRETACEOUS

DAKOTA FORMATION. The Dakota formation has been reported to contain little or no selenium (1,13). This formation, like the Lakota, is believed to be an unfavorable environment for the deposition and retention of the element in important amounts. The lack of seleniferous vegetation on the formation confirms this conclusion.

GRANEROS FORMATION. The thick Graneros shales of the Black Hills and elsewhere probably contain, in common with other marine beds, small amounts of selenium. A few available analyses confirm this conclusion (1,4,5). Highly seleniferous plants have not been found growing on the formation, nor on soils derived from it. The Graneros is dominantly non-calcareous. Observations by the authors suggest that, for the most part, non-calcareous formations do not produce toxic soils and vegetation.

GREENHORN FORMATION. A preliminary investigation of the selenium content of the Greenhorn formation suggests that it contains a low concentration of selenium. However, it probably does contain more of the element than the underlying formations.

Byers, et al. (6) reported the selenium content at various positions within the Greenhorn formation in Pueblo county, Colorado, to range between 0.2 p.p.m. and 3.0 p.p.m. Vegetation from these beds, however, contained selenium up to 260 p.p.m. These results are somewhat lower than the determinations on unleached samples from the Irish Creek well reported from this laboratory (8) (Table 3) which show a range between 0.0 p.p.m. and 6.0 p.p.m. with concentrations of 3.0 p.p.m. or more at several positions in the formation.

Composite samples collected in Fall River county (Table 4) and Butte county (Table 5) confirm the opinion of the authors that the selenium content of the

TABLE 3. Greenhorn Formation Irish Creek Well Core (8) S. E. 1/4, Sec. 17, T. 15 N., R. 20 E., Ziebach Co., S. D.

Depth Feet	*Selenium Content p.p.m.*	*Depth Feet*	*Selenium Content p.p.m.*
2334-2349	2.7	2515-2529	2.8
2349-2363	1.5	2529-2557	1.0
2363-2365	no analysis	2557-2572	3.0
2365-2375	4.0	2572-2608	0.0
2375-2393	6.0	2608-2625	1.88
2393-2416	4.3	2625-2649	0.0
2416-2492	3.5	2649-2670	2.2
2492-2515	0.8	2670-2680	2.5

TABLE 4. Greenhorn Formation, S. W. 1/4, Sec. 13, T. 9 S., R. 2 E., South of Edgemont, Fall River Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G64	36-44	0.0			
G63	26-36	1.6	*Mentzelia decapetala* Pursh	V66	1.6
G62	16-26	1.3			
G61	6-16	3.2	*Astragalus racemosus* Pursh	V65	13.8
G60	0-6	1.7			

TABLE 5. Greenhorn Formation, N. E. 1/4, Sec. 27, T. 9 N., R. 2 E., Butte Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G256	50-60	0.0			
G255	40-50	0.8	*Mentzelia decapetala* Pursh	V267	1.0
G254	30-40	1.0	*Mentzelia decapetala* Pursh	V266	8.0
G253	20-30	0.0	*Mentzelia decapetala* Pursh	V265	0.0
G252	10-20	0.0	*Grindelia squarrosa* (Pursh) Dunal.	V263	2.0
G251	0-10	0.0	*Astragalus racemosus* Pursh	V264*	4.0
Unsampled interval 92 feet					
G250	40-49	0.0	*Grindelia squarrosa* (Pursh) Dunal.	V262	3.4
G249	30-40	0.0			
G248	20-30	0.6	*Stanleya bipinnata*	V260†	60.0
G247	10-20	0.0	*Grindelia squarrosa* (Pursh) Dunal.	V258	4.0
			Astragalus racemosus Pursh	V259	125.0
G246	0-10	0.5	*Grindelia squarrosa* (Pursh) Dunal.	V257	1.4

* On lower 5 feet. † Collected on G247 also.

Greenhorn formation in South Dakota is so low that toxic soils are not likely to be developed from it. However, in South Dakota as elsewhere, certain positions within this formation support the growth of "converter" plants although the selenium content of these plants is relatively low.

TABLE 6. Carlile Formation, Irish Creek Well Core (8), S. E. ¼., Sec. 17, T. 15 N., R. 20 E., Ziebach Co., S. D.

Depth Feet	*Selenium Content p.p.m.*	*Depth Feet*	*Selenium Content p.p.m.*
1950-1975	0.7	2165-2204	0.4
1975-2000	0.0	2204-2243	0.5
2000-2035	0.5	2243-2278	3.0
2035-2050	1.5	2278-2310	0.5
2050-2081	0.4	2310-2315	3.0
2081-2134	0.5	2315-2334	3.0
2134-2165	0.0		

CARLILE FORMATION. Available analyses of this formation indicate that it is low in selenium, although rarely selenium free (6,8). The samples of Carlile from the Irish Creek well (Table 6) contain 0.0 to 3.0 p.p.m. of selenium. No cases of selenium poisoning have been observed on this formation in South Dakota. Furthermore, the formation does not support the growth of seleniferous plants in this state.

NIOBRARA FORMATION. The chalky, and calcareous marls and shales of the Niobrara formation are the most persistently seleniferous beds of the Great Plains region. Very few analyses of bedrock or soils derived from the formation are selenium free. Most outcrops expose highly seleniferous beds in South Dakota (Tables 7-21).

The formation in South Dakota, Kansas, and Nebraska has been divided into two members a lower one, the Fort Hays, and upper member, the Smoky Hill. These members differ in selenium content where identification has been made.

FORT HAYS MEMBER. The Fort Hays member of the Niobrara is commonly low in selenium and other investigators apparently are in agreement with this view (5). Data previously published on eastern South Dakota also supports this conclusion (8). Chalky beds, at or near the base of the Niobrara formation, around the Black Hills also appear to be relatively low (Tables 7 and 9) although those analyzed contain selenium enough to cause some trouble and seleniferous vegetation grows on these beds. Positive identification of these beds as Fort Hays has not been made, however.

Smoky Hill Member. The Smoky Hill member of the Niobrara formation is the most persistent highly seleniferous succession of beds outcropping on the Great Plains. Data previously published (5, 6, 8) support this conclusion. In the present survey the member has been studied and adequately sampled. (Table 7 to 21 inclusive). Selected successions of composite analyses of the Niobrara, mostly Smoky Hill, presented in Fig. 12 show that although variation in parts of the Smoky Hill occur, selenium is an important constituent wherever the member is exposed. Study of the tables indicates that the lower part of the Smoky

Hill member, in general, contains less selenium than the upper part of the member. (See Tables 10 and 11 and Table 12 samples 6Y-9Y, 10 and 11.)

Particular attention is directed to a set of composite samples collected in Sec. 17, T. 104 N., R. 71 W., Lyman county, (Table 13). These samples cover the uppermost 82 feet of the upper Smoky Hill in this area. The average selenium content of this considerable thickness of beds is 32.9 p.p.m. The lowest analysis of a 10-foot composite is 16.0 p.p.m. which is a relatively high concentration. The highest is 45.0 p.p.m. selenium. The average of the succession of 30 feet of beds lying in the interval 22 to 52 feet below the top of the Niobrara is 42.7 p.p.m. selenium, without doubt the highest average selenium concentration of any succession of this thickness known at any position at any place.

Other significant successions of beds of the upper Smoky Hill are those from SE 1/4, Sec. 31, T. 7 N., R. 6 E., Meade county (Table 14), one in the SE1/4, Sec. 35 T. 1 N., R. 8 E., Pennington county (Table 15) and one in the SW 1/4, Sec. 18, T. 10 S., R. 3 E., Fall River county (Table 16). All of these analyses indicate that the upper portion of the Smoky Hill is highly seleniferous.

Pierre Formation. The Pierre formation probably contains selenium, at least in minute amounts, throughout most of the succession and at most locations. Wide variation in selenium content at various positions within the formation are

TABLE 7. Fort Hays Member of the Niobrara Formation, Carlile Contact, Sec. 33, T. 8 S., R. 1 W., 3/4 mile N. Junction 18 and 85, Niobrara Co., Wyo.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G14	10	Niobrara	3.4	*Astragalus racemosus* Pursh	V13	526.0
		Contact				
G15	8	Carlile	3.0			

TABLE 8. Fort Hays Member of the Niobrara Formation (8)

No.	*Lab. No.*	*Remarks*	*Selenium Content p.p.m.*
1	1281	Composite, upper 5 feet of member. Lake Henry Spillway, Scotland, Bon Homme Co., S. D.	3.0
2	1287	10 foot composite, Quarry, Spirit Mound, Clay Co., S. D.	1.0
3	1290	10 foot composite, Spirit Mound above quarry, Clay Co., S. D.	1.5
4	1291	Composite, 8-10 feet of beds below uppermost 5 feet (No. 1) Spillway, Lake Henry, Scotland, S. D.	0.3
5	1295	Basal Fort Hays, 10 foot composite N. W. 1/4, Sec. 9, T. 93 N., R. 52 W., Clay Co., S. D.	0.0
6	1297	N. E. 1/4, N. E. 1/4, Sec. 12, T. 94 N., R. 54 W., Yankton Co., S. D.	0.0

TABLE 9. Niobrara Formation (Probably Fort Hays Member), Elev. 2810 at (0-10), S. W. 1/4, Sec. 6, T. 8 N., R. 5 E., 1/8 mile N. 212, below Miller Butte samples, Butte Co., S. D.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G210	0-10	Elev. 2810 ft.	5.5	*Astragalus racemosus* Pursh	V213	50.0
				Mentzelia decapetala Pursh	V214	2.0
				Grindelia squarrosa (Pursh) Dunal.	V215	2.0
				Mentzelia decapetala Pursh	V216	3.2
G212	20-24		5.0			

TABLE 10. Niobrara Formation (lower) Smoky Hill Member, N. E. 1/4, Sec. 6, T. 8 N., R. 5 E., Hill by Miller Butte, Butte Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G227	90-100	2.2			
G226	80-90	0.0			
G225	70-80	1.8			
G224	60-70	8.0	*Grindelia squarrosa* (Pursh) Dunal.	V229	7.0
G223	50-60	4.1			
G222	40-50	8.0	*Astragalus racemosus* Pursh	V228	625.0
G221	30-40	8.0			
G220	20-30	5.0			
G219	10-20	8.7			
G218	0-10	8.6	*Stanleya bipinnata* (on wash)	V230	385.0

TABLE 11. Niobrara Formation (lower) Smoky Hill Member (red bed contact), (See Figure 11), 8.5 miles W. of Pine Ridge, Shannon Co., S. D.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content*	*Vegetation*	*Lab. No.*	*Selenium Content*
G108	8½-18½	Gray bed	.7			
G107	4-8½	Red bed	3.5			
G106	0-4	Mixed Niobrara and Red beds	1.5			
		Contact				
G105	20-25	Yellow Niobrara	11.6			
G104	10-20	Yellow Niobrara	7.0	*Astragalus racemosus* Pursh	V102	100.0
G103	0-10	Yellow Niobrara	7.3			
G111	10-20	Niobrara	8.3	*Astragalus racemosus* Pursh	V112	600.0
G112	18 feet	Concretions	.5	Stanleya bipinnata	V113	40.0
G110	0-10	Niobrara	5.0			

FIG. 11. (See Table 11) Niobrara Formation (red bed contact)
1. White River 3. Red bed on mixed Niobrara and red beds
2. Gray bed 4. Yellow Niobrara

TABLE 12. Smoky Hill Member of the Niobrara Formation (8)

No.	*Lab. No.*	*Remarks*	*Selenium Content p.p.m.*
1Y	47	Abandoned cement plant, N. E. ¼, Sec. 17, T. 93 N., R. 56 W., Yankton Co., S. D.	3.0
2Y	48		7.0
3Y	49		9.0
4Y	50		11.0
5Y	51	Numbers 1Y to 9Y inclusive are 10 foot composites in stratigraphic order with 9Y at base, 1Y at top	16.0
6Y	52		5.0
7Y	53		3.0
8Y	54		2.0
9Y	55		2.5
10	1288	Lower Smoky Hill, composite of 10-12 feet, N. E. ¼, N. E. ¼, Sec. 6 T. 94 N., R. 53 W., Yankton Co., S. D.	3.5
11	1289	Basal Smoky Hill, Spillway, Lake Henry, Bon Homme Co., S. D., composite of 5 feet	6.5
12	1272	Uppermost Smoky Hill, in contact with Sharon Springs, center Sec. 23, T. 95 N., R. 58 W.	1.3
13	1272	Upper, white, N. E. ¼, N. E. ¼, Sec. 9, T. 94 N., R. 35 W.	4.0

TABLE 13. Niobrara Formation, Sec. 17, T. 104 N., R. 71 W., Railroad cut at Oacoma, west end of Missouri River Bridge, Lyman Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G608	70-82	26.0			
G607	60-70	24.0			
G606	50-60	16.0	*Gutierrezia sarothrae* (Pursh) Britt. and Rusby	V609*	160.0
G605	40-50	41.0	*Aster multiflorus* Ait.	V610*	34.0
			Astragalus racemosus Pursh	V611*	1420.0
G604	30-40	42.0	*Mentzelia decapetala* Pursh	.V612*	2.6
G603	20-30	45.0			
G602	10-20	35.0			
G601	0-10	29.0			

* Collected at 30 to 50 feet.

TABLE 14. Niobrara Formation, Smoky Hill (upper) Member, S. E. 1/4, Sec. 31, T. 7 N., R. 6 E., Meade Co., S. D.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G164	60-65		6.3	*Astragalus racemosus* Pursh.	V181	2,640.0
				Gutierrezia sarothrae (Pursh) Britt. and Rusby	V182	46.4
G163	50-60		27.0	*Astragalus racemosus* Pursh.	V179	1,160.0
		Gypsum from joints (secondary)	4.3	*Gutierrezia sarothrae* (Pursh) Britt. and Rusby	V180	44.0
G162	40-50		16.0	*Astragalus racemosus* Pursh.	V177	880.0
				Gutierrezia sarothrae (Pursh) Britt. and Rusby	V178	18.0
G161	30-40		15.0	*Astragalus racemosus* Pursh.	V175	1,960.0
				Aster multiflorus Ait.	V183	52.0
				Gutierrezia sarothrae (Pursh) Britt. and Rusby	V176	8.0
G160	20-30		9.0	*Astragalus racemosus* Pursh.	V172	760.0
				Aster multiflorus Ait.	V173	48.0
				Gutierrezia sarothrae (Pursh) Britt. and Rusby	V179	8.8
G159	10-20		18.5	*Aster multiflorus* Ait.	V170	165.0
				Gutierrezia sarothrae (Pursh) Britt. and Rusby	V171	22.0
G158	0-10		21.0	*Astragalus racemosus* Pursh.	V166	4,100.0
				Aster multiflorus Ait.	V167	90.0
				Gutierrezia sarothrae (Pursh) Britt. and Rusby	V168	14.0

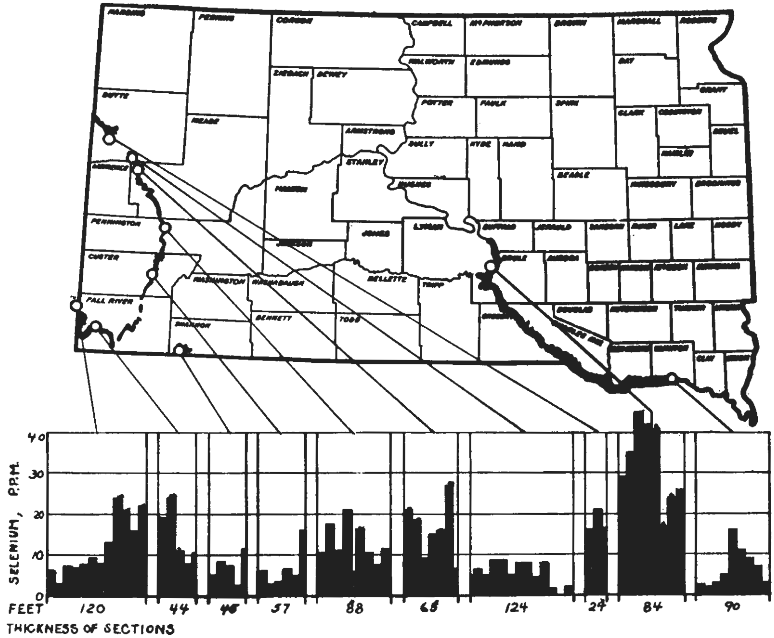

FIG. 12. Map shows general outcrop areas of the Niobrara formation in black. Circles locate sections sampled. Graph shows selenium content of the sections sampled.

TABLE 15. Niobrara Formation, Smoky Hill (upper) Member, S. E. 1/4, Sec. 35, T. 1 N., R. 8 E., Rapid Creek, Pennington Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G141	83-88	5.7			
G140	73-83	21.0			
G139	63-73	11.0			
G138	53-63	17.2			
G137	43-53	10.4	*Astragalus racemosus* Pursh	V142	150.0
G146	33-43	11.2			
G145	21-32	7.2	*Mentzelia decapetala* Pursh	V147	1.2
			Stanleya bipinnata (on wash)	V148	525.0
G144	10-20	10.6			
G143	0-10	16.2	*Aster multiflorus* Ait. (on wash)	V149	19.2

TABLE 16. Niobrara Formation, Smoky Hill Member, uppermost beds—in contact with Sharon Springs (Table 22), S. W. 1/4, S. W. 1/4, Sec. 18, T. 10 S., R. 3 E., Fall River Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G74	40-44	10.5			
G73	30-40	8.0			
G72	20-30	11.0	*Stanleya bipinnata*	V69	1140.0
G71	10-20	24.0			
G70	0-10	19.0			

TABLE 17. Niobrara Formation, N. W. 1/4, Sec. 26, T. 10 N., R. 2 E., 8.5 miles N. Mobile Station at Belle Fourche, Butte Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G235	20-25	16.5			
G234	10-20	21.0	*Stanleya bipinnata*	V237	2260.0
			Agropyron smithii Rydb.	V239	3.0
G233	0-10	16.0	*Grindelia squarrosa* (Pursh) Dunal.	V236	12.0

TABLE 18. Niobrara Formation, S. E. 1/4, Sec. 16, T. 4 S., R. 10 E., 2.8 miles E. of Fairburn, Custer Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G131	50-57	16.0			
G130	40-50	5.0	*Stanleya bipinnata*	V135	575.0
G129	30-40	6.3	*Astragalus racemosus* Pursh	V136	315.0
G128	20-30	3.3			
G127	10-20	2.7	*Mentzelia decapetala* Pursh	V134	4.0
G126	0-10	6.0			

TABLE 19. Niobrara Formation, S. W. 1/4, Sec. 32, T. 8 S., R. 1 E., Fall River Co., S. D.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G11	20-30	Shale	1.6	*Astragalus racemosus Pursh.*	V12	80.0
G10	10-20	Shale	7.0			
G9	0-10	Shale	3.3			

TABLE 20. Niobrara Formation, Irish Creek Well Core (8), S. E. 1/4, Sec. 17, T. 15 N., R. 20 E., Ziebach Co., S. D.

Depth Feet	*Selenium Content p.p.m.*
1680-1720	15.0
1720-1742	13.0
1742-1753	14.0
1753-1842	16.0
1842-1878	22.0
1878 Bentonite	113.0
1878-1900	12.0
1900-1939	11.5
1939-1950	10.0

TABLE 21. Niobrara and Sharon Springs Contact, S. E. 1/4, Sec. 33, T. 8 S., R. 1 W., Niobrara Co., Wyo.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G28	1 ft.	Sharon Springs	21.0			
		(contact)				
G27	110-120	Niobrara	22.0			
G26	100-110		16.0			
G25	90-100		21.0	*Astragalus racemosus* Pursh.	V41	500.0
				Stanleya bipinnata	V42	136.0
G24	80-90		24.0	*Stanleya bipinnata*	V40	150.0
G23	70-80		13.0	*Stanleya bipinnata*	V39	376.0
G22	60-70		8.0	*Stanleya bipinnata*	V38	240.0
G21	50-60		9.2	*Stanleya bipinnata*	V37	200.0
G20	40-50		7.5	*Astragalus racemosus* Pursh.	V35	186.0
				Stanleya bipinnata	V36	626.0
G19	30-40		7.0	*Stanleya bipinnata*	V34	550.0
G18	20-30		7.3	*Astragalus racemosus* Pursh.	V32	320.0
				Stanleya bipinnata	V33	476.0
G17	10-20		0.6	*Astragalus racemosus* Pursh.	V30	460.0
				Stanleya bipinnata	V31	350.0
G16	0-10		6.1	*Astragalus racemosus* Pursh.	V28	2,700.0
				Stanleya bipinnata	V29	520.0

indicated by this and previous investigations. Important and significant variations from place to place are also indicated. Preliminary work has shown that although the selenium content of much of the Pierre is low, probably no greater than that in many other marine deposits, that in certain members it is unusually high and that even in these important variations in selenium content occur (8). The Sharon Springs member was found to be highly seleniferous and the Mobridge (Interior of this report) locally contains much selenium. Notation was also made of high selenium content in the upper part of the Virgin Creek. The evidence presented in this bulletin corroborates and amplifies these preliminary findings.

Sharon Springs Member. The Sharon Springs member of the Pierre formation is one of the most seleniferous successions in South Dakota, and probably elsewhere in the Great Plains province. The dark fissile shales of the lower Sharon Springs contain a high concentration of selenium, wherever they have been sampled. The less fissile beds of the upper Sharon Springs, for the most part, are only moderately seleniferous although beds containing much selenium have been found among them. Analyses of the beds of this member are presented in Tables 22 to 28 inclusive and important sections are shown graphically in Figure 13.

A representative section sampled at the mouth of Bull Creek, Lyman county (Table 26) gave an average selenium content for 50 feet of beds of 11.3 p.p.m. even though the average of the upper 30 feet was only 3.5 p.p.m. The lower 20 feet are notably high in selenium with an average of 24 p.p.m. Around the Black Hills, the lower Sharon Springs is more than double the thickness at the mouth of Bull Creek but the average selenium content is essentially the same, being 11.6 p.p.m. (Table 22) southeast of Provo, Fall River county. The total selenium content of the lower Sharon Springs south of the Black Hills is thus approximately twice that along the Missouri river, as suggested by analyses. These sets of analyses compared each include the entire lower Sharon Springs at the two localities. Other sets around the Black Hills do not sample the lower Sharon Springs completely (Tables 23, 24 and 25) but indicate high selenium content. The Brennan section (Table 24) averages 16.9 p.p.m. for the uppermost 20 feet whereas 2 miles south of Buffalo Gap the upper 50 feet averages 9.9 p.p.m. selenium (Table 23).

The upper Sharon Springs, wherever it has been adequately sampled, contains much less selenium than the lower beds. At the mouth of Bull Creek, Lyman county, where the entire succession was compositely sampled excepting the lower 20 feet (Table 26) gave an average of 2.8 p.p.m. of selenium for 76 feet of beds.

TABLE 22. Sharon Springs Member of the Pierre Formation, N. ½, Sec. 19, T. 10 S., R. 3 E., S. E. of Provo, Fall River Co., S. D.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G90	150-156		0.9			
G89	140-150		4.2			
G88	130-140		3.5			
G87	120-130		4.0			
G86	110-120		4.0			
G85	100-110		19.2			
G84	90-100		9.0			
G83	80-90		17.5			
	80-83	Bentonite	.8			
G82	70-80		18.0	*Prunus melanocarpa* (A. Nels) Rydb.	V92	1.0
G81	60-70		13.2			
G80	50-60		12.4			
G79	40-50		10.6			
G78	30-40		9.6			
G77	20-30		20.0			
G76	10-20		8.5			
G75	0-10		24.0			

This is about one-fourth the average of the lower Sharon Springs at the same location. The representative succession southeast of Provo, composited over 50 feet of beds, gave an average selenium content of 2.6 p.p.m. which, although not strictly comparable, is again approximately one-fourth the average content of the lower Sharon Springs at the same place. Two miles south of Buffalo Gap, the lower 30 feet of the upper Sharon Springs gave an average of 7.6 p.p.m. There is the possibility here, however, that the lower 10 feet, which contained 13.0 p.p.m., may belong with the lower Sharon Springs. Analyses of samples from a core of the Irish Creek well (8) (Table 28), taken at intervals, are high in selenium with the exception of one taken between 1605 and 1647 feet which contained only 4.5 p.p.m. of selenium.

TABLE 23. Sharon Springs Member of the Pierre Formation, 2 miles S. of Buffalo Gap on line between Sec's. 5 and 8, T. 7 S., R. 7 E., Fall River Co., S. D.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G122	70-80		4.1			
G121	60-70		5.8	*Astragalus racemosus* Pursh.	V125	11.0
G120	50-60		13.0			
G119	40-50		7.8			
G118	30-40		11.2			
G117	20-30		12.0			
	20-22½	Bentonite	0.6			
G116	10-20		10.5			
G115	0-10		8.5			

TABLE 24. Sharon Springs Member of the Pierre Formation, S. E. ¼, Sec. 13, T. 1 S., R. 8 E., Pennington Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G155	50-58	3.0	*Aster multiflorus* Ait.	V156	0.0
G154	40-50	3.6			
G153	30-40	6.1	*Aster multiflorus* Ait.	V157*	1.0
G152	20-30	4.8			
G151	10-20	21.0			
G150	0-10	12.8			

* On wash from entire section.

The reason for the differences in the selenium content of the lower and upper Sharon Springs is not apparent. The selenium content in the upper beds may have been proportionally low when the sediments were deposited. On the other hand, leaching since exposure may be responsible for differences in analyses. The upper Sharon Springs appears to be less impervious to water than the lower beds, and the upper Sharon Springs probably has leached deeper and at a more rapid rate than the lower beds of the member. It is the present view of the authors, however, that the primary selenium content of the upper Sharon Springs was originally fairly low. Soils developed on these beds retain sufficient selenium, however, to render certain areas toxic.

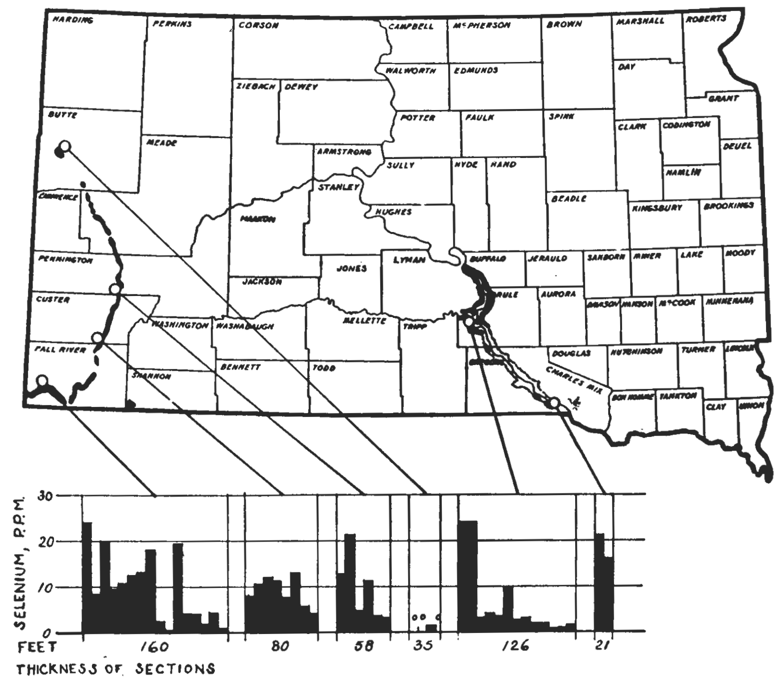

FIG. 13. Map shows general outcrop of Sharon Springs member of the Pierre formation. Circles locate sections sampled. Graph shows selenium content of sections sampled.

TABLE 25. Sharon Springs Member of the Pierre Formation, S. E. ¼, S. W. ¼, Sec. 8, T. 11 N., R. 3 E., 2.6 miles N. of Indian Creek on S. D. 85, Butte Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	
G272	30-35	0.0	
G271	20-30	1.3	No Vegetation
G270	10-20	0.0	
G269	0-10	0.0	

TABLE 26. Sharon Springs Member of the Pierre Formation, Sec. 32, T. 103 N., R. 72 E., Lyman Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
K14	120-126	1.5			
K13	110-120	0.8			
K12	100-110	0.7			
K11	90-100	2.0			
K10	80-90	2.0			
K9	70-80	2.9			
K8	60-70	2.6			
K7	50-60	10.0			
K5	40-50	3.4			
K4	30-40	4.2			
K3	20-30	3.0			
K2	10-20	24.0			
K1	0-10	24.0	*Astragalus racemosus* Pursh.	K6	200.0

TABLE 27. Sharon Springs Member of the Pierre Formation (8)

No.	*Remarks*	*Selenium Content p.p.m.*
1	Abandoned cement plant, N. E. 1/4, Sec. 17, T. 93 N., R. 56 W., Yankton Co., S. D.	45.0
2	Composite, upper 10 feet, south end of Rosebud bridge, Gregory Co., S. D.	21.0
3	Composite, lower 11 feet, south end Rosebud bridge, Gregory Co., S. D.	16.0
4	Composite, upper 15 feet, Oacoma Hill Lyman Co., S. D.	0.0

TABLE 28. Sharon Springs Member of the Pierre Formation (8), S. E. 1/4, Sec. 17, T. 15 N., R. 20 E., Irish Creek Well Core, Ziebach Co., S. D.

Depth Feet	*Selenium Content p.p.m.*
1445-1502	18.0
1502-1535	12.5
1535-1554	10.5
1554-1605	10.0
1605-1647	4.5
1647-1680	10.0

Sully Member. Gregory zone: The Gregory marl zone was previously found to be low in selenium content, even where the rock was fresh and unweathered (8). These findings are believed to indicate the selenium content correctly. Since the zone is too thin to form more than very restricted outcrops, it was not further investigated in the present study.

TABLE 29. Sully Member of the Pierre Formation, Gregory Zone (8), S. E. 1/4, Sec. 17, T. 15N., R. 20 E., Irish Creek Well Core, Ziebach Co., S. D.

Depth Feet	*Selenium Content p.p.m.*
1372-1388	0.0
1388-1423	0.7
1423-1445	1.5

Agency shale: Previous investigation of the selenium content of the Agency shale indicate that this succession contains selenium in very small amounts (8). Further and more adequate sampling during the present investigations corroborates previous evidence. Of particular interest is the composite sampling of 100 feet of beds of the type section near Cheyenne Agency (Table 30) which shows an average of analyses of only 0.5 p.p.m. of selenium. The maximum was only 2.1 p.p.m.

TABLE 30. Agency Shale (Type Section) of the Sully member of the Pierre Formation, N. W. 1/4, Sec. 6, T. 12 N., R. 32 E., South bank of Missouri River at Whitlock's Crossing, west side of bridge, Dewey Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	
G429	90-100	0.0	
G428	80-90	0.0	
G427	70-80	0.0	
G426	60-70	0.5	No Vegetation
G425	50-60	1.0	
G424	40-50	0.0	
G423	30-40	0.5	
G422	20-30	2.1	
G421	10-20	1.0	
G420	1-10	0.0	

TABLE 31. Sully Member of Pierre Formation, Agency Shale (8)

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*
1887	15-30	Samples from Railway cut, Ft. Pierre, Stanley county, S. D. Composites of thickness as indicated	2.0
1864	0-15		0.3

TABLE 32. Sully Member of the Pierre Formation, Agency Zone (8), S. E. 1/4, Sec. 17, T. 15 N., R. 20 E., Irish Creek Well Core, Ziebach Co., S. D.

Depth Feet	*Selenium Content p.p.m.*
1130-1186	1.0
1186-1247	0.7
1247-1274	1.3
1274-1331	5.0
1331-1372	0.0

Oacoma beds: The selenium content of the Oacoma beds has been previously studied (8) and found to contain selenium in amounts varying between 0.0 p.p.m. and 5.0 p.p.m. (Tables 33 and 34). Further studies of this thin zone have not been made during this investigation.

TABLE 33. Sully Member of the Pierre Formation, Oacoma Zone (8)

No.	*Lab. No.*	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*
1T	1886	30-35	Samples numbered 1T to 3T inclusive are a stratigraphic series, each a	0.0
2T	1871	15-30	composite of beds as indicated. 1T at top, 3 T at base.	0.4
3T	1882	0-15		
1P	1889	30-35	Samples numbered 1P to 3 P inclusive are a stratigraphic series, each a	2.2
2P	1867	15-30	composite of beds as indicated. 1P at top, 3P at base. Ft. Pierre,	2.5
3P	1865	0-15	below Verendrye monument.	
1M	42A		South end Rosebud Bridge, 25 foot composite, including some Agency.	0.5
2M	43		Rosebud Bridge, Gregory county, S. D.	2.0
3M	33		Gregory Co., S. D.	3.0
4M	35		Gregory Co., S. D.	5.0
5M	34		Lyman Co., S. D.	Trace

TABLE 34. Sully Member of the Pierre Formation, Oacoma Zone (8), S. E. 1/4 , Sec. 17, T. 15 N., R. 20 E., Irish Creek Well Core, Ziebach Co., S. D.

Depth Feet	*Selenium Content p.p.m.*
1042-1076	1.2
1076-1101	0.5
1101-1130	1.0

Verendrye beds: The Verendrye beds of the Sully member of the Pierre have likewise been found to be low in selenium content. Adequate samplings at widely scattered locations (Tables 35, 36 and 37) did not result in any analysis greater than 2.0 p.p.m. for any 10 foot composite. It was observed, however, that a zone within the member supports *Astragalus racemosus* of relatively low selenium content (44.0 p.p.m.). This zone was identified by these plants and by lithology east, northeast, and north of Newell and north of Belle Fourche and is possibly continuous between these points.

TABLE 35. Sully Member of the Pierre Formation, Verendrye Zone, Sec. 36, T. 7 N., R. 17 E., Four Corners Bridge, Cheyenne River, Meade Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	
G354	30-40	0.6	
G353	20-30	1.0	No Vegetation
G352	10-20	1.2	
G351	0-10	0.5	

TABLE 36. Sully Member of the Pierre Formation, Verendrye Zone (8)

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*
1868	65-78	Samples 1 to 6 are composites of the type section of the Verendrye covering	1.3
1885	50-65	intervals as indicated; 6 at base of section. Fort Pierre, Stanley Co., S. D.	2.0
1881	35-50		1.0
1870	30-35		1.5
1883	15-30		0.5
1884	0-15		0.0
	0-25	Sec. 10, T. 96 N., R. 67 W., Charles Mix Co., S. D. 25 feet composite.	0.0

TABLE 37. Sully Member of the Pierre Formation, Verendrye Zone (8), S. E. 1/4, Sec. 17, T. 15 N., R. 20 E., Irish Creek Well Core, Ziebach Co., S. D.

Depth Feet	*Selenium Content p.p.m.*
959-979	1.0
979-998	1.3
998-1017	1.0

Virgin Creek Member. Lower Virgin Creek: The Virgin Creek member of the Pierre is characteristically low in selenium at most places and at most positions (Tables 38 to 42 inclusive). Analyses of 10-foot composites of 140 feet of the member at the type locality (Table 38) are thought to be typical of the selenium content. Inspection of these analyses indicate a narrow range from 0.0 p.p.m. up to a maximum of only 2.5 p.p.m. The average selenium content of 140 feet of beds is 1.0 p.p.m.

TABLE 38. Virgin Creek Member (Type Section) of the Pierre Formation, Sec. 29, T. 16 N., R. 29 E., One mile S. E. of Promise, S. D., on Virgin Creek, Dewey Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	
G443	130-140	1.0	
G422	120-130	(not analyzed)	
G441	110-120	2.0	
G440	100-110	0.0	No Vegetation
G439	90-100	1.5	
G438	80-90	1.5	
G437	70-80	0.0	
G436	60-70	2.5	
G435	50-60	0.5	
G434	40-50	0.4	
G433	30-40	1.0	
G432	20-30	0.0	
G431	10-20	1.2	
G430	0-10	0.0	

Although the selenium content of the member as a whole is low, certain beds in the upper part of the member, as least locally, are sufficiently high in selenium content to cause considerable concern. A zone of calcareous shale, two or more thin beds of nearly pure chalk, containing three bentonite beds two to three inches thick, lies approximately 30 feet above the base of the upper Virgin Creek in Lyman and Stanley counties. It is only about 10 feet thick. This zone was sampled as a composite, 23.6 miles west of Fort Pierre and in the spillway on the Dean farm in the NE¼,SE¼, Sec. 28, T. 3 N., R. 31 E. The first composite contained only 1.5 p.p.m. and the second 2.0 p.p.m. selenium. Bed to bed analyses of the Dean succession gave selenium contents, as indicated in Table 39. Although none of these beds are extremely rich in selenium, the maximum being 6.0 p.p.m. plants growing on this zone absorb much selenium. Furthermore, the Virgin Creek is relatively thin in this area and the seleniferous Interior is thus topographically near this zone. This zone has been observed where serious difficulties have been experienced in livestock poisoning. The authors regard this zone as dangerous in Lyman and Stanley counties, where it is favorably exposed.

The uppermost Virgin Creek near Landing Creek in Gregory county is also highly seleniferous. Analyses of the upper 25 feet as composites from the NW¼ Sec. 22, T. 100 N., R. 72 W. are listed in Table 42. The average selenium content of these dark gumbo forming shales is 26 p.p.m. The lower 10 feet of this set yielded 52.0 p.p.m. selenium, the highest average selenium content of any 10-foot composite discovered in this investigation. Evidence thus indicates that in Lyman, Stanley and Gregory counties the upper half of the Virgin Creek contains much selenium, and is an important source of selenium in soils and plants of this area.

TABLE 39. Virgin Creek Member of the Pierre Formation, S. E. 1/4, Sec. 28, T. 3 N., R. 31 E., Spillway at Dean Farm, Stanley Co., S. D.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	
G374		Chalk	6.0	
G373		Bentonite	5.0	No Vegetation
G372		Shale	4.3	
G371		Bentonite	2.0	
G370		Shale	5.5	
G369	3 1/4-5 1/4	Chalk	0.5	
G368	3-3 1/4	Bentonite	0.0	
G367	0-3	Chalky shale	5.0	

TABLE 40. Virgin Creek Member of the Pierre Formation (8)

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*
1873	15-25 (composite)	24.85 miles west of Ft. Pierre on U. S. Highway No. 14. Lower Virgin Creek	3.0
1888	0-15 (composite)	24.85 miles west of Ft. Pierre on U. S. Highway No. 14. Lower Virgin Creek.	2.0
	10 ft. (composite)	Road cut, Sec. 10, T. 96 N., R. 67 W., Charles Mix Co., S. D.	3.5
1894	10 ft. (composite)	Midland Hill, north of Midland, Haakon Co., on U. S.Highway 14. Composite of uppermost 10 feet of formation	3.0

TABLE 41. Virgin Creek Member of the Pierre Formation (8), S. E. 1/4, Sec. 17, T. 15 N., R. 20 E., Irish Creek Well Core, Ziebach Co., S. D.

Depth Feet	*Selenium Content p.p.m.*
670-864	1.0
864-897	1.5
897-921	1.0
921-959	1.5

There is the possibility that the high selenium content of the upper Virgin Creek is due to secondary enrichment by downward moving waters which have leached selenium from the Interior member. The impervious character of the Virgin Creek is favorable to this possibility. Were this the case, however, a considerable percentage of the selenium should probably be soluble as it is in the salt crusts having a similar origin. When investigated, however, the selenium in the upper

Virgin Creek appeared to be mostly in an insoluble form. Although secondary genesis of the selenium in the upper Virgin Creek is not precluded, syngenetic deposition seems to be most probable.

Interior Member. Selenium concentration in the Interior member of the Pierre is highly variable. Preliminary investigation indicated great variation, particularly in selenium content at various points in the outcrop area (8). Field and laboratory work of the present investigation verify this view and furnish considerable additional data on the nature of this variation. In a general way, the selenium content varies from high in the eastern and southeastern portion of the outcrop area to low in the western and northwestern portion (Figure 14).

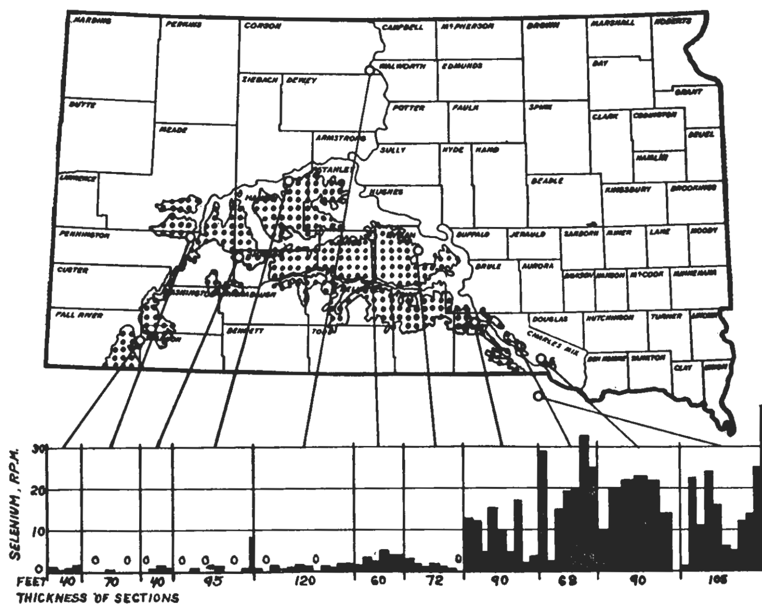

FIG. 14. Dotted areas on map show general outcrop of the Interior member of the Pierre formation. Circles locate sections sampled. Graph shows selenium content of sections.

The highest selenium content of these beds, according to analyses, is in Charles Mix, Gregory, and Lyman counties South Dakota, and in the adjacent counties in Nebraska (Tables 42 to 45 inclusive). The average selenium content of the entire member, a total of 90 feet, was 18.5 p.p.m. in Sec. 3, T. 96 N., R. 67 W. (Table 44). In section 33, T. 98 N., R. 68 W., the average of 68 feet of beds (Table 45) was 19.7 p.p.m. The average selenium content of 105 feet of beds in SE$\frac{1}{4}$, NW$\frac{1}{4}$, Sec. 30, T. 33 N., R. 11 W., Boyd county, Nebraska was 19.1 p.p.m. (Table 43). These representative successions indicate that the reserve selenium stored in the Interior of this area is very great and that conditions of outcrop and that factors in transference or retention of selenium in derived soils and absorption by plants determine whether or not seriously toxic areas are produced on it. It is fortunate indeed that this member is covered in many places in this area, and that optimum conditions are rarely, if ever, completely realized.

TABLE 42. Interior Member of the Pierre Formation, (Virgin Creek Contact), East of Dixon Experiment Plots, Sec. 22, T. 100 N., R. 72 W., Gregory Co., S. D.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G509	80-90	Interior	3.8			
G508	70-80	Interior	2.0	*Bouteloua curtipendula* (Michx.) Torr.	V512	0.0
G507	60-70	Interior	17.0			
G506	50-60	Interior	4.6			
G505	40-50	Interior	10.0			
G504	30-40	Interior	15.4			
G503	20-30	Interior	4.5			
G502	10-20	Interior	12.5			
G501	0-10	Interior	13.0	*Astragalus racemosus* Pursh.	V511	4,800.0
		Contact				
G500	20-25	Virgin Creek	6.0			
G499	10-20	Virgin Creek	10.0			
G498	0-10	Virgin Creek	52.0			

TABLE 43. Interior Member of the Pierre Formation, S. E. 1/4, N. W. 1/4, Sec. 30, T. 33 N., R. 11 W., Spencer Dam near Spencer, Nebr., Boyd Co., Nebr.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G549	98-105		40.0	*Bouteloua curtipendula* (Michx.) Torr.	V546	1.0
				Aster multiflorus Ait.	V547	3.2
				Mentzelia decapetala Pursh.	V548*	6.0
G545	90-98		25.0			
G544	80-90		13.8			
G543	70-80		12.0			
G540		Yellow chalk at 72½ feet	1.5			
G542	60-70		5.0			
G541	50-60		6.0			
G533	40-50		16.0	*Astragalus racemosus* Pursh	V534	4160.0
G532	30-40		24.0			
G530	20-30		11.0	*Astragalus racemosus* Pursh.	V529	1100.0
G528	10-20		22.5	*Aster multiflorus* Ait.	V531	180.0
G527	0-10		1.3			
G557		Well core at 0-20 ft. down	2.3			
G558		Well core at 23 ft. down	6.0			

* Collected on upper part of section.

North of this area of highest selenium concentration the selenium content of this member falls off fairly rapidly although certain intervals contain much selenium. A succession, incomplete at the top, of 70 feet of Interior beds in Sec. 22, T. 100 N., R. 72 W., northern Gregory county (Table 42) had an average selenium content of 9.2 p.p.m., half or less than half the concentration south of this locality. Analyses of parts of the Interior in Lyman and Stanley are inadequate to show the selenium content of the member as a whole or to indicate the average selenium content of the member. (Tables 47 to 51 inclusive). They are, however, evidence of the decrease in selenium content to the northwest. Sufficient selenium is present in the Interior of these counties to produce soils which support toxic vegetation and cause serious losses where conditions are favorable.

Although the average selenium content appears to decrease still further to the west, beds supply sufficient selenium for the growth of toxic plants at least as far west as Secs. 13 and 14, T. 5 N., R. 21 E. (Table 52). A set of composite samples of 197 feet of beds of the Interior in Jackson county (Table 53) appears to be typical of the member in western South Dakota. Here all analyses are low

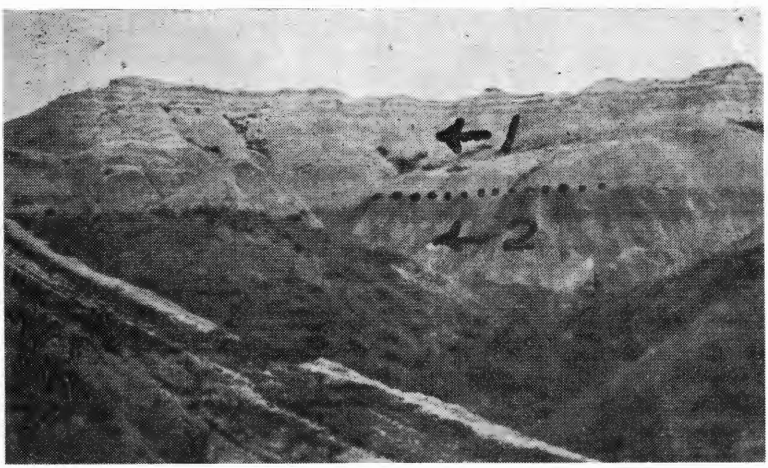

FIG. 15. (See Table 55) Interior member of the Pierre formation overlain by the Chadron formation. 1. Chadron. 2. Interior. Dotted line indicates contact.

with no 10 foot interval containing more than 1.0 p.p.m. selenium. The set sampled in Sec. 7, T. 1 S., R. 20 E. Jackson county along Bad Bear Creek represents additional beds probably below those cited in Table 54. Particular attention should be directed to analyses (Table 55) of Interior beds at Dillon Pass (Fig. 15). These show that high concentrations of selenium occur at certain positions within the member in this area, sufficient to supply "converter" plants with considerable quantities of selenium. The uppermost five feet of this succession is of particular interest both from the aspect of selenium content (20.0 p.p.m.) and because of the position immediately below the Oligocene (Chadron) clays. This high concentration of selenium in the Interior is not in keeping with that of the Interior elsewhere in the western outcrop area. Since the terrestrial Chadron immediately overlies this zone of high selenium content, there is the possibility that the selenium is associated with plant growth or other causes for secondary enrichment in Oligocene rather than with primary concentration in Interior time. There is some support for this hypothesis in the soil-like aspect of the overlying Chadron clay.

TABLE 44. Interior Member of the Pierre Formation (8)

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*
1H	75-90	High Bare Hill, Sec. 3, T. 96 N., R. 67 W.; Charles Mix Co., S. D.	14.0
2H	65-75	Samples 1H to 6H are composites of beds as indicated, in stratigraphic	22.0
3H	45-60	order, with 1H at the top, 6H at the base.	23.0
4H	30-45		22.0
5H	15-30		20.0
6H	0-15		10.0

TABLE 45. Interior Member of the Pierre Formation, Sec. 33, T. 98 N., R. 68 W., Across river from Mulehead Ranch, Charles Mix Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G568	60-68	25.0			
G567	50-60	32.5			
G566	40-50	19.6			
G565	30-40	19.4			
G564	20-30	15.0			
G563	10-20	2.1			
G562	0-10	29.0			
G561	Wash	10.0	*Stanleya bipinnata*	V569	190.0

TABLE 46. Interior Member of the Pierre Formation, Sec. 17, T. 100 N., R. 72 W., Gregory Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G517	40-52	4.5			
G516	30-40	10.0			
G515	20-30	4.0			
G514	10-20	1.2	Oats (heads)	V518	8.0
G513	0-10	1.3			

TABLE 47. Interior Member of the Pierre Formation (Virgin Creek Contact) N. E. 1/4, N. W. 1/4, Sec. 15, T. 106 N., R. 76 W., John Eymer Farm, Lyman Co., S. D.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G600	5 ft.	Interior	5.6			
G597	5 ft.	Interior	10.0	*Aster multiflorus* Ait.	V599	13.0
				Agropyron smithii Rydb.	V598	0.0
G592	5 ft.	Interior	1.8			
		Contact				
				Astragalus racemosus Pursh.	V594	2460.0
				Aster multiflorus Ait.	V595	10.0
G588	30-32	Virgin Creek	1.5	*Aster multiflorus* Ait.	V591	16.0
G587	20-30	Virgin Creek	6.0			
G586	10-20	Virgin Creek	0.0	*Astragalus racemosus* Pursh.	V589	3.5
G585	0-10	Virgin Creek	0.0	*Aster multiflorus* Ait.	V590	0.0

TABLE 48. Interior Member of the Pierre Formation, Reed Farm. Sec. 2, T. 107 N., R. 78 W., Lyman Co., S. D.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G410	30-40		0.0			
G408	20-30		0.5			
G407	10-20		1.0			
G406	0-10		1.8			
G413	20-32		1.1			
G412	10-20		1.9			
G411	0-10		3.0	*Astragalus* sp.?	V414	0.0
G405	5 ft. Random	Chalky	9.0			
G404	10 ft. Random	Chalky	6.7			

TABLE 49. Interior Member of the Pierre Formation, Dean Farm, S. E. 1/4 N. E. 1/4, Sec. 29, T. 3 N., R. 31 E., Stanley Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G402	50-60	4.0	*Astragalus racemosus* Pursh.	V403	250.0
G401	40-50	4.0			
G400	30-40	5.0			
G399	20-30	2.2			
G398	10-20	3.2			
G397	0-10	1.5			

TABLE 50. Interior Member of the Pierre Formation (8)

No.	*Lab. No.*	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*
1K	1892	55-70	Samples 1K to 4K are composites of beds as indicated, in stratigraphic	0.0
2K	1891	40-55	succession, with 1K at top, 4K at base. Taken 1.8 miles south of	1.0
3K	1876	20-40	Junction of U. S. Highway 14 and S. D. Highway 63, on U. S. 14,	1.3
4K	1878	0-20	Stanley Co., S. D.	2.3
1M			Sec. 2, T. 107 N., R. 78 W. Lyman Co., S. D.	29.0
2M			2 feet below surface, Sec. 2, T. 107 N., R. 78 W., Lyman Co., S. D.	12.0
3M	1890		Composite of 17 feet of beds, 16.2 miles west of Ft. Pierre, S. D.	3.0
4M	1893		Hill north of Midland, U. S. Highway No. 14, composite of 15 feet of beds.	1.0
5M	1880		Roadcut, 8 miles east of Stamford on U. S. 16, composite of 5 feet of beds.	1.5
6M	1895		½ mile west of Junction, U. S. Highways 16 and 83, on Highway 16, 10 foot composite.	3.0

TABLE 51. Interior Member of the Pierre Formation, Dean Farm, Cut, N. W. ¼ N. E. ¼, Sec. 33, T. 3 N., R. 31 E., Stanley Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G390	20-25	0.0	*Aster multiflorus* Ait.	V392	6.0
G389	10-20	1.0	*Grindelia squarrosa* (Pursh) Dunal.	V393	0.0
G388	0-10	1.8	*Astragalus racemosus* Pursh.	V391	10.0

TABLE 52. Interior Member of the Pierre Formation, Sect. 13 and 14, T. 5 N., R. 21 E., Ferguson Ranch, on Plum Creek, Haakon Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G472	90-95	8.5	*Astragalus racemosus* Pursh.	V481	224.0
G471	80-90	1.0	*Astragalus racemosus* Pursh.	V480	72.0
G470	70-80	0.0	*Astragalus racemosus* Pursh.	V478	3.0
G469	60-70	0.0	*Juniperus virginiana* L.	V479	0.0
G468	50-60	1.3	*Astragalus racemosus* Pursh.	V476	4.4
G467	40-50	0.0	*Astragalus racemosus* Pursh.	V475	30.0
G466	30-40	0.0			
G465	20-30	1.0			
G464	10-20	0.0	*Astragalus racemosus* Pursh.	V474	4.0
G463	0-10	0.0			
G461	30-40	0.0			
G460	20-30	0.0			
G459	10-20	0.0			
G458	0-10	0.0	*Astragalus racemosus* Pursh.	V462	0.0

TABLE 53. Interior Member of the Pierre Formation, N. E. 1/4, Sec. 16, T. 1 S., R. 19 E., east of Cottonwood in Jackson Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G322	195-97	0.0			
G321	185-95	0.0			
G320	175-85	0.0			
G319	165-75	0.5			
G318	155-65	0.0	*Astragalus racemosus* Pursh.	V323	16.0
G316	150-55	0.5			
G315	140-50	0.5			
G314	130-40	0.0			
G313	120-30	1.0			
G312	110-20	0.0			
G311	100-10	0.5			
G310	90-100	1.0			
G309	80-90	0.0			
G308B	75-80	0.0			
G308A	70-73	0.5			
G307	60-70	0.5			
G306	50-60	0.5			
G305	40-50	0.0			

TABLE 54. Interior Member of the Pierre Formation, Center of Sec. 7, T. 1 S., R. 20 E., Jackson Co., S. D., along Bad Bear Creek

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G299	30-38	1.0			
G298	20-30	1.5			
G297	10-20	0.8	*Astragalus racemosus* Pursh.	V300	10.0
G296	0-10	0.0			

TABLE 55. Interior Member of the Pierre Formation (Contact with Chadron.) (See Fig. 15.) 19.3 miles west of Cedar Pass Lodge—Dillon Pass

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G337	2-6	Gray Chadron	.5			
G336	0-2	Red Chadron	0.0			
		Contact				
G335	80-85	Interior	20.0			
G334	70-80		1.5			
G333	60-70		4.0			
G332	50-60		6.0			
G331	40-50		2.0	*Astragalus racemosus* Pursh.	V339	10.0
G330	30-40		.6	*Astralagus racemosus* Pursh.	V338	64.0
G329	20-30		1.7	*Astragalus racemosus* Pursh.	V343	641.0
G328	10-20		1.0	*Astragalus racemosus* Pursh.	V341	75.0
G327	0-10		0.0	*Astragalus racemosus* Pursh.	V340	48.0
				Astragalus racemosus Pursh.	V342*	32.0

* Below 0-10

TABLE 56. Interior Member (Type Section) of the Pierre Formation, Sec 29, T. 18 N., R. 30 E., Corson Co., road cut at west end Mobridge Bridge, Corson Co., S. D.

Lab. No.	*Depth Feet*	*Remarks*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G456	110-120		2.0			
G455	100-110		1.9			
G454	90-100		1.0			
G453	80-90		1.4	*Aster multiflorus* Ait.	V457	0.0
G452	70-80	Upper 3 ft. only	0.0			
G451	60-70		1.5			
G450	50-60		1.7			
G449	40-50		1.0			
G448	30-40		0.5			
G447	20-30		1.5			
G446	10-20		0.0			
G445	0-10		1.0			

TABLE 57. Interior Member of the Pierre Formation, Irish Creek Well Core (8), S. E. 1/4, Sec. 17, T. 15 N., R. 20 E., Ziebach Co., S. D.

Depth Feet	*Selenium Content p.p.m.*
335 1/2-393	0.5
393-400	0.0
400-427	0.6
427-491	1.4
491-500	5.0
500-522	3.0
522-531	2.5
531-557	1.1
557-586	0.8
586-612	1.0
612-642	1.2
642-670	0.6

TABLE 58. Interior Member of the Pierre Formation, N. E. 1/4, Sec. 16, T. 1 S., R. 19 E., east of Cottonwood in Jackson Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G304	30-35	0.7			
G303	20-30	1.5	*Mentzelia decapetala* Pursh.	V317	1.0
G302	10-20	0.0			
G301	0-10	0.0			

TABLE 59. Interior Member of the Pierre Formation, N. E. 1/4, Sec. 31, T. 2 N., R. 13 E., Pennington County, 1/4 mile west of Wicksville on U. S. Highway 14.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	
G281	60-70	0.0	
G280	50-60	0.0	
G279	40-50	1.2	No Vegetation
G278	30-40	0.5	
G277	20-30	0.0	
G276	10-20	0.0	
G275	0-10	0.0	

TABLE 60. Interior Member of the Pierre Formation, N. W. 1/4, Sec. 3, T. 10 S., R. 9 E., Near U. S. Highway 18 in eastern Fall River Co., S. D.

Lab. No.	*Depth Feet*	*Selenium Content p.p.m.*	*Vegetation*	*Lab. No.*	*Selenium Content p.p.m.*
G54	30-40	1.6			
G53	20-30	0.8	*Mentzelia decapetala* Pursh.	V55	1.6
G25	10-20	0.6			
G51	0-10	1.2			

Cause of Areal Variation in Selenium Content of the Interior Member

Evidence seems to show that selenium in the bedrock, and the Interior member of the Pierre as well, was for the most part, deposited contemporaneously with deposition of the sediments in which it occurs. Reduction in selenium content has also been associated with variations in thickness of the Interior (Mobridge) (8). Further studies, however, suggest that decrease in selenium content is not commensurate with increase in thickness since present data indicate that areal reduction in selenium content is proportionately greater than increase in thickness. An association between selenium and sedimentary facies also appears to exist. Not only in the case of the Interior, but also in the Niobrara formation, and to a lesser degree in the Greenhorn formation, selenium in unusual amounts appears to be associated with calcareous sediments.

Furthermore, pyrite (iron sulphide) is commonly associated with selenium in these beds as evidenced by the invariable occurrence of secondary gypsum in partially weathered outcrops of these beds. Small but numerous crystals of pyrite have also been observed in well cuttings from the Interior member. Although the amount of organic matter in the Interior has not been determined, Rubey (19) has investigated Cretaceous sediments and has found that organic matter tends, in a general way, to vary directly in amount with carbonates and pyrite. He found organic matter to be particularly abundant in the Greenhorn and Niobrara formations. Although the Sharon Springs member is only slightly calcareous, it is notably high in organic matter. Thus there appears to be an association between carbonate, sulphide, selenium, and organic matter.

It may be, then, that areas of Cretaceous sea bottom on which organic matter was accumulating in unusual amounts were the sites of greater chemical reduction that elsewhere and that as a result greater amounts of calcium carbonate, sulphide, and selenium were deposited (Figure 16).

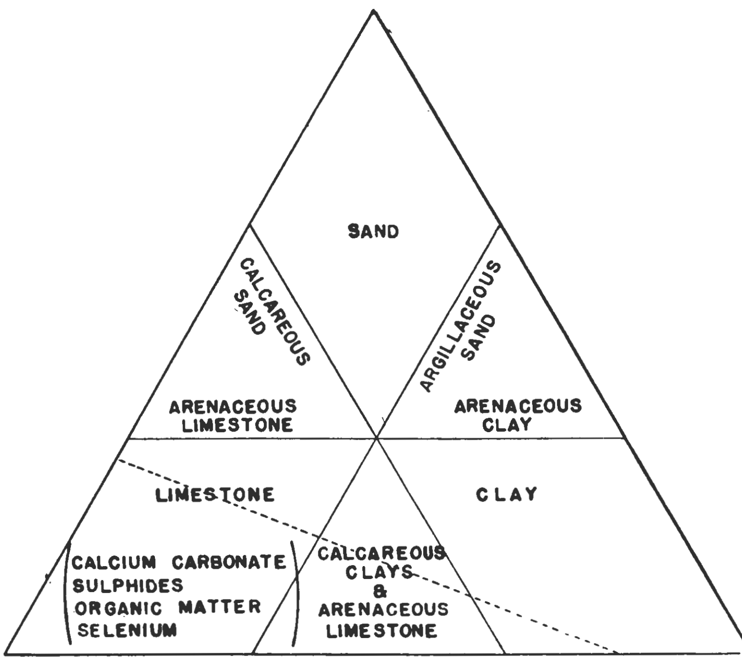

FIG. 16. Diagram to show possible relation of selenium deposition to lithologic facies.

Elk Butte Member. Investigation of selenium content of beds of the Elk Butte member of the Pierre are too incomplete to draw general conclusions. Those which have been made indicate that beds at this position, for the most part at least, are low in selenium content (Table 61). A single 10 foot composite near Wewela contained 4.0 p.p.m. Converter plants have not been observed on the member at any position and established cases of selenium poisoning have not been recorded or observed. It is the present view of the authors that the Elk Butte member is not likely to produce areas of seleniferous vegetation.

Fox Hills Formation. But little study has been made of the selenium content of the Fox Hills formation. It is believed, however, that the formation is low in selenium. The sandy portions are not likely to contain more than small concen-

TABLE 61. Elk Butte Member of the Pierre Formation (8)

Lab. No.	*Depth Feet*	*Location*	*Selenium p.p m.*
G573	0-10	Composite samples as indicated collected	0.6
G574	10-20	2½ to 3 miles north of Wewela, S. D., in	4.0
G575	20-30 (partial)	stratigraphic order, listed beginning at base of section.	0.0
G576	43-45		0.0
G577	45-80	Slope mantle derived from member, composited.	1.0
	30	Composite of beds, 3.6 miles north of Junction of Highways 18 and 281 on Highway 281	0.5

trations, in fact, analyses made in this laboratory indicate that they are selenium free (Table 62). Limestone concretions contained 1.5 p.p.m. selenium and coal from outcrops in Meade county contained 1.3 p.p.m. No composite samples have been collected.

LANCE FORMATION. The Lance formation contains selenium but, so far as known, only in very small amounts. Much of the formation is selenium free. Available analyses (Table 62) suggest that small amounts of selenium are probable in coals, lignitic shales, and in calcareous beds of the formation. Even here the element is likely to be present in concentrations of less than 1.0 p.p.m. Collections of composite samples have not been made.

TABLE 62. Selenium Content of Fox Hills, Lance and Fort Union Formations (1)

Formation	*Description*	*Selenium content p.p.m.*
Fox Hills	Fossiliferous sandstone	0.00
Fox Hills	Limestone concretions	1.50
Fox Hills	Coal	1.30
Fox Hills	Sandstone, iron stained	0.00
Fox Hills	Sandstone	0.00
Fox Hills	Basal portion	0.00
Lance, Hell Creek	Coal	0.00
Lance, Hell Creek	Fossil bone	0.00
Lance, Hell Creek	Shale	0.00
Lance, Hell Creek	Lignitic shale	1.00
Lance, Ludlow	Pyritic coal	0.00
Lance, Ludlow	Fossiliferous shale	0.00
Lance, Ludlow	Coal	.50
Lance, Ludlow	Ferruginous sand	0.00
Lance, Ludlow	Lignitic shale	.75
Lance, Ludlow	Pyritic concretion	0.00
Lance, Cannonball	Sandstone	0.00
Lance, Cannonball	Limestone	.50
Fort Union	Coal	.50
Fort Union	Siliceous, plant fossils	0.00

FORT UNION. Meager data available on the selenium content of the Fort Union suggests that the content is low (Table 62). The sandy character of most of the formation suggests sedimentation in an environment not suited to selenium deposition. Coals, however, may be expected to contain the element in small amounts.

CHADRON FORMATION. The Chadron formation contains some selenium, at least in some places in the lower part. It is probable that considerable variation in selenium content occurs in contemporaneous beds. Thus, a bed of gray clay which becomes a striking maroon red has been observed to lie at or near the base of the formation in many places at widely separated points in western South Dakota. In Shannon county, 8.5 miles west of Pine Ridge, where this bed lies on Niobrara the selenium content was 3.5 p.p.m. In the Big Badlands at Dillon Pass, this or a similar bed lies on the Interior member of the Pierre. At this place a composite sample yielded no selenium. The gray clay immediately overlying the red bed at the first location contained 0.7 p.p.m. in a 10 foot composite and at Dillon Pass a 4 foot composite of gray clay immediately overlying the red clay contained 0.5 p.p.m. selenium on analysis (Table 55). Thus the Chadron, probably contains sufficient selenium to render vegetation toxic but plants are extremely sparse on it. However, *Astragalus racemosus* has been observed growing on this formation.

BRULE FORMATION. The Oreodon beds of the Brule formation contain selenium, perhaps in considerable amounts. Investigation is inadequate to determine either stratigraphic or geographic distribution within this formation. Analyses of 12 feet of beds divided into two six foot composites yielded an average selenium content of 6.5 p.p.m. selenium. The upper six feet contained 9.0 p.p.m. selenium. Thus this portion of the formation 5.2 miles west of Cedar Pass Lodge in the Big Badlands is more than moderately seleniferous. Volcanic ash from White River, probably Brule, yielded no selenium (1).

MIOCENE AND PLIOCENE FORMATIONS. No data was secured during this investigation on the selenium content of Miocene and Pliocene formations. Previously published analyses of samples from the Arikaree sandstone and from Miocene volcanic ash yielded no selenium (1). Coarse sediments such as these are believed not to be likely to contain much selenium.

Tertiary Intrusive Igneous Rocks. No attempt has been made to obtain conclusive data on the selenium content of Tertiary intrusive igneous rock masses. Samples from two intrusions in Wyoming, Sundance Mountain and Devils Tower, each contained selenium. The former contained 1.0 p.p.m. and the latter 0.25 p.p.m. of the element. These analyses are of considerable interest since they show the occurrence of selenium in rocks of igneous origin.

Pleistocene. Investigation of glacial deposits to determine their selenium content has not been made. They are not likely to contain selenium in important amounts. Since glacial deposits are largely of local derivation, some selenium is probable wherever till is derived from older seleniferous rock. Cases of selenium poisoning have not been observed on glacial drift. Analyses of Pleistocene collected along Randall Creek, Gregory county, and near Lowry, Walworth county, were selenium free.

Factors Concerned in the Surface Distribution Of Selenium

The outcrop of a seleniferous formation locates the places where toxic areas are likely to occur. The outcrop, however, does not designate a uniformly toxic area. Parts of it may be highly toxic, parts only slightly toxic, and much of it may not be toxic. Students of the selenium problem are in accord with the idea that toxic areas are scattered and distributed in a seemingly erratic way. There is agreement also that toxic areas are definitely associated with certain geological formations. The relation to stratigraphic distribution has been discussed (Pages 27 to 60); the occurrence of selenium in soils and in plants will also be considered (Pages 67 to 85). During the field work, which is the basis for most of the data of this report, factors which determine surface distribution of toxic areas were noted. Some of the more important of these are discussed in the following pages.

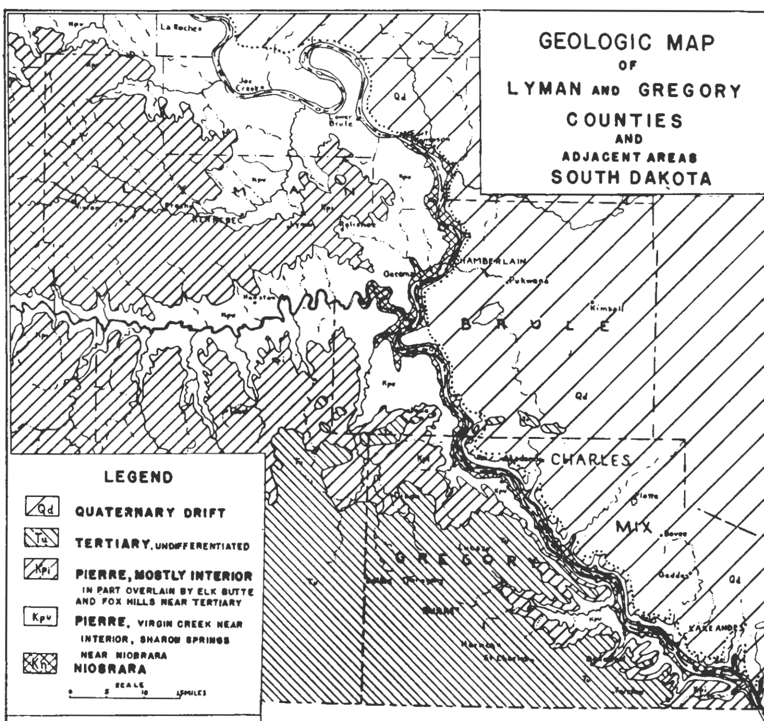

FIG. 17

WIDTH OF OUTCROP

The wider an outcrop of seleniferous bedrock is, the more probable it is that toxic areas will occur on it, and the narrower the outcrop is, the less likely it is that it may cause other than local trouble. Thickness of formation, structure, and topography govern the width of the outcrop of any formation.

The thickness of seleniferous zones or beds thus becomes a factor of first importance. Everything else being equal thin formations produce narrow outcrops and thick ones produce wide outcrops.

The structure or attitude of bedrock also determines in part the width of the outcrop of the formation. In most parts of South Dakota bedrock lies in a nearly horizontal attitude. In certain areas, however, particularly around the Black Hills, beds dip at fairly high angles. The relatively steep dip of the Niobrara formation around the Black Hills narrows the outcrop greatly, thus greatly restricting the area in which this highly seleniferous formation is exposed. This is illustrated graphically in Figure 18. On the other hand, the horizontality of the Interior member of the Pierre formation along the Missouri river, coupled with its thickness, permits wide surface distribution of that member. In regions of horizontal strata wide areas of thick beds are exposed if the surface is flat.

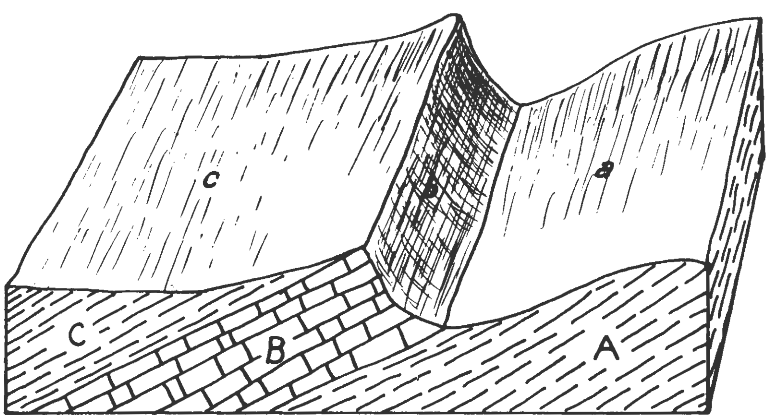

FIG. 18. Block diagram of an area underlain by three tilted formations, A, B, and C. Formation B is seleniferous. Note that surface area b is rendered seleniferous by the outcrop of formation B.

Topography or surface character is in part responsible for the width of outcrop. On areas of flat topography or very low relief thin formations may outcrop widely. Where relief is high, that is where slopes are steep and long, outcrops of horizontal rocks are relatively narrow. Surface slopes increase or decrease the width of outcrop, the dip of the rocks as it is related to direction of slope being a determining factor. Along valleys, where beds are horizontal, outcrops are restricted and narrow where the seleniferous bed has been exposed and re-covered (Figure 19). An excellent example of this condition is shown by the restricted surface distribution of the Niobrara formation along the Missouri river.

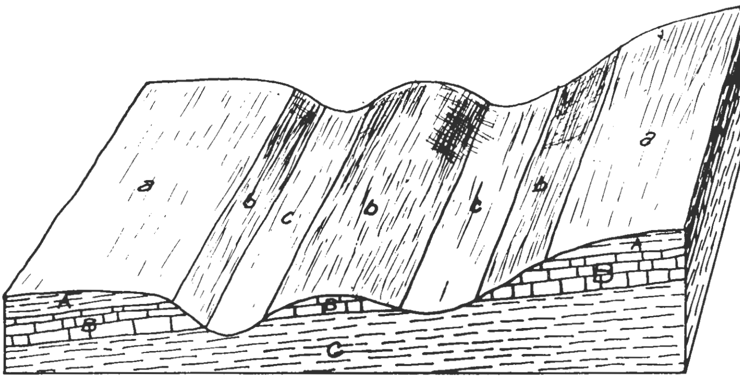

FIG. 19. Block diagram of an area underlain by three formations one of which (B) is seleniferous. Note effect of topography on width of outcrop b.

SLUMPING, SLIDING, CREEPING

The width of the area in which a formation occurs at the surface may be modified by certain processes. This is particularly true when formations are exposed along slopes. In such situations gravity causes beds to creep, slide, and slump down the slope. (Figure 20). Beds of the Pierre formation are particularly adapted, by their physical nature, to these processes. Slumping, sliding, and creeping of seleniferous beds may greatly extend the surface areas occupied by them. Along the Missouri river, in Charles Mix and Gregory counties, the area occupied by the Interior member of the Pierre formation, a highly seleniferous succession in these counties, is doubled or more than doubled in many places. On the other hand non-seleniferous formations may slump or creep over seleniferous formations, thus decreasing the area occupied by seleniferous beds. In the case of the Interior, however, because of the massive character of the beds, the net result is probably to increase the surface area rather than to decrease it.

DEPOSITS DERIVED FROM SELENIFEROUS FORMATIONS

Formations exposed at the surface are broken down by physical and chemical processes, transported and deposited. In humid regions chemical weathering is most important in rock disintegration, whereas in regions of low humidity, physical disruption is increasingly important. Where materials derived from seleniferous beds are transported for short distances, considerable selenium may be retained and incorporated into the resulting deposit. Wind and water are the important agents of transportation and deposition over the Great Plains region.

Along steep slopes the cutting power of streams is great, particularly of small streams which flow during rains. When the base of the slope is reached, however, the transporting power is mostly lost and deposits are made. These deposits, known as alluvial fans (Figure 21), if derived from seleniferous formations, may contain much selenium because the source is immediate and the possibility of mixture with non-seleniferous dilutants is less likely. Investigation of some of these

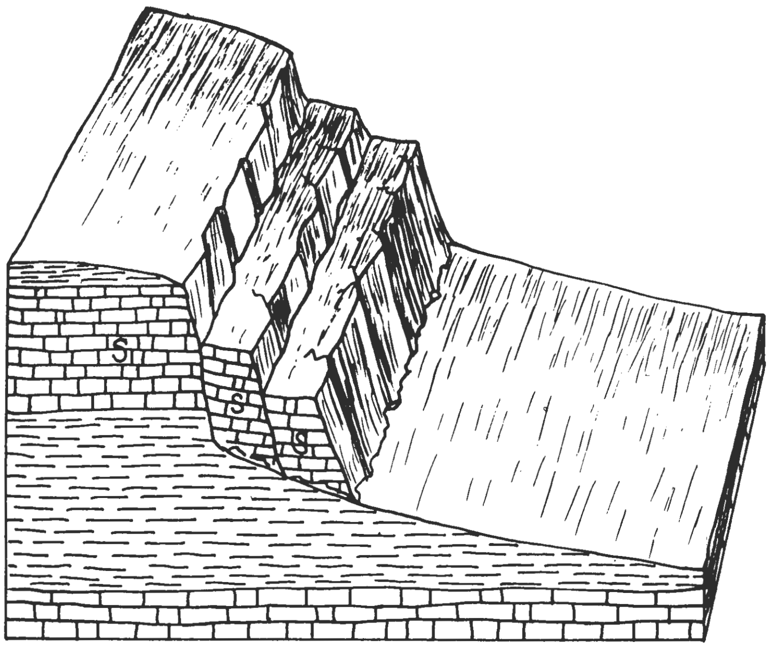

FIG. 20 Block diagram to show how slumping may increase surface area occupied by a seleniferous bed (S).

deposits proves that they are highly seleniferous in some cases, and that highly seleniferous vegetation grows on them.

Alluvial deposits along streams may be regarded with suspicion if drainage is chiefly from seleniferous bedrock. These may be particularly dangerous since seleniferous materials may be thus transferred to very gentle slopes and valley bottoms, the desirable environment for some species of *Aster* which do not grow well on steep hard slopes. Some of these Asters are highly seleniferous.

Wind blown materials derived from seleniferous bedrock may themselves be seleniferous. The Interior member of the Pierre formation along the west side of the Missouri river is especially susceptible to wind erosion with subsequent deposition. The calcareous nature of these beds of the Interior may be wholly or in part responsible for flocculation of weathered Interior into silt and sand sized aggregates which are transported by drifting. The resulting deposits are made at relatively short distances from the wind eroded sources. Considerable dilution from the introduction of non-seleniferous materials occurs. Nevertheless, some aeolian deposits in Lyman county derived from nearby Interior were found to contain sufficient selenium to produce toxic vegetation.

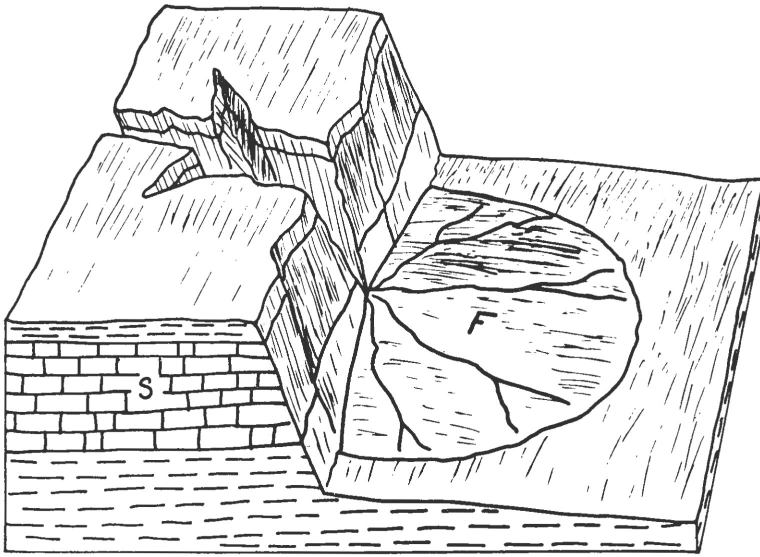

FIG. 21. Block diagram showing alluvial fan (F) derived chiefly from a seleniferous formation (S).

NON-SELENIFEROUS DEPOSITS COVERING SELENIFEROUS ROCK

Seleniferous bedrock is covered by non-seleniferous or only slightly seleniferous materials in many places. Water-laid silts, sands, and gravels along ancient and recent valleys effectively cover much of the outcrop of the Niobrara formation around the Black Hills (Figure 22). Most of this formation appears to be thus covered in the Belle Fourche irrigation project. Much of the Niobrara along the Missouri river is also covered by thick alluvian which produces no toxic vegetation.

East of the Missouri river selenium poisoning is reported only rarely because of the glacial drift, which covers the seleniferous formations.

Leaching and secondary deposition of selenium: Selenium is removed from bedrock by leaching. Water which falls as rain passes downward through soil and bedrock. As it passes downward soluble substances are removed and are transported in solution. Movement is both by gravity and capillary action. Some selenium is removed together with other soluble salts in the process of leaching. Probably most of the selenium thus dissolved, over long periods of time as least, is removed from the soils and rocks in the process. The fact that seleniferous bedrock contains much more selenium than the derived soils (Pages 68 to 70) is indicative of loss of selenium through leaching. Considerable amounts of selenium in undrained pools is further evidence of leaching. Selenium in secondary gypsum sug-

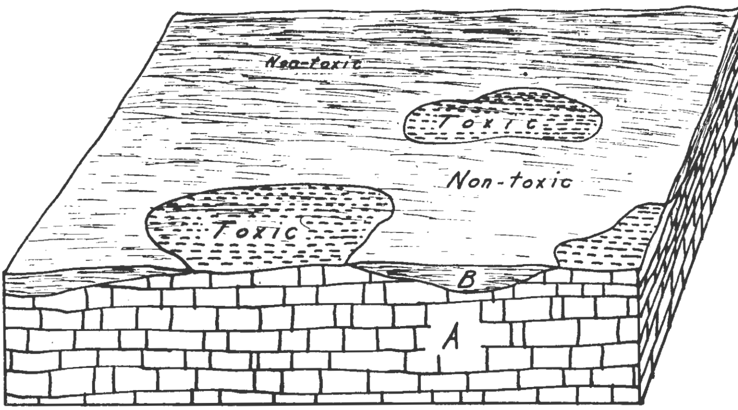

FIG. 22. Block diagram showing relation between toxic and non-toxic areas. A—Seleniferous formation. B—Non-seleniferous material.

gests removal of primary selenium from the bedrock. There is the possibility that in humid regions all of the selenium from soils and surficial bedrock is eventually removed.

In regions of relatively low rainfall, however, where the rate of evaporation is high, there is the possibility that much selenium is redeposited in secondary selenium compounds. Where ground water containing selenium seeps to the surface, or approaches near enough to the surface by capillarity for evaporation to occur, redeposition of selenium is possible. Seleniferous salt crusts resulting from this process have been observed in many places. In some of these, selenium was highly concentrated and was several times that of the bedrock from which the salts had been leached. Furthermore, much of the selenium in these salt crusts is in soluble form.

A tendency toward concentration in certain soil horizons has been suggested by Byers (4). This zone probably is due to evaporation of water held and raised through capillary openings in the soil.

In regions of low rainfall the removal of selenium from bedrock and soil up-slope permits redeposition down-slope. Thus selenium is likely to be concentrated at the bases of slopes or above beds impervious to ground water. Salt crusts high in selenium have been found near the bases of bedrock slopes even where the bedrock was fairly low in selenium content. The same process may also increase the selenium content of alluvial deposits in valleys where subsurface drainage comes down from seleniferous soils or bedrock. Such redeposition of selenium at lower, less dry locations cannot be quantitatively estimated but may possibly be of great importance since selenium is thus moved to an environment where moderately seleniferous plants such as *Aster* grow.

Selenium in Soils of South Dakota

In a large part of the area discussed in this report, conditions of climate and erosion have resulted in a slow process of soil formation. This is especially true in the region around the Black Hills. Although the shales outcropping in these areas are partially weathered, it is difficult in many cases to determine whether or not the material on the outcrop should be classified as soil. In this bulletin, the term soil is used only when definite accumulations of organic matter were apparent in the surface layer of material, and when at least six inches of the surface material had been weathered to such an extent that stratifications originally present in the parent material were practically obliterated.

Several samples of soil have been analyzed for total selenium at this laboratory. It has been found that soils containing more than 10.0 p.p.m. are found in very few instances, even in areas where selenium poisoning is known to be a serious problem. Soils containing more than 5.0 p.p.m. are found occasionally. Soils whose profiles are fairly well developed usually contain less than 5.0 p.p.m. of selenium even in highly seleniferous areas. (These statements concern samples taken to a depth of six inches.)

In the seleniferous areas near the Missouri river which occupy parts of Gregory, Lyman, and Stanley counties, most of the soils producing toxic vegetation are derived from the Interior member of the Pierre formation. The seleniferous zone in the upper Virgin Creek member of the Pierre is also important in forming seleniferous soils, but the area of soils derived from this member is not as great as the area of soils derived from the Interior member. Several small outcrops of the Niobrara formation are found along the river, but soils derived from this formation are uncommon in this area.

In the seleniferous areas around the Black Hills, a considerable portion of the highly seleniferous soils have been derived from the Niobrara formation. A considerable area of partially weathered Niobrara bedrock, which can not properly be classified as soil in this report, is also found in this region. This material supports some plant growth, especially highly seleniferous plants, and livestock which graze upon it suffer from selenium poisoning in many cases. There are spots in this area where the Niobrara formation underlies a thin layer of alluvium which is of low selenium content. Plants growing in the alluvium may extend through it into the Niobrara formation below it and become seleniferous (Figure 23).

The Sharon Springs member of the Pierre formation is highly seleniferous in this region. The lower Sharon Springs is composed of a black carbonaceous shale which weathers very slowly. Little if any soil has been formed from the lower Sharon Springs in this area. The upper Sharon Springs has weathered to form soil in some parts of the area, and selenium poisoning has been observed in cattle grazing on it. The Interior member of the Pierre formation is very low in selenium in this region, and soils weathered from it contain very small amounts of the element. The Greenhorn formation has been found to contain some selenium, but because of the low average selenium content, and the narrowness of its outcrop it seldom weathers to a seleniferous soil.

Although selenium occurs in other formations than those which have been discussed above, they do not weather into seleniferous soils in South Dakota.

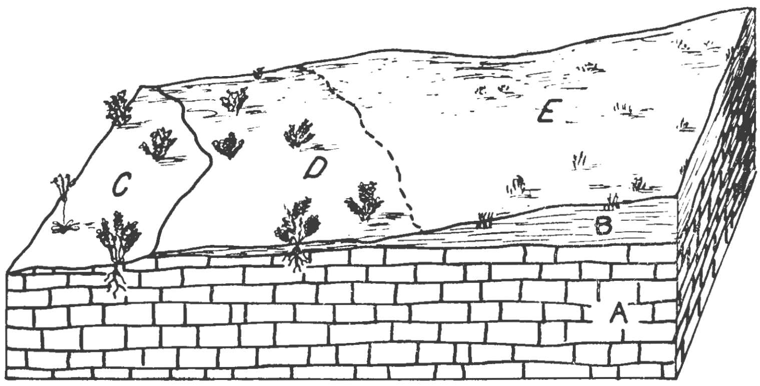

FIG. 23. Block diagram of an area underlain by a highly seleniferous bedrock A, partially covered by a non-seleniferous bed B. Note that the toxic area includes not only the outcrop C, but also the area under thin cover D which is penetrated by the roots of the plants.

Factors Determining the Selenium Content of Soils

Soils are the result of the modification of parent rock materials. They are produced in place on bedrock or on materials which have been derived from bedrock and later transported and deposited. In soil formation, rock is decomposed mechanically and chemically. Addition of organic matter and chemical interaction between rock derivatives and solutions of organic substances along with processes of illuviation and eluviation produce soils. The character of the parent material is an important factor in determining the physical and chemical properties of the soil. In regions of low humidity, such as in the Great Plains area, the effect of parent material on the resulting soils is probably greater than in regions of high precipitation. Leaching is less rapid and less effective here than in regions of high rainfall and secondary deposition of salts in the soil results from leaching and subsequent evaporation.

The chemical constituents of bedrock may thus remain in the soils resulting from the breakdown of these rocks. Sodium salts are contained in the soils derived from sodium rich parts of the Pierre shale, and calcium salts are characteristic of soils derived from calcareous beds. Small amounts of selenium compounds from bedrock are also retained in the soils derived from these rocks. It is the view of the authors that the greater portion of the original or primary selenium of the bedrock is lost by leaching during the weathering of rocks and the formation of the soil. An indication of the loss of selenium during the process of soil formation may be obtained from studies of the selenium content of the Boyd soils and that of the Interior member of the Pierre formation. It is apparent from the description of the Boyd soils given in the 1938 U.S.D.A. Yearbook of Agriculture (36) that this series of soils is derived from the Interior member. Most, if not all, of the soil of section 4, T. 108 N., R. 79 W., Lyman county, is derived from the Interior. Exhaustive selenium analyses of soils from this section have been made by Byers (4). The average selenium content of the Boyd clay on this section is 2.9 p.p.m. The average of the analyses of composite samples of the Interior north of Landing Creek (section 22, T. 100 N., R. 72 W.) involving 90 feet of beds is 9.2 p.p.m. of selenium (Table 42). The average selenium content of 90 feet of beds in section 3, T. 96 N., R. 67 W., Charles Mix county, is 18.5 p.p.m. (Table 44). The latter succession is much fresher and probably less leached than the former. Using the first average and comparing it with the average of the analyses of the Boyd soil, a loss of approximately 60 percent of the original selenium is indicated. Comparison with the higher bedrock average suggests a loss of 84 percent of the original selenium. A tentative range in the loss of selenium during soil formation may thus be given as 60-84 percent, although the lower figure is probably much too conservative.

Because of the impervious nature of most of the soils found in seleniferous areas, it is felt that leaching may not in itself remove any large fraction of the soluble selenium. However, percolation of water into the surface of the soil, solution of the selenium, and redeposition at the surface upon subsequent evaporation may be important in that it aids in the removal of selenium by surface runoff. Beath, Eppson, and Gilbert (37) report depositions of soluble selenium at various levels in a soil horizon. It is apparent, therefore, that leaching, in itself, must play some part in decreasing the selenium content of surface soils. The rate of removal by leaching and surface runoff depends primarily on the amount of rainfall and the solubility of the selenium.

The amount of soluble selenium present in weathering rock probably depends to some extent on the degree of oxidation of the selenium. Knight and Beath (13), state, however, that "It is doubtful if ordinary weathering processes, bacterial action, etc., have any appreciable effect upon converting the naturally occurring selenium complexes of the semi-arid areas into available form." They suggest "converter" plants as the most important factor in the solution of selenium. Beath, Eppson, and Gilbert (38) found that selenium in highly seleniferous plants is partially volatile, and the remainder is largely water soluble. Upon the death of these plants the selenium is returned to the soil or rock in which the plant grew, or is carried off by water and redeposited. The rate of removal of selenium by plants depends on the kind of plants and the volatility and solubility of the selenium in the plants.

During the formation of soils, there is probably considerable mixing of the parent material, especially in loessial and alluvial soils. Even in residual soils it is probable that considerable loess and alluvium is present. In the weathering of a soil from seleniferous rock, the selenium content of the soil depends in part, therefore, on the degree of mixing of parent materials as well as the selenium content of the parent materials.

Topography, also, is an important factor in determining the selenium content of soils. On a level surface, the amount of surface runoff would be small as compared to that on a slope. If the level surface were below a seleniferous rock outcrop, its selenium content would undoubtedly be increased by the redeposition of soluble selenium leached from the rock outcrop, and from the deposition of materials from the seleniferous rock by water, wind or gravity. The selenium content of the soils formed on slopes is, in part at least, dependent upon the nature of the parent material and the kind of plants occurring up the slope from them.

Although these factors are important in causing variations in the selenium content of soils, it is difficult to determine to what extent each of them has been active in producing seleniferous soils.

Factors Influencing the Availability of Selenium to Plants And Absorption of Selenium by Plants

Several factors are important in determining the amount of selenium a plant will absorb from a soil, and because these factors can cause large variations in the selenium content of a plant it is necessary that they be taken into consideration, whenever possible, in interpreting data concerned with this problem.

The most important factors include the following: 1. the kind of plant analyzed; 2. the stage of growth of the plant when analyzed; 3. the chemical form of the selenium in the material in which the plant grew; 4. plant associations; 5. variations in geology; and 6. other factors such as the total selenium content of the material in which the plant grew, climate, part of the plant analyzed, drying of the plant for analysis, thrift and age of the plant when analyzed, selenium accumulations in subsoils, and possibly others. The following is a discussion of these factors and how they effect the selenium content of plants:

KIND OF PLANTS ANALYZED

Plants growing in the same soil, within short distances of each other, under the same conditions of climate, often vary greatly in their selenium content. Beath, Draize, and Gilbert (2) found that certain plants such as woody aster will absorb selenium from a soil from which crop plants will not absorb the element. Later work by Beath, Eppson, and Gilbert (37, 38), Knight and Beath (13), Byers (4, 5), and Byers et al. (6) has shown that some types of plants such as the *Astragali* absorb large amounts of selenium from soil, while other plants such as our common crop plants absorb only small amounts of the element. Beath and his associates (2, 37, 39) and Miller and Byers (40) have classified plants on the basis of their ability to absorb selenium from soils. Those plants which are capable of absorbing large amounts of selenium from soils from which common crop plants and grasses absorb only small amounts of the element, Beath and co-workers call "converter" plants. These will be discussed more fully later. Some plants grow only where there is selenium in the soil and these they call "indicator" plants. Plants which normally absorb only relatively small amounts of the element are usually referred to as non-seleniferous. Thus, the kind of plant growing in a soil determines to some extent the selenium content of the plant. The following data shows the importance of this factor. All of the plants analyzed from each location were collected within an area of about four square rods, on the same geological formation, on the same day. The results of the analyses are shown in the following table.

TABLE 63. Comparison of the Selenium Content of Different Species of Plants

Sample No.	*Location*	*Kind of Plant* *Scientific Name*	*Common Name*	*Se content p.p.m. (Dry basis)*
V183-A	S½ SE¼	*Stanleya bipinnata*		2380.0
V184	Sec. 30,	*Aster multiflorus* Ait.	White aster	320.0
V185	T. 7 N.,	*Artemisia canadensis* Michx.	Sage brush	6.8
V186	R. 6 E.,	*Grindelia squarrosa* (Pursh) Dunal.	Gum weed	260.0
V187	Meade	*Agropyron smithii* Rydb.	Western wheat grass	27.0
V188	county	*Gutierrezia sarothrae* (Pursh) Britt. and Rusby	Broom snakeweed	220.0
V189		*Astragalus racemosus* Pursh.		760.0
V375	NE¼SE¼	*Astragalus racemosus* Pursh.		500.0
V376	Sec. 28,	*Grindelia squarrosa* (Pursh) Dunal.	Gum weed	10.0
V377	T. 3 N.,	*Xanthium pennsylvanicum* Waller	Cockleburr	4.0
V378	R. 31 E.,	*Agropyron smithii* Rydb.	Western wheat grass	0.0
V379	Stanley	*Salsola pestifer* A. Nels.	Russian thistle	4.0
V380	county	*Heliathus* sp.	Sunflower	0.0
V381		*Lygodesmia juncia* (Pursh) D. Don.	Prairie pink	1.0
V382		*Lepadenia marginata* (Pursh) Niewl.	Snow-on-the-mountain	3.0
V383		*Melilotus officinalis* (L.) Lam.	Yellow sweet clover	4.0
V384		*Brauneria augustifolia* (D.C.) Heller	Purple coneflower	1.0
V385		*Solidago pallida* (Porter) Rydb.	Goldenrod	4.0
V386		*Astragalus mollissimus* Torr.	Wooly loco	1.0
V387		*Amaranthus retroflexus* L.	Pig weed	0.0
V535	SE¼NW¼	*Hordeum montanense* Beal.	Foxtail	7.0
V536	Sec. 30,	*Lepadenia marginata* (Pursh) Niewl.	Snow-on-the-mountain	1.6
V537	T. 33 N.,	*Aster multiflorus* Ait.	White aster	14.0
V538	R. 11 W.,	*Chenopodium album* L.	Lamb's quarter	1.0
V539	Boyd county, Neb.	*Panicum capillare* L.	Witch grass	1.4

Since the more important factors which cause variations in the selenium content of plants are eliminated from the study represented by the data in Table 63, it becomes apparent that variations in the selenium content of different kinds of plants are great, and must therefore be carefully considered in a study of this problem.

STAGE OF GROWTH OF THE PLANTS WHEN ANALYZED

Byers (4) lists the stage of growth of the plant when it is examined as a factor to be considered in the interpretation of data concerning selenium studies.

Beath, Eppson and Gilbert (38) state that the stage of growth of the plant when analyzed is one of the factors to be considered in examining data concerning highly seleniferous plants. They present data to illustrate the fact .

During the summer of 1938 the authors made studies of the selenium content of several plants at various stages of growth. In making these studies, the following procedure was followed in collecting the plants and preparing them for analysis.

A well-marked location was selected for making the study of each species of plant. The plants were cut off just above the level of the ground, several plants being taken at random over an area of about one to two square rods depending on conditions at the location where the plants were taken. Plants were taken from the same location at various times during the growing season. Before the plants were analyzed for selenium they were dried at 50-60° C. for 48 hours. All analyses are reported on a dry basis.

TABLE 64. Selenium Content of Western Wheat Grass *Agropyron smithii* Rydb. (*A. occidentale* Scribn.)

Location	*Lab. No.*	*Date Collected*	*Stage of growth or height of plant*	*Se content of plant. p.p.m. Dry basis*	*Remarks*
SW 1/4	B43	5-24-38	10-12 inches	73.0	This group of plants was
NW 1/4	C54	6-2-38	14-16 inches	50.0	taken within a large patch of
Sec. 20,	D64	6-27-38	Fertilizing	44.0	*A. multiflorus.*
T. 100 N.,	E7	7-9-38	Fertilized	13.0	
R. 72 W.,	V520	8-8-38	Early maturity	36.0	
Gregory	K24	10-1-38	Late maturity	7.8	
county					
SW 1/4	C53	6-2-38	14-16 inches	28.0	This group of plants was
NW 1/4	D63	6-27-38	Fertilizing	15.0	taken where there were no
Sec. 20,	E8	7-9-38	Fertilized	6.0	*A. multiflorus* growing.
T. 100 N.,	V521	8-8-38	Early maturity	10.0	
R. 72 W.,					
Gregory					
county					
NW 1/4	A7	5-7-38		22.0	This group of plants was
SW 1/4	B39	5-24-38	12-14 inches	23.0	taken within a large patch
Sec. 22,	C50	6-2-38	14-16 inches	36.0	of *A. multiflorus.*
T. 100 N.,	D35	6-27-38	Ferilizing	26.0	
R. 72 W.,	E6	7-9-38	Fertilized	11.0	
Gregory	V495	8-8-38	Early maturity	12.0	
county	K21	10-1-38	Late maturity	15.6	
NW 1/4	A8	5-7-38		84.0	This group of plants was
SW 1/4	B37	5-4-38	12-14 inches	8.0	taken where there were no
Sec. 22,	C49	6-2-38	14-16 inches	70.0	*A. multiflorus* growing.
T. 100 N.,	D36	6-27-38	Fertilizing	3.0	
R. 72 W.,	E11	7-9-38	Fertilized	11.6	
Gregory	V496	8-8-38	Early maturity	8.0	
county	K18	10-1-38	Late maturity	6.4	

Examination of the data in Table 64 shows that there is a tendency for western wheat grass *(A. Smithii)* to decrease in selenium content in the later stages of growth. It will be noted that in the last case two of the samples (laboratory numbers B37 and D36) show selenium contents which do not fit in favorably with the rest of the data. In these cases the plot from which the plants were picked was not too well situated, and it is possible that all of the samples in this case are not comparable.

TABLE 65. Selenium Content of Asters. *Aster multiflorus* Ait.

Location	*Lab. No.*	*Date Collected*	*Stage of growth or height of plant*	*Se content of plant. Dry basis p.p.m.*
SW 1/4	A11	5-7-38		1800.0
NW 1/4	B42	5-24-38	10-12 inches	1620.0
Sec. 20,	C57	6-2-38	14-16 inches	780.0
T. 100 N.,	D60	6-27-38	24-30 inches	330.0
R. 72 W.,	E10	7-9-38		230.0
Gregory	V519	8-8-38	Bud	400.0
county	K20	10-1-38	Mature	900.0
NW 1/4	A6	5-7-38		128.0
SW 1/4	B38	5-24-38	10-12 inches	125.0
Sec. 22,	C48	6-2-38	14-16 inches	270.0
T. 100 N.,	D37	6-27-38	24-30 inches	76.0
R. 72 W.,	E5	7-9-38		28.0
Gregory	V494	8-8-38	Bud	14.0
county	K22	10-1-38	Mature	35.0

From Table 65 it is apparent that *Aster multiflorus* is more highly seleniferous early in its growth than it is at later stages, but the above data indicate a rise in its selenium content toward maturity.

TABLE 66. Selenium Content of Gum Weed *Grindelia squarrosa* (Pursh) Dunal.

Location	*Lab. No.*	*Date Collected*	*Stage of growth or height of plant*	*Se content of plant. Dry basis p.p.m.*
SW1/4	A10	5-7-38		11.0
NW1/4	B41	5-24-38	10-12 inches	18.0
Sec. 20,	C56	6-2-38	12-14 inches	32.0
T. 100 N.,	D61	6-27-38	24-30 inches	30.0
R. 72 W.,	K23	10-1-38	Post-blossom (mature)	90.0
Gregory				
county				
N1/2	D4	6-27-38	12-14 inches	
SW 1/4			Preblossom	160.00
Sec. 35,	F23	8-4-38	Blossom	230.0
T. 108 N.,	K17	10-2-38	Mature	230.0
R. 78 W.,				
Lyman				
county				

TABLE 67. Selenium Content of Sweet Clover *Melilotus officinalis*

Location	*Lab. No.*	*Date Collected*	*Stage of growth or height of plant*	*Se content of plant. Dry basis p.p.m.*
SW¼	B44	5-24-38	10-12 inches	11.0
NW¼	C55	6-2-38	16-18 inches	24.0
Sec. 20,	D62	6-27-38	Blossom (early)	26.0
T. 100 N.,	E1	7-9-38	Full blossom	15.2
R. 72 W.,	V523	8-8-38	Early maturity	4.0
Gregory county	K19	10-1-38	Mature	1.2

The data in Tables 66 and 67 indicate that the selenium content of *Grindelia squarrosa* increases in later stages of growth, whereas that of sweet clover increases until the blooming stage and then it decreases.

The selenium content of three grain crops at various stages was studied in the greenhouse and one study on wheat was made in the field. The results of the study are given in Table 68.

TABLE 68. Selenium Content of Crop Plants at Different Stages of Growth

Crop	*Days of Growth*	*Stage or height when taken for analysis*	*Selenium content (dry basis)* Stems p.p.m.	Roots p.p.m.	Heads p.p.m.
Wheat		4-6 inches, seedling	17.0	15.0	
(Triticum[1]		8-12 inches, seedling	27.0	9.5	
vulgare)		Fertilized	17.0	4.6	20.0
Field		Dough	6.0	0.0	15.2
conditions		Mature			16.0
Wheat	22	5 inches, seedling	62.5	40.0	
(Triticum	49	Headed	3.53	17.55	
vulgare)	74		2.8	7.1	4.8
Greenhouse conditions					
Oats	26	Seedling	0.0	5.0	
(Avena	34	Heading	0.0	2.4	0.0
sativa)	41	Pollenating	0.0	4.8	0.0
Greenhouse	58	Early maturity	3.8	12.7	7.25
conditions					
Barley	26	Seedling	5.3	8.3	
(Hordeum	34	Heading	6.1	11.4	
vulgare)	41	Pollenating	6.4	9.7	7.9
Greenhouse	58	Early maturity	5.5	10.5	3.6
conditions					

[1] Number of days of growth not determined because date of planting not known.

From these results it appears that grains are not alike as concerns comparative amounts of selenium they contain at various stages of growth. Wheat apparently decreases in selenium content at later stages, whereas oats increases. Barley remains fairly constant.

CHEMICAL FORM OF SELENIUM IN THE SOIL

Perhaps the most important factor in determining how much selenium any one plant will absorb from the soil is the chemical form in which the selenium occurs in the soil. Because selenium normally is found in such small quantities in soil, it has been difficult to determine its chemical forms.

Byers and Knight (41) state that although they made no attempt to identify the selenium compounds present in the soil, two types of compounds, water soluble and ammonia soluble, seemed to occur. Williams and Byers (42) and Knight and Beath (13) analyzed several pyritic materials and found that selenium was present in them in varying amounts. It would appear then, that in soils containing pyritic concretions selenium may be present as pyrites in which selenium is substituted for sulfur. Williams and Byers (43) and Beath, Eppson, and Gilbert (38) found that little if any selenium occurs naturally in the elemental form in soils. Williams and Byers (43) also found that the major part of the selenium in soils probably occurs as a very insoluble basic iron selenite, the chemical composition of which they have been unable to determine exactly. They also found that small amounts of selenium occurred as the selenate, probably as calcium selenate, and that some of the selenium apparently occurs in organic form.

Moxon (1) reports that when 200 grams of naturally seleniferous soil was leached free of calcium with 3 percent hydrochloric acid solution and then extracted with 4 percent ammonium hydroxide solution, the ammonia extract contained 42.1 percent of the total selenium, which he considered to be organic. Byers (5), however, states that it appears certain that but little selenium is associated with the organic matter after it has become humified. Beath, Eppson, and Gilbert (38) and Olson and Moxon (44) present data which indicates that considerable organic selenium occurs naturally in soils.

Preliminary work at this laboratory indicates that there is a large difference in the absorption of various forms of selenium by plants, when these forms of selenium are added to non-seleniferous soils. Olson and Moxon (44) have presented data showing that the water soluble and organic selenium content of soils may be used as a relative measure of the availability of selenium to crop plants.

TABLE 69. Availability of Different Forms of Selenium

Crop grown	*Se added* *p.p.m.*	*Selenium content (p.p.m.) of plants grown in soil containing Se in form of:* Na_2SeO_4	$CaSeO_4$	Na_2SeO_3	$Fe(OH)SeO_3$[1]	*FeSe*	*Se*	*Organic*[2]
Corn	2.0	269.0	lost	0.0	1.6	0.0	0.0	
Corn[3]	2.0	84.0	125.0	6.0	3.6	2.0	0.0	
Barley	2.0	92 3	197.6	10.4	10.0	0.0	0.0	180.0
Wheat	2.0	504.0	400.0	12.0			2.8	
Astragalus racemosus	10.0	2357.0	2717.0	650.0	726.0	5.0		
Stanleya bipinnata	10.0	1429.0		573.0	625.0	15.2	1.0	

[1] Exact formula not known.
[2] Water extract of *Astragalus racemosus*.
[3] Second crop.

In order to determine what difference there might be in the availability of different chemical forms of selenium to plants various chemical forms of the element were added to non-seleniferous soils and the plants grown in the soils were analyzed for selenium. The results of the study are given in Table 69.

From the data in Table 69 it is apparent that selenium in the soil in the form of selenates is readily available to plants. When it is present in the form of selenites it is relatively unavailable to common crop plants but it is available to "converter" plants. This is in agreement with the work of Franke and Painter (45) and Knight and Beath (13), who found that the selenite is bound by soils whereas the selenate is not. The other inorganic forms of selenium are apparently not readily available to plants. Beath, Eppson, and Gilbert (38) found *Astragalus bisulcatus* and *Astragalus pectinatus* to be capable of absorbing large amounts of selenium from a non-seleniferous soil which had been treated with 25 p.p.m. of elemental selenium. However, they allowed their plants to grow for a longer period of time in the soil before analyzing them for selenium. It would seem, then, that young "converter" plants cannot absorb large amounts of very insoluble forms of selenium whereas older "converter" plants can.

In order to determine whether the rate of absorption of the different forms of soluble selenium would vary, corn plants which had been germinated in white sand and grown for a few days in a selenium-free culture solution were placed in a culture solution containing KNO_3, $Ca(NO_3)_2$, and a buffer containing K_2HPO_4 and KH_2PO_3 in the proper proportions to give a pH of 6.1 (46), and one of the following forms of selenium at a concentration of 0.4 p.p.m. of selenium: sodium selenate, sodium selenite, sodium selenide, and an alcohol soluble, partially purified, extract of *Astragalus racemosus*. After four days the plants were removed and the roots were washed well with water. The plants were then dried at 50-60° C. for twenty-four hours and analyzed for selenium. At the time the plants were removed, the solutions showed no visible signs of any selenium reduction, and no molds nor algae were present. Results of the analyses are given in Table 70.

TABLE 70. Absorption of Different Forms of Selenium

Pot No.	*Form of Selenium*	*Selenium content of plants (Dry basis) p.p.m.*
1	Sodium selenate	277.0
2	Sodium selenate	238.0
3	Sodium selenite	157.0
4	Sodium selenite	125.0
5	Sodium selenide	112.0
6	Sodium selenide	132.0
7	Organic	146.0
8	Organic	152.0

The results given in Table 70 indicate that the rate of absorption of selenium in its different forms, even when concentrations in solution are equal, may be another factor in determining the selenium content of plants.

PLANT ASSOCIATIONS

Highly seleniferous plants have been studied by Beath and co-workers (2,13, 37, 38, 39) in some detail. They have presented considerable data showing that these plants are capable of absorbing large amounts of selenium from soils in which the element is not available to crop plants, and that the subsequent death and decomposition of these plants is effective in producing a soil of high available selenium content.

Data presented in this paper under "Forms of Selenium in the Soil" indicates at least one step in the conversion of unavailable to available selenium. Whereas selenium in the form of the selenite is not absorbed from soil by common crop plants, it is absorbed by *Astragalus racemosus* and *Stanleya bipinnata* in large amounts. The crop plants are capable of absorbing the extract from *Astragalus racemosus*. From this it may be concluded that selenium occurring in the soil in the form of selenites may become available to crop plants through the action of "converter" plants.

A field study of this factor was made during the summer of 1938. Samples of *Agropyron smithii* taken within a patch of *Aster multiflorus* plants and analyzed for selenium averaged 35.75 p.p.m. of selenium. Samples of the same kind of grass taken within 20 feet of the patch of asters averaged 14.75 p.p.m. of selenium. This illustrates the effect of associated vegetation on the selenium content of plants.

VARIATIONS IN GEOLOGY

The selenium content of plants has been shown to vary with the geological formation on which they grew (8, 38). As the result of the work presented in this paper, it has been found that there is considerable variation in the selenium content of plants growing on the same geological formation. An example of this is the seleniferous zone near the top of the Virgin Creek member of the Pierre formation. This zone supports an abundant growth of our common "converter" plants, and some of the most seleniferous soil in the state has been formed from it. The rest of the member is apparently of no importance in the selenium problem. Similar variations occur in other formations.

The Interior member of the Pierre formation in South Dakota is a good example of geological material of the same age which varies in selenium content at different geographical locations (Fig. 14). This is discussed on pages 49 to 58 of this bulletin. The selenium content of the Interior member decreases from east to west and south to north and so does the selenium content of plants growing on the member.

Byers et al. (6) give data showing how a formation may vary in selenium content from bed to bed. Figure 23 shows how bed to bed variation in the formation may cause variation in the selenium content of plants growing on the formation.

OTHER FACTORS

TOTAL SELENIUM CONTENT OF THE SOILS. Naturally, unless a soil contains selenium the plants growing on it cannot contain selenium. On the other hand, the presence of selenium in soils in rather large amounts is not a sure indication that plants growing in the soil will absorb enough of the element to be determined by present methods of analysis. Lakin, Williams, and Byers (47) have studied soils of relatively high selenium content which are not known to produce plants of high enough selenium content to be injurious to animals. The analysis of soils for total selenium therefore is merely a guide in determining whether or not the soils are possible sources of danger from selenium poisoning.

CLIMATE. Although no conclusive work concerning the effect of climate on the selenium content of plants has been reported it seems that climate does cause variations. Byers (5) presents data indicating that selenium content of plants decreases with increasing rainfall. Franke and Painter (45), however, have reported that the selenium content of plants was higher during seasons of higher precipitation.

THE PART OF THE PLANT ANALYZED: Beath, Eppson, and Gilbert (38) and Byers and co-workers (5, 6, 47) have found that the selenium contents of different parts of the same plant may vary considerably. The selenium content of some of our crop plants has been found to depend upon the part of the plant analyzed (see Table 68, page 74).

DRYING OF PLANT FOR ANALYSIS. Beath, Eppson, and Gilbert (38) have found that when highly seleniferous plants are dried for analysis they may lose a considerable part of their selenium. They found, however, that drying had little if any effect on the selenium content of common crop plants and grasses. The loss of selenium from the highly seleniferous plants was found to vary considerably.

THRIFT AND AGE OF PLANT WHEN ANALYZED. Beath, Eppson, and Gilbert (38) have found that the selenium content of plants is affected by the thrift of the plant, and by the age of the plant(as determined by the size and physical character of the root).

SELENIUM ACCUMULATION IN SUBSOILS. Beath, Eppson, and Gilbert (37) report accumulations of soluble selenium at various levels in a soil horizon and suggest this as a possible cause for variations in the selenium content of plants. Byers et al. (6) point out that the cause of the variation in the selenium content of soil horizons is probably the selenium content of the parent material from which the different horizons were weathered. However, it appears that concentration of soluble selenium at certain levels probably is more important in causing variations in the selenium content of crop plants than is the variation in total selenium content of the soil.

SULFUR CONTENT OF THE SOIL. Considerable work has been done on the sulfur inhibition of selenium uptake by plants in the greenhouse with culture solutions and artificially selenized soils (48, 49, 50, 51), but work with naturally seleniferous soils, both in the field and under controlled conditions, has shown that sulfur applications do not inhibit the absorption of selenium (13, 45). The authors are of the opinion that the sulfur content of the soil is of little importance in determining the selenium content of plants growing on it.

Other factors probably influence selenium absorption by plants, but as yet little work has been done in determining their importance.

Selenium Content of Grasses in South Dakota

Considerable data concerning the selenium content of some of the more important grasses of South Dakota have been assembled during the past few years. By combining the data obtained by this laboratory with that published by Byers (4, 5) it has been found that western wheat grass *(Agropyron smithii)* is apparently the most highly seleniferous of the important grasses in the state. A summary of the data assembled is presented in Table 71. In examining the data it must be kept in mind that several of the factors important in causing variations in the selenium content of plants have not been taken into consideration, so that no rigid comparison can be made. However, one point that seems to stand out clearly is that western wheat grass is relatively seleniferous as compared to the other grasses. This is an important factor in South Dakota because western wheat grass, *Agropyron smithii*, grows well in seleniferous areas. This grass is used extensively for hay as well as for grazing, and because of its ability to absorb relatively large amounts of selenium, it should be grazed cautiously in highly seleniferous areas.

TABLE 71. A Comparison of the Selenium Content of Some Grasses Common to Western S. D.

			Selenium content of plants (Dry basis)		
Common Name	*Scientific Name*	*No. of analyses reported*	*Range*	*p.p.m. Average*	*Av. for species*
Western Wheat Grass	*Agropyron smithii*[1]	75	0.0-84.0	12.11	
Western Wheat Grass	*Agropyron smithii*[2]	20	0.0-60.0	15.15	11.46
Western Wheat Grass	*Agropyron smithii*[3]	40	1.0-50.0	8.40	
Buffalo Grass	*Buchloe dactyloides*[1]	5	0.0-0.5	0.17	
Buffalo Grass	*Buchloe dactyloides*[2]	3	0.0-12.0	7.33	2.65
Buffalo Grass	*Buchloe dactyloides*[3]	1		1.00	
Blue Grama	*Bouteloua gracilis*[1]	8	0.0-3.6	1.40	1.40
Side Oat Grama	*Bouteloua curtipendula*[1]	9	0.0-32.0	4.41	
Side Oat Grama	*Bouteloua curtipendula*[3]	8	1.0-8.0	2.75	3.57
Needle grass	*Stipa sp.*[1]	3	0.0-2.0	1.01	
Needle grass	*Stipa sp.*[2]	22	0.5-40.0	6.70	5.61
Needle grass	*Stipa sp.*[3]	24	1.0-10.0	5.17	
Little bluestem	*Andropogon scoparius* Michx.[2]	51	0.0-2.0	0.75	
Little bluestem	*Andropogon scoparius* Michx.[3]	25	0.0-6.0	2.12	1.10

1 Data from this laboratory
2 Data from Byers (4)
3 Data from Byers (5)

CONVERTER PLANTS IN SOUTH DAKOTA

Several of the plants which may be classified as selenium "converters" occur in South Dakota, but those which occur most commonly are: *Astragalus racemosus, Stanleya bipinnata, Gutierrezia sarothrae, Aster multiflorus* and *Grindelia squarrosa*.

Figure 24 illustrates the importance of "converter" plants in the selenium problem. Selenium, as it occurs in relatively unweathered bedrock, is essentially unavailable to common crop plants and grasses. Even where soils have developed from seleniferous rock, the element remains relatively unavailable to common plants unless "converter" plants have been active during the formation of the soil. The "converter" plants are capable of absorbing selenium which is not available to other plants, and they absorb the element in relatively large amounts. Al-

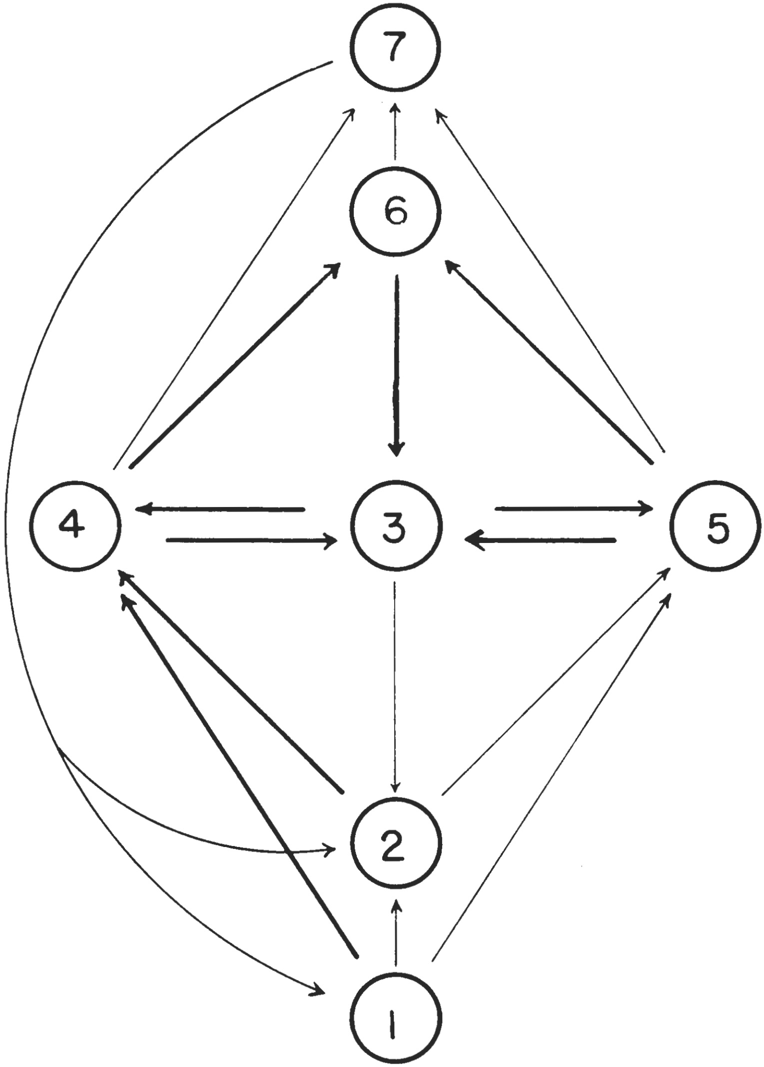

FIG. 24. The role of "converter" plants in the selenium cycle. Selenium in: 1. Parent rock; 2. Soil (inorganic); 3. Soil humus; 4. "Converter" plants; 5. Other plants; 6. Animals; 7. Atmosphere.

though some of the selenium in certain of these plants is volatile, and therefore escapes into the atmosphere, most of it is retained by the plant. When the plant dies it becomes incorporated as humus in the material in which it grew. The selenium it contained is then available to crop plants. Once the selenium has been converted to organic form, ordinary crop plants are probably able to maintain it in that form.

TABLE 72. Selenium Content of Converter Plants

	Selenium content of plants in parts per million (Dry basis)				
Location	*Astragalus racemosus*	*Aster multiflorus*	*Stanleya bipinnata*	*Gutierrezia sarothrae*	*Grindelia squarrosa*
NW¼ Sec. 4, T. 9 S., R. 1 E., Fall River Co.	24.0	7.2			
SE¼ Sec. 33, T. 8 S., R. 1 W., Fall River Co.	2700.0		520.0		
Same location	460.0		350.0		
Same location	320.0		476.0		
Same location	186.0		626.0		
Same location	500.0		136.0		
NW¼ SW¼ Sec. 8, T. 11 S., R. 3 E., Fall River Co.	490.0	3.6			7.4
SE¼ Sec. 16, T. 4 S., R. 10 E., Custer Co.	550.0		860.0		
SE¼ Sec. 31, T. 7 N., R. 6 E., Meade Co.	4100.0	90.0		14.0	
Same location	2880.0	165.0		22.0	
Same location	760.0	48.0		8.8	
Same location	1960.0	52.0		8.0	
Same location	880.0			18.0	
Same location	1160.0			44.0	
Same location	2640.0			46.4	
SE¼ Sec. 30, T. 7 N., R. 6 E., Meade Co.	760.0	320.0	2380.0	220.0	260.0
SW¼ Sec. 6, T. 8 N., R. 5 E., Butte Co.	50.0				2.0
NE¼ Sec. 6, T. 8 N., R. 5 E., Butte Co.	625.0				7.0
NE¼ Sec. 27, T. 9 N., R. 2 E., Butte Co.	125.0				4.0
Exact location unknown, Stanley Co.	24.0	5.0	250.0		
NE¼ SE¼ Sec. 28, T. 3 N., R. 31 E., Stanley Co.	500.0				10.0
NW¼ NE¼ Sec. 33, T. 3 N., R. 31 E., Stanley Co.	10.0	6.0			0.0
NE¼ NW¼ Sec. 15, T. 106 N., R. 76 W., Lyman Co.	3.5	0.0			
SE¼ Sec. 16, T. 106 N., R. 76 W., Lyman Co.	2460.0	10.0			12.4
Sec. 17, T. 104 N., R. 71 W., Lyman Co.	1420.0	34.0		160.0	

TABLE 73. Summary of Table No. 72

Plant	Avg. Se content p.p.m.	Average Se content of *A. racemosus* plants at same location p.p.m.	Comparative Se uptake p.p.m. using *A. racemosus* as 100
Stanleya bipinnata	699.75	687.5	101.78
Aster multiflorus	61.73	1240.9	4.97
Gutierrezia sarothrae	60.10	1840.0	3.27
Grindelia squarrosa	37.85	627.5	6.03

As previously stated, plant collections made during the summer of 1938 were made in such a manner that several of the factors causing variations in selenium content were eliminated. It seems, therefore, that some conclusions may be made as to the relative selenium content of our common "converter" plants and their selenium content at several locations. In order that the comparisons might be as valid as possible, they are made only where the plants were taken on the same date, from the same 10-foot section of the same formation, at a given location. Some factors, however, could not be eliminated, and must be kept in mind when interpreting this data.

Astragalus racemosus occurs at each location. Comparing the average selenium content of the other plants with the average selenium content of these *Astragalus* plants taken at the same location, results as shown in Table 73 are obtained.

Although the number of samples used in the comparison in Table 73 is small, it seems that some conclusions may be drawn from them. *Astragalus racemosus* and *Stanleya bipinnata* seem to be about equal in their ability to absorb selenium. The other three plants studied absorb considerably less selenium when growing under the same conditions.

SELENIUM CONTENT OF PLANTS AS RELATED TO THE VARIOUS GEOLOGICAL FORMATIONS

Moxon et al. (8) have made a study of the selenium content of plants on various geological formations in the state. A close relationship between the geological formation, type of vegetation, and selenium content of the vegetation was found to exist. These authors arrived at the following conclusions:

1. The Greenhorn formation is low in selenium in South Dakota. It does, however, contain some of the element, and *Astragalus racemosus* and *Stanleya bipinnata* occur occasionally on some beds of the formation. However, the formation is not considered important in selenium poisoning.

2. The Carlile formation is found to contain small amounts of selenium, and plants containing selenium are found growing on it in a few instances, but no dangerous seleniferous areas are believed to be found on it.

3. The Niobrara formation is the most highly seleniferous geological formation occurring in the state. *Astragalus racemosus* and *Stanleya bipinnata* are found growing on it abundantly, and the selenium content of these plants is high. Of the large number of plants analyzed from this formation during the summer of 1938, none were selenium-free. Several cases of selenium poisoning have been reported and observed on the Niobrara formation.

4. The Pierre formation varies in selenium content between and within its various members. The Sharon Springs member, although it contains large amounts

of selenium, is considered relatively unimportant in the formation of seleniferous areas because the lower part of the formation breaks down very slowly and seldom supports much vegetation. The upper part of the formation weathers more readily and in some instances may produce seleniferous areas. The Sully member of the formation contains some selenium, but not enough to make it important in the selenium problem. The lower Virgin Creek is low in selenium, whereas, a zone near the top of the member is highly seleniferous and where this part of it is exposed and relatively unweathered both *Astragalus racemosus* and *Stanleya bipinnata* are found growing in abundance on it. This zone is the parent material of some of the most seleniferous soil in the state. The Interior (Mobridge) member has a very low selenium content in its western and northern outcrops in the state, but near the Missouri River in the southern half of the state it becomes very highly seleniferous. The Interior (Mobridge) member in this region weathers into a very tillable and fertile soil and much of it is farmed. Perhaps most of the seleniferous soil of the state which is cultivated is derived from this member. Very little work has been done on the Elk Butte member of the Pierre, but apparently it is unimportant in the selenium problem in this state.

The White River formation has been found to contain a small amount of selenium, and *Astragalus racemosus* plants have been found growing on it (Figure 25) at several locations. Two samples of the plant found growing on the Oreodon beds of the White River formation, one in Jackson county and one in Pennington county, contained 4.0 and 10.0 parts per million of selenium respectively. *Gutierrezia sarothrae* also occurs in relative abundance on this formation, but no samples have been analyzed for selenium at this laboratory. The White River formation is not considered to be of importance in the selenium problem in South Dakota.

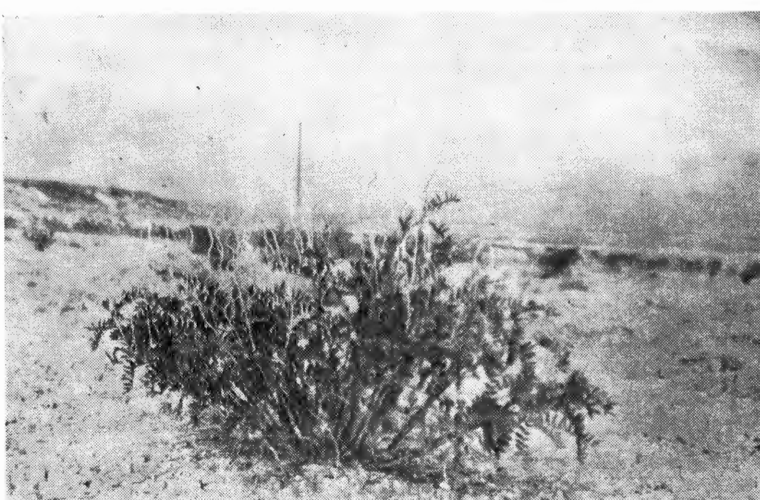

FIG. 25. *Astragalus racemosus* growing on the White River formation. Note absence of other vegetation.

RELATIONSHIP BETWEEN THE SELENIUM CONTENT OF PLANTS AND THE MATERIAL IN WHICH THEY GROW

In order to determine to what extent plants might be used in determining how seleniferous the material in which they grew might be, the following study was made.

TABLE 74. Selenium Content of Converter Plants on Three Different Formations

Formation	Geol. Spl. No.	Depth In Feet	Se Content of Geol. Sample	PLANT SAMPLED: *A. racemosus* Spl. No.	*A. racemosus* Se Content p.p.m.	*S. bipinnata* Spl. No.	*S. bipinnata* Se Content p.p.m.	*A. multiflorus* Spl. No.	*A. multiflorus* Se Content p.p.m.	*G. sarothrae* Spl. No.	*G. sarothrae* Se Content p.p.m.	*M. decape* Spl. No.	*M. decape* Se Con p.p
Niobrara	G25	90-100	21.0	V41	500.0	V42	136.0						
	G24	80-90	24.0			V40	150.0						
	G23	70-80	13.0			V39	376.0						
	G22	60-70	8.0			V38	240.0						
	G21	50-60	9.2			V37	200.0						
	G20	40-50	7.5	V35	186.0	V36	626.0						
	G19	30-40	7.0			V34	550.0						
	G18	20-30	7.3	V32	320.0	V33	476.0						
	G17	10-20	0.6	V30	460.0	V31	350.0						
	G16	0-10	6.1	V28	2700.0	V29	520.0						
	G164	60-65	6.3	V181	2640.0					V182	46.4		
	G163	50-60	27.0	V179	1160.0					V180	44.0		
	G162	40-50	16.0	V177	880.0					V178	18.0		
	G161	30-40	15.0	V175	1960.0			V183	52.0	V176	8.0		
	G160	20-30	9.0	V172	760.0			V173	48.0	V174	8.8		
	G159	10-20	18.5	V169	2880.0			V170	165.0	V171	22.0	.	
	G158	0-10	21.0	V166	4100.0			V167	90.0	V168	14.0		
Greenhorn	G256	50-56	0										
	G255	40-50	0.8									V267	1.
	G254	30-40	1.0									V266	8.
	G253	20-30	0									V265	
	G252	10-20	0	V264	4.0					V263	2.0		
	G251	0-10	0										
	G250	40-49	0							V262	3.4		
	G249	35-40	0										
	G248	20-30	0.6										
	G247	10-20	0	V259	125.0					V258	4.0		
	G246	0-10	0.5							V257	1.4		
Pierre	G331	40-50	2.0	V339	10.0								
(Interior	G330	30-40	0.6	V338	64.0								
member)	G329	20-30	1.7	V343	641.0								
	G328	10-20	1.0	V341	75.0								
	G327	0-10	0	V340	48.0								
	G472	90-95	8.5	V481	224.0								
	G471	80-90	1.0	V480	72.0								
	G470	70-80	0	V478	3.0								
	G469	60-70	0	V477	0								
	G468	50-60	1.3	V476	4.4								
	G467	40-50	0										
	G466	30-40	0	V475	30.0								
	G465	20-30	1.0										
	G464	10-20	0	V474	4.0								
	G463	0-10	0										

During the sampling of several geological sections, plant samples were taken on each part of the section where geological samples were taken. The plants collected were growing in relatively unweathered material, such as that taken for analysis. Several factors causing variation in selenium content of plants were eliminated by the method of collection but several others were not controllable. Some of the results of the work are listed in Table 74.

An examination of the data in Table 74 reveals that there is no direct correlation between the selenium content of the plants and the selenium content of the material in which they grew, even though several factors causing variations are eliminated. There are several reasons for this lack of correlation. One of the most important of these reasons is the variation in selenium content of the formations within the 10 feet that were composited for each sample. It was often difficult to obtain samples of plants that were representative of the whole 10-foot bed on which they were collected, and because of the variation in selenium content of the rock, considerable variation might result. The age, thrift, and length of roots of the plants varied somewhat between samples, and this is in part responsible for the lack of correlation.

It is interesting to note that in some cases where selenium could not be detected in the rock samples, analyses of plants showed traces to be present. There are several reasons which may be suggested for this apparent discrepancy. If the formation contained only a small amount of selenium distributed throughout the whole ten feet where it was sampled, the amount of selenium in a 10-gram sample such as that used for analysis may have been too small to detect. It is possible, too, that selenium may be concentrated in very thin bands in some of the formations, so that when a 10-foot section is sampled the composite might not contain enough selenium to be detected upon the analysis of a ten gram sample. Furthermore, that part of the formation on which the plant sample was collected might contain no selenium, but the plant root may have extended downward into another part of the formation which did contain selenium.

DISTRIBUTION OF IMPORTANT CONVERTER PLANTS IN SOUTH DAKOTA

Although, with the information on hand, it is not possible to accurately map the distribution of "converter" plants in South Dakota, a considerable number of observations have been made relative to their distribution. The following discussion is based largely on these observations.

Astragalus racemosus has never been found growing where the soil or rock is selenium-free. Trelease and Trelease (52) have shown selenium to be a stimulating and possibly an essential element for the growth of some indicator plants, one of which was *Astragalus racemosus*. A few analyses of this species of plant have been made where the selenium content was zero, but Beath[1] states that in such a case the plant would at some stage of its growth contain selenium. Growing under natural conditions, the plant seems to require relatively unweathered material for best growth, although it has been found in a few cases on fairly well-developed soil.

1. (Personal communication).

Astragalus racemosus has been reported on the Greenhorn, Carlile, and Niobrara formations, the Sharon Springs, Sully, Virgin Creek, and Interior members of the Pierre formation, and on Brule and Chadron beds of the White River formations in South Dakota, and it may occur on others also. It occurs most frequently on the Niobrara formation, and upper Virgin Creek and the Interior members of the Pierre formation. Its occurrence is quite frequent on the Sharon Springs member of the Pierre formation too, but this member is of such a nature that it rarely supports much vegetation at all, except on its upper beds. *Astragalus racemosus* is the most important "converter" plant in the area surrounding the Black Hills, and in this area it is important in causing the death of animals from acute selenium poisoning.

Stanleya bipinnata has never been found growing on non-seleniferous material in South Dakota, and Trelease and Trelease (52) report it as being one of the plants which may require selenium for normal growth. Thomas Nuttall in his book, Genera of North American Plants (volume 2, page 72, 1818), makes the following statement concerning *Stanleya*: "its large, and glaucous leaves, so much like some of the cultivated varieties of *Brassica oleracea,* has induced us to collect them as an article of diet, but to more than half of those who had partaken of this deleterious vegetable, after being boiled, it proved a violent emetic."

He states further, "Commencing, (as we observed) near the confluence of Paint Creek and the Missouri, growing on the talus of broken calcareous cliffs, from hence it occurs locally for two or three hundred miles farther up the river, so that it appears only to occupy a limited belt which traverses the Missouri."[1] Since selenium is known to cause vomiting in dogs (53) it is probable that it was the cause of the emetic action of the *Stanleya* mentioned by Nuttall. It is of interest to note that he observed the plant growing on chalky cliffs and talus from the cliffs. Around the Black Hills in South Dakota, *Stanleya* has been found growing only on the Niobrara and Greenhorn formations. Both of these formations are chalky. East toward the Missouri river, the plant is found also on the the Interior and upper Virgin Creek members of the Pierre formations, both of which are chalky to some extent.

Stanleya is much more abundant in the region around the Black Hills than in the region to the east of it. Observations made at the contact of the Niobrara with adjacent formations reveal that although there may be an abundant growth of the plant on the Niobrara and its relatively unweathered wash to within a very few feet of the contact or the border of the wash material, it will not extend beyond the Niobrara-Carlile contact and will not grow in the non-seleniferous Carlile formation. Figure 26 shows diagrammatically the occurrence of *Astragalus racemosus* and *Stanleya bipinnata* on various formations.

Aster multiflorus is scattered fairly widely over the entire state. It apparently grows as well where there is no selenium in the soil as where there is selenium in the soil. It appears to require more moisture and a more well developed soil for vigorous growth than do *Astragalus racemosus* and *Stanleya bipinnata*. It is, therefore, more abundant in the seleniferous regions along the Missouri river than in those farther west. The plant probably occurs on all formations where the soil

1. The authors are indebted to O. A. Stevens, Associate Professor of Botany and Plant Pathology, North Dakota Agricultural College, Fargo, N. Dak., for calling their attention to this statement.

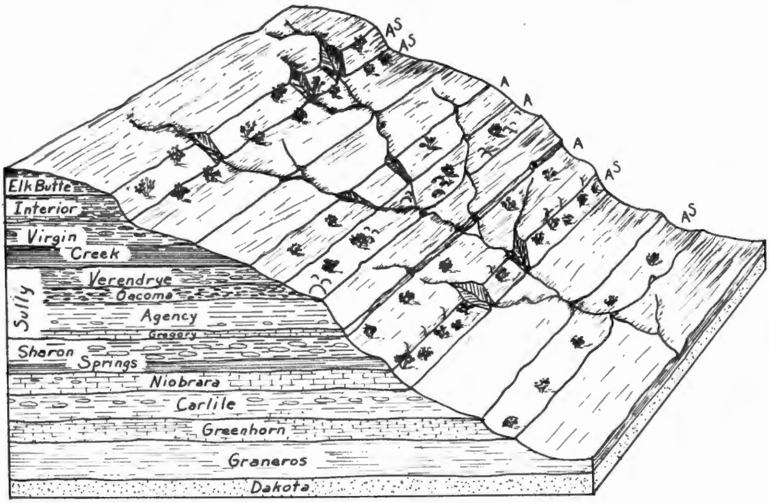

FIG. 26. Block diagram showing formations which support *Astragalus racemosus* and *Stanleya bipinnata.* A—*Astragalus racemosus;* S—*Stanleya bipinnata.*

has been fairly well developed and where the rainfall is not too limited. When it is found growing in the region around the Black Hills, *Aster multiflorus* usually exhibits poor growth.

Gutierrezia sarothrae has not been studied by the authors in as great detail as have other plants discussed here. It occurs on several formations, and probably will grow where there is no selenium present, although this is not definitely known. It grows best in relatively unweathered material, and it appears to do well under drought conditions. It is more abundant in the region surrounding the Black Hills than it is farther east.

Grindelia squarrosa occurs widely distributed over the whole state. It grows best on fairly well-developed soils, but will grow on relatively unweathered material. Its occurrence apparently is not related to the occurrence of selenium. Observations show that it is more or less sporadic in its occurrence from year to year. During the summer of 1938 it was abundant over the state, but it appears that in the summers preceding 1938 its occurrence was much less frequent. This is probably due to differences in moisture conditions. These plants grow much better in the seleniferous regions along the Missouri river than in those around the Black Hills.

IMPORTANCE OF CONVERTER PLANTS IN THE STATE

The regions surrounding the Black Hills of South Dakota consist of relatively unweathered material, and few well-developed soils are found. In this region, ranching is more predominant than farming. It is felt, therefore, that in this region highly seleniferous plants are more important in causing deaths in livestock, due to acute selenium poisoning, than they are in producing seleniferous soils. Although there is considerable ranching in the region along the Missouri river, the soils are fairly well-developed, and much of the land is farmed. Because it occurs much more frequently in this area, *Aster multiflorus* is probably the most important "converter" plant in the region of the Missouri river. Around the Black Hills, *Astragalus racemosus* and *Stanleya bipinnata* are the most important highly seleniferous plants, both from the standpoint of conversion and livestock poisoning.

The Selenium Cycle

In the Great Plains the most important seleniferous rocks are those of Upper Cretaceous time, especially those of the Pierre and Niobrara formations. These rocks of marine origin are, however, not the primary source of selenium. Selenium from some earlier source must have been present in the erosion cycle at the time that the sediments were being deposited to form these formations. The primary source of selenium is a matter of speculation at the present time. We do, however, know that selenium occurs in such ancient rocks as those of the Whitewood formation. Selenium has also been found in pyrites and other minerals, from pre-Cambrian rocks (4, 42) and (Table 1, page 28) and in igneous rocks and sublimates from volcanic gases in Hawaii (6).

Although the primary source of selenium is of great academic interest, especially to geologists and geochemists, it probably is of less real importance than other parts of the selenium cycle. Without doubt, the movement of selenium in the cycle at the present time is of more importance to those who are studying the selenium problem from the standpoint of agriculture or public health.

As a starting point in the diagrammatic scheme for the selenium cycle (Fig. 27 it is assumed that the primary source of selenium is igneous rock. Weathering and erosion have broken the igneous rocks down and a part of the material has found its way into the old sea in which the sedimentary rocks, of Upper Cretaceous time, were deposited. Thus we find selenium in the Pierre and Niobrara formations of the Great Plains area. It is the selenium which is present in these formations today that gives us the most concern. The selenium of these sedimentary rocks becomes available to converter plants and is also carried through soil forming processes to appear in soil where it is available to converter plants and, to a limited extent, to crop plants. The selenium absorbed by converter plants is, of course, partially returned to the soil upon decay of the plant and it is then available to crop plants.

Animals which feed upon seleniferous plants retain a part of the selenium in their bodies and excrete a part of the selenium, which finds its way into soils, sedimentary rocks, and water. Animals also eliminate a limited quantity of selenium in the form of volatile compounds which ultimately find their way back into the soil or rocks by way of ground or running water, or the ocean.

Whatever the primary source of selenium may be, breakdown of seleniferous rocks by weathering and leaching has permitted removal of some of the selenium to the oceans. The fact that ocean water contains no more than a trace of selenium while marine sediments, both ancient and modern, contain appreciable quantities of the element indicates that selenium is rapidly precipitated when it reaches the ocean. The mechanism for this precipitation is indicated by the work of Strock (54) and Byers and associates (6) who found that, in the presence of colloidal ferric hydroxide, selenium (selenite) is rapidly removed from solution as an insoluble iron compound. Marine sediments are, thus, more or less of a trap or reservoir for selenium. The selenium is retained in the marine sediments and remains there until elevation by diastrophism and subsequent erosion of overlying deposits brings these selenium containing sediments back to the surface where they are exposed to the processes of weathering and leaching.

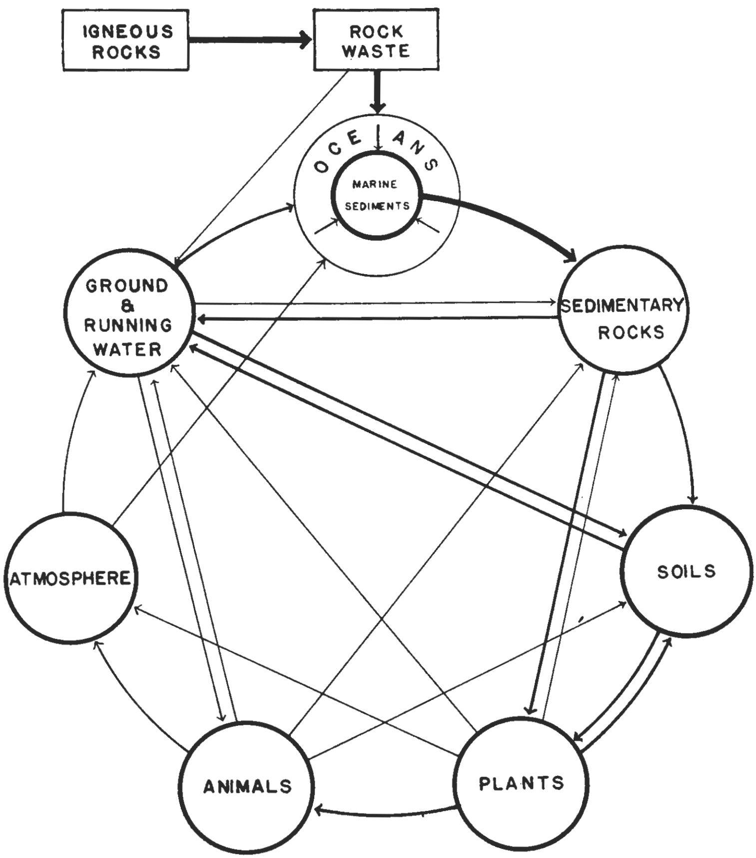

FIG. 27. Selenium Cycle.

During the processes of soil formation and accompanying leaching much of the selenium is carried away by ground and running water and finds its way back to the ocean where it is redeposited. Positive proof of the loss of selenium from soils and rocks is given by Williams and Byers (55). They found that drainage water from irrigated districts in Colorado contained considerable quantities of selenium while the supply of irrigation water contained no selenium or at most less than one part per billion. The selenium leached from these districts is being carried by the Colorado river, to the Gulf of California. No data on the selenium content of the deposits from the bottom of the Gulf of California are available.

Williams and Byers (56) have reported on the selenium content of sea-bottom deposits collected off the coasts of Alaska and Siberia. The selenium content of the nine samples which they analyzed contained from 0.03 p.p.m. to 0.70 p.p.m. with an average content of 0.273 p.p.m.

Twelve samples of deposits from the Gulf of Mexico were obtained through the courtesy of Dr. A. C. Trowbridge of the department of geology, University of Iowa. These samples had been collected by the U. S. Fish Hawk at the following locations:

Number	Latitude	Longitude	Depth in Fathoms
42	28° 47′ 42″	89° 29′ 41″	50.0
45	28 54 36	89 28 27	17.2
62	28 55 11	89 32 15	24.0
70	28 47 03	89 32 05	50.0
76	28 47 42	89 29 41	50.0
81	28 48 36	89 31 12	48.0
86	28 57 15	89 32 08	26.3
162	28 55 14	89 20 45	12.2
190	28 57 31	89 19 58	8.4
354	28 47 59	89 17 55	62.0
501	28 55 33	89 08 26	35.0
506	28 51 00	89 05 39	100.0

The samples were not large enough for individual determinations so they were composited for analysis. The composite sample contained 0.77 p.p.m. of selenium. This is almost three times the average value for the samples from the Alaska and Siberia coasts and is comparable to the concentration of selenium in most of the marine sediments of Paleozoic and Mesozoic age.

Estimates based on the selenium content of unweathered sections of the Interior member of the Pierre formation and the selenium content of soil derived from this member indicate that the loss of selenium during the soil forming process ranges from 60 to 85 percent. The higher value is probably more typical in the Great Plains area.

There is adequate evidence that plants absorb selenium both from soils and sedimentary rocks. At the death of the plants the selenium finds its way back to the soils and rocks. However, a part of the selenium absorbed by plants finds its way into ground and running water and a part is volatilized into the atmosphere. Ultimately these fractions are largely returned to the sea and deposited in marine sediments.

It is likely that transference of selenium through the cycle is even more complex than indicated by the selenium cycle in Figure 27, due to the intricate and complex changes in chemical composition, particularly in the organic portion of the cycle.

Control Measures

Probably the most effective control measure for application in the most toxic areas would be the detailed mapping of seleniferous formations and seleniferous soils on individual farms and ranches. The mapping of the areas would have to be done by persons familiar with the selenium problem and would need to be confirmed by adequate analyses for selenium. Instances were encountered, during the course of the field work, where the fencing off of two or three acres on a farm would eliminate the source of considerable livestock trouble. In other cases it would, of course, require the withdrawal of larger areas from the production of livestock feed. These areas should not be used for cash, food, or feed crops but could safely and ethically be used for seed or fiber crops.

Although some experimental work carried out under greenhouse conditions has suggested that sulfur applications to soils will decrease the absorption of selenium from these soils by plants (48, 49, 50, and 51) experiments carried on in the field have demonstrated that sulfur applications are of little or no value in this respect (13,45).

Investigations under way in this laboratory show that it is possible to counteract the toxic effects of seleniferous feeds by supplying a small amount of certain other elements in the drinking water. To date this study has not reached a stage where it can be safely recommended for livestock under farm conditions.

The tolerance levels for selenium in poultry feeds have been worked out here at the Experiment Station (57,58,59) and now it is possible to advise poultrymen whether or not to use the feeds which they send in for selenium analysis. Work has started on tolerance levels of selenium for farm animals.

It has been observed that some seleniferous grains lose large percentages of their selenium during storage (60). Many farmers follow the practice of mixing their selenium-containing feeds with selenium-free feeds which they purchase outside of the seleniferous areas.

Summary

1. The rocks of the several geological formations are described briefly, and a correlation between the geological formations of this state and those of nearby states is made.

2. Analyses of several samples of rocks from many of the geological formations indicate that selenium is usually present in the rocks of South Dakota, but in most of the rocks it is found only in very small amounts. There are, however, some formations or beds within formations which contain a relatively large amount of the element, and where these formations or beds are exposed selenium poisoning in livestock may occur. The most consistently highly seleniferous formation in South Dakota is the Niobrara. Fortunately its outcrop covers only a very small area within the state. The lower Sharon Springs member of the Pierre formation is also consistently highly seleniferous, but it is resistant to weathering and therefore seldom forms soils, and vegetation is seldom found growing on it. The upper Sharon Springs contains enough selenium to be considered dangerous from the standpoint of selenium poisoning. Although the relatively fresh out-

crops of the member seldom support much vegetation, soils weather from it and these soils support the growth of considerable vegetation. For the most part the Virgin Creek member of the Pierre formation is not highly seleniferous, but near the Missouri river in the southern half of the state the uppermost part of the member contains considerable selenium and highly seleniferous soils have weathered from it. The Interior member of the Pierre formation is highly seleniferous in the area along the Missouri river in the southern half of the state, and in this area it forms seleniferous soils. However, its selenium content decreases rapidly toward the northwest.

3. Factors concerned in the surface distribution of selenium are discussed and illustrated.

4. Data concerning the selenium content of soils indicate that during the formation of soils from bedrock there is a considerable loss of selenium. The reason for this loss and other factors determining the selenium content of soils are discussed.

5. Factors influencing the availability of selenium to plants and the absorption of selenium by plants are discussed.

6. The selenium contents of six grasses, western wheat grass, buffalo grass, sideoat grama, blue grama, needlegrass, and little bluestem, are compared. Western wheat grass is found to be considerably more seleniferous than are the other grasses with which it is compared. The selenium contents of the important "converter" plants of the state, *Astragalus racemosus, Stanleya bipinnata, Aster multiflorus, Gutierrezia sarothrae,* and *Grindelia squarrosa* are also compared.

7. The relationship between the selenium content of the geological formations and the selenium content of plants growing on them is discussed. It is found that in general the selenium content of the formation determines the type of plants and the selenium content of the plants which grow on the formation.

8. Based on available data, a hypothetical selenium cycle is presented.

9. Control measures for selenium poisoning are discussed briefly.

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