

THE GEOLOGICAL SURVEY OF WYOMING

HORAGE D. THOMAS, STATE GEOLOGIST

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SOME ROCKS AND SOILS OF HIGH SELENIUM CONTENT

BY

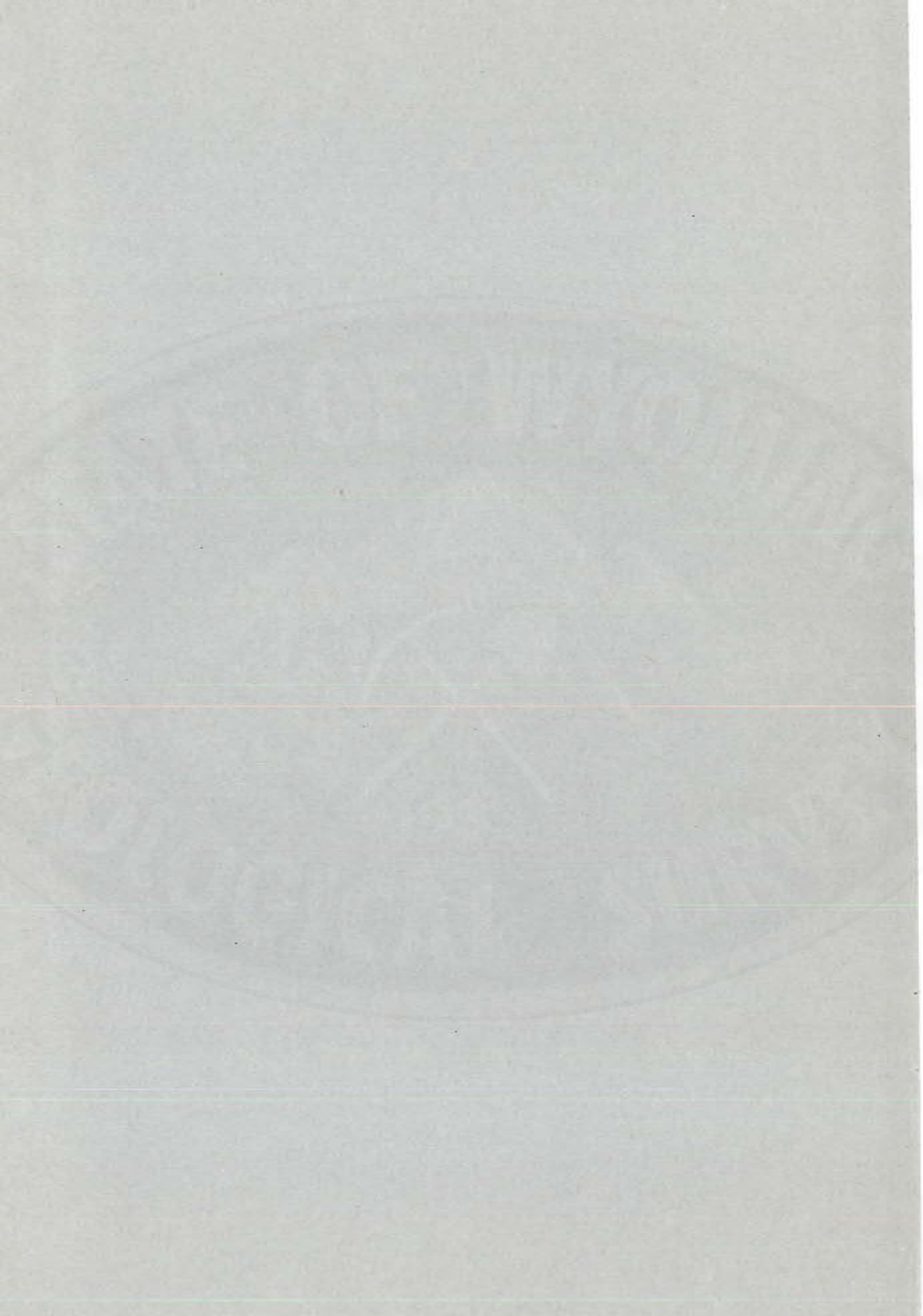
O. A. BEATH, ARTHUR F. HAGNER and C. S. GILBERT



UNIVERSITY OF WYOMING

Laramie, Wyoming

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SOME ROCKS AND SOILS OF HIGH SELENIUM CONTENT

By O. A. Beath, Arthur F. Hagner, and C. S. Gilbert

ABSTRACT

Critical seleniferous areas in the western states are correlative with the available, or water soluble, form of selenium. Selenate selenium is the dominant form in the rocks and soils considered in this paper. Rocks and ores studied include tuffs, sandstone, vanadiferous siltstone, phosphate rock, shales, and vanadium-uranium ores. A typical toxic soil from eastern Wyoming is described and an appraisal is made of the toxic character of native vegetation associated with seleniferous rocks and soils. Quantitative analyses of two tuffs are given and quantitative correlation of selenium and vanadium in two samples of vanadiferous siltstone is reported on. The selenium-accumulating properties of different kinds of vegetation are discussed. The possibility of using seleniferous vegetation in locating mineralized areas is considered.

INTRODUCTION

Primary selenium occurrences in the arid and semi-arid regions of the western states are distributed in various types of rocks and soils. Seleniferous vegetation has been found growing on Paleozoic, Mesozoic, Cenozoic, and Recent deposits. The oldest formation in Wyoming known to support native seleniferous plants is the Amsden, the lower part of which is of Mississippian age. The Amsden formation was recently found to support the seleniferous *Astragalus grayi* (Gray's vetch) and *Stanleya tomentosa* (Prince's Plume), (Sec. 5, T. 39 N., R. 91 W., Fremont Co., Wyo.). (Fig. 1 and 2). In tracing selenium occurrences from older rocks to those of Recent age, it is evident that no consistent pattern can be followed. Certain formations are definitely seleniferous while others are not. The correlation of geological formations with seleniferous plant occurrences has been investigated by several workers (Beath, 1-10), (Byers, 11-13), (Hershey, 18), (Lakin, 19), (Moxon, 22, 23), (Olson, 24), (Trelease, 26, 27), (Williams, 29, 30).

SOME ASPECTS OF SELENIUM OCCURRENCES

Seleniferous soils and vegetation have been identified in many regions of the western United States. In addition, such areas extend into the Canadian provinces of Alberta, Saskatchewan, and Manitoba and south into Mexico. Soils capable of supporting seleniferous plants have been found only in arid and semi-arid regions where the mean annual rainfall is less than 20 inches.

Selenium *indicator* plants are a special group of native plants that can be relied upon to contain significant amounts of selenium, and hence their presence indicates the occurrence of selenium in the soils upon which they grow. The capacity of such plants to concentrate a large amount of selenium in their framework often results in an *accumulation* of selenium several hundred times greater than the soil concentration. There are a large number of native plants aside from the indicators that are capable of accumulating high selenium values when rooted in a selenium-containing soil. Their growth, however, is not

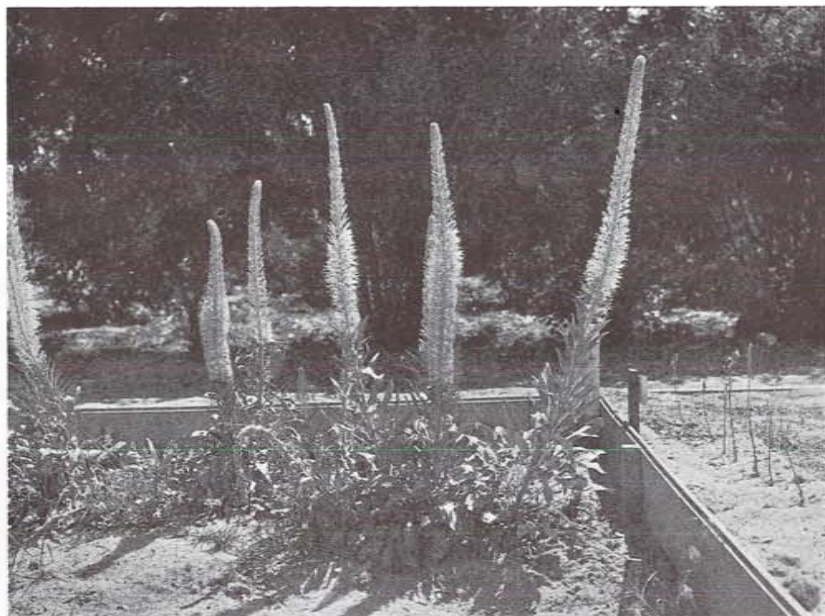


Figure 1. *Stanlea tomentosa* Parry. A positive selenium accumulator.
Near Lysite, Wyoming.



Figure 2. *Astragalus grayi* Parry. Typical of a large group of positive selenium
accumulators. Shirley Basin, Wyoming.

restricted to these special conditions, consequently their usefulness as true indicators is negligible. In general, seleniferous plants are abundant and widely distributed. They cover vast areas in the sparsely settled regions of the western United States that are devoted to raising cattle and sheep, and are responsible for losses of livestock estimated at millions of dollars annually.

Selenium in its naturally occurring states is not universally available to farm crops and forages. There are areas, however, where soils carry some available selenium. In most cases these toxic areas are localized. A soil containing 1 to 10 parts per million of total selenium is definitely seleniferous. If none is present in an available form, then only those native plants with selenium-absorbing tendencies will be seleniferous. Soils with a selenium content from 10 to 30 ppm. have a high concentration, and values above 30 ppm. are considered very high. In terms of available or water soluble selenium it is not possible to state what constitutes a minimum value. Seleniferous grass has been found that yielded 50 ppm. in soil that contained only 0.5 ppm. water soluble selenium. It is generally known, however, that a soil with 1 to 5 ppm. of available selenium can be depended upon to support seleniferous grasses and forages.

Only a few samples of native soils have been tested for the form of water soluble selenium. In these the selenate form of selenium was dominant. A very considerable amount of work remains to be done to establish the form of naturally occurring selenium compounds in the toxic areas of the Western States.

Sodium selenite introduced into a surface foot of soil (40 ppm. selenium) and allowed to react a few years under cropping conditions was much less soluble at the end of an 8 year test. For its complete recovery, strong oxidizing reagents were required. The total selenium was essentially the same as originally introduced. The portion soluble in water at the conclusion of the experiment amounted to only 4 ppm., 3 ppm. of which were selenite selenium and 1 ppm. was selenate.

Whereas considerable attention has been directed to volcanic rocks as a primary source of selenium, the writers have evidence to show that certain tuffs are not only high in selenium, but support an abundance of highly seleniferous vegetation. On the other hand, many volcanic rocks upon chemical examination show some selenium, but no toxic plants of significance have been reported growing on them or in soils derived from them.

SELENIUM-BEARING TUFFS

Location and Field Relations

The seleniferous volcanic exposures discussed in this paper are located in sections 2, 3, 10, and 11, T. 39 N., R. 91 W., Fremont County, Wyoming. Locally the area is known as the "Lysite poison draw." The area occupied by the tuffs and alluvial wash derived from them is essentially similar topographically to the surrounding region. The continuity of vegetative cover is such that an observer would not recognize any particular change in plant density

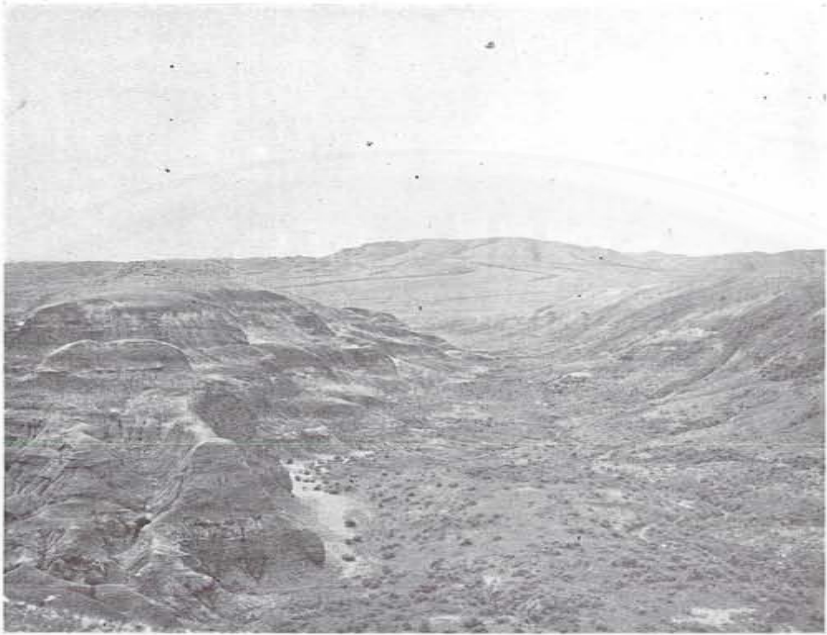


Figure 3. Seleniferous stratified tuff in draw near Lysite, Wyoming.



Figure 4. Seleniferous tuff in center of photo. Background is Tensleep formation with Amsden at base. Near Lysite, Wyoming.

or kind in passing across the poison draw from a point outside. Livestock operators have long recognized the danger of the area and know fairly well where the boundary between safe and unsafe vegetation is located.

In 1934, an investigation was made of the poisonous plants in the region. Chemical analyses demonstrated that the active toxicant is selenium and that plants growing in the poison draw are much more seleniferous than corresponding species outside the area. At the time of this investigation it was believed that the geological formation involved was the Wind River (Lower Eocene). During 1944, an intensive study was made of the geological features and plants in the region. Field observations (Tourtelot, 25) indicate that the poison draw involves rocks of Middle or Upper Eocene age. Type rock specimens from several horizons were taken for study and the petrographic work on this material was done by A. F. Hagner.

Near the head of the main poison draw, erosion has dissected a portion of the outcrop and produced an abrupt prominence about 75 feet high. (Fig. 3 and 4). From this exposure it was possible to collect rock specimens of the individual beds. Where slopes are steep the surface is covered with finely divided disintegrated rock. Beneath this mantle, however, the rocks are massive and compact. Individual beds vary in color; some are white, gray, or green, others range from red to brown. The thickness of individual beds ranges from 3 to 20 feet.

Selenium analyses were run on all the rock specimens taken from representative exposures. In general, a wide variation was found in selenium content, both in the total amount and in the water soluble form. The results suggest that during the time the beds were deposited the source material differed in selenium content. The original source of the tuffs in the Lysite area may have been active volcanoes of the Yellowstone Park region.

A considerable amount of alluvium and representative kinds of vegetation were collected for selenium analyses. Because of more favorable conditions for plant growth, the alluvium supports a greater density and diversity of plants than is found associated with the tuffs proper. From the point of view of livestock poisoning, the alluvium is a major consideration in the poison draw area.

The lack of vegetation on some exposures of tuff may be due to the fact that the available selenium is present in too great a concentration for plants to survive. Further information on this point is needed to arrive at definite conclusions.

Description of Individual Tuffs

The selenium-bearing tuffs were examined in hand specimen and with the petrographic microscope. The rocks are light-colored, fine-grained, and loosely compacted. Microscopically they consist of mixtures of crystals, lithic fragments, and glass, the proportions varying with the sedimentary bed or layer.

Lithic fragments are subrounded and range in size from $1/10$ to $1/2$ mm. across. Crystals are angular to sub-angular and range from $1/50$ to $1/4$ mm. across; most of them are between $1/8$ and $1/4$ mm. Although too small for accurate identification, the lithic fragments are mostly plagioclase and glass and have a trachytic structure. The glass is usually partly devitrified and altered to clay.

The crystals are almost all plagioclase feldspar and range in composition from 45 to 61 percent anorthite; most of them contain around 55 percent. Anorthite content was determined with a universal stage measuring extinction angles in the zone normal to (010). It was possible to measure from 4 to 8 crystals in each slide, with the exception of the finest grained tuff (Bed 1), in which case only 2 crystals were suitable.

Chemical analyses of Beds 2 and 3 (Table 1) are similar to trachyte except for the low potash content and the high silica in Bed 3. It is believed that the former is due to the absence of potash feldspars. The absence of quartz, except for an occasional grain, suggests that the high silica in Bed 3 is largely present in the glass. These differences are certainly to be expected in non-uniform rocks or in aggregates of different rocks, minerals, and glass, such as tuffs.

The following descriptions are based on a microscopic study of crushed fragments and thin sections of one representative specimen from each of the beds mentioned. Minor lithologic variations occur within individual beds but are not considered here. The numbers refer to sedimentary beds and range from the lowest in the succession, Bed 1, to the highest, Bed 5.

Bed 1. This is a white, extremely fine-grained vitric tuff, somewhat over half of which is glass and the remainder crystals and lithic fragments with a slightly greater percentage of the former. Glass shards are found in places, but, for the most part, the glass is considerably altered to clay. Crystals are predominately labradorite which is euhedral to anhedral, shows albite twinning, and contains from 54 to 55 percent anorthite. Scattered grains of quartz, sericite, and biotite occur throughout the slide. The crystals range in size from $1/4$ to $1/50$ mm. across, the average being approximately $1/30$ mm. Lithic fragments appear to be trachyte or andesite and average $1/4$ mm. across. A few veinlets transect the rock and consist of plagioclase, quartz, and glass.

Bed 2. This is a buff, lithic-crystal tuff with the principal constituents labradorite crystals and lithic fragments. The labradorite is subhedral to anhedral, shows albite twinning, and has an anorthite content of 52 to 57 percent. It is occasionally zoned and crystals range in size from $1/4$ to $1/20$ mm. across, most of the crystals being $1/4$ to $1/8$ mm. in size. The lithic fragments appear to be trachyte and range in size from a fraction of a mm. across to 1 mm. by $1/2$ mm. Minor minerals include occasional grains of biotite, magnetite, apatite, and kaolin. The glass is partly altered and devitrified and a small amount of limonite occurs throughout the slide.

Bed 3. This is a green, crystal-lithic tuff containing chiefly labradorite and lithic fragments with a minor amount of glass. Labradorite grains are

subhedral to anhedral, have albite twinning, and average $1/8$ to $1/16$ mm. in diameter. Anorthite content ranges from 46 to 58 percent. The mineral is slightly altered to sericite and kaolin. Lithic fragments appear to be trachyte or andesite, are subrounded, and average about $1/4$ to $1/2$ mm. across. A few grains of biotite and magnetite are present. The glass is partly devitrified.

Bed 4. This is a gray, crystal-lithic tuff composed largely of labradorite crystals and lithic fragments, with a small amount of glass. Labradorite is euhedral to anhedral, shows well-developed albite twinning, and is occasionally zoned. Anorthite content ranges from 48 to 58 percent. The mineral is fresh with only incipient alteration to kaolin. Crystals range in size from a small fraction of a mm. to $1/2$ mm. in length, and $1/4$ mm. across. Minor amounts of magnetite, ilmenite, and apatite are present. Some of the ilmenite is partly altered to leucoxene. The lithic fragments range in size from a fraction of a mm. to 1 mm. in length and are up to $1/2$ mm. across. Although too small to be indentified with certainty, they appear to be trachyte or andesite.

Bed 5. This is a pale-brown tuff with about 40 percent labradorite and lithic fragments distributed as individual grains in a groundmass of glass. Labradorite is subhedral to anhedral, shows albite twinning, and is little altered. It has an anorthite content of 50 to 58 percent. The lithic fragments show varying degrees of alteration to clay. Both labradorite and lithic fragments average about $1/8$ mm. across. An occasional crystal of biotite and a small amount of magnetite and limonite are present.

Selenium Content of Tuffs

The selenium content of the tuffs examined was found to range from 12.5 to 187 parts per million. In some practically all the selenium is soluble in water; in others only part is soluble. The form of selenium that is soluble in water is dominantly the selenate. Only traces of selenite selenium are present.

Bed 1. This is the lowest bed exposed. Analysis of samples from the surface foot showed the total selenium content to be 112.0 ppm. The quantity soluble in water was 94.3 ppm., of which 92.5 ppm. were selenate and 1.8 ppm. selenite. These data show that about 84 per cent of the total selenium in the rock is water soluble. *Atriplex nuttallii* (saltbush), a woody perennial rooted in the rock, was found to be highly seleniferous.

Bed 2. A composite sample for analysis was taken from the vertical face of the exposure of Bed 2. It carried 187.0 ppm. total selenium. A water extract yielded 180.0 ppm., of which 173.0 ppm. were selenate and 7.0 ppm. were selenite. In this bed, approximately 96 percent of the total selenium was soluble in water. No native plants were growing in the immediate vicinity of the exposure. A quantitative analysis was made of this tuff. (Table 1).

Bed 3. This bed occupies a position about midway between the lowest and highest outcrops. Its total selenium content was found to be 175.0 ppm. The quantity soluble in water was 152.0 ppm., of which 144.0 ppm. were selenate and 8.0 ppm. were selenite. Approximately 87 percent of the total selenium was water soluble. No native plants were observed growing on this bed. A quantitative chemical analysis was made of the tuff (Table 1).

Bed 4. The total selenium in this tuff was only 29 ppm. The amount soluble in water was not determined.

Bed 5. This is the uppermost rock exposed. Total selenium was 12.5 ppm. Solubility was not determined.

Seleniferous Vegetation Associated With Tuffs

The dominant selenium indicator plants in the poison area are *Astragalus grayi* and *Xylorrhiza parryi* (Fig. 3 and 4). Representative plant collections were made and analyzed and the results are tabulated in Table 2.*

*In determining the total amount of selenium in plants and soils the procedures followed were those outlined in Association Official Agricultural Chemists, 1940. In the estimation of water-soluble forms of selenate, selenite, and organic selenium, the method of Byers (13) was followed.

TUFF FROM LYSITE AREA

Quantitative Analysis
C. S. Gilbert, Analyst

Table 1

	Bed 2	Bed 3
SiO ₂	58.86%	67.98%
Al ₂ O ₃	18.69	15.01
CaO	4.83	3.69
MgO	1.24	0.59
FeO	0.08	0.26
Fe ₂ O ₃	4.38	3.46
TiO ₂	0.69	0.50
K ₂ O	1.44	1.57
Na ₂ O	4.31	3.98
SO ₃	0.08	0.06
P ₂ O ₅	0.30	0.00
H ₂ O (below 110°)	4.25	1.90
H ₂ O (above 110°)	2.08	1.33
TOTAL	101.23	100.33

Minor Constituents

MnO	50.0 ppm.	0.0 ppm.
V	100.0 ppm.	0.0 ppm.
Co	5.0 ppm.	10.0 ppm.
Ni	6.3 ppm.	29.4 ppm.
Se	187.0 ppm.	175.0 ppm.

Table 2		
Name of Plant	Stage of Growth	Selenium ppm.
<i>Hymenoxis floribunda</i>	Flower	575
<i>Atriplex nuttallii</i>	Seed	524
<i>Agropyron smithii</i>	Flower	41
<i>Comandra pallida</i>	Flower	162
<i>Astragalus grayi</i>	Flower	4,420
<i>Xylorrhiza parryi</i>	Flower	1,850
<i>Castilleja chromosa</i>	Seed	3,152

The data in Table 2 show that vegetation in the poison area is seleniferous and in an amount large enough to be poisonous to livestock. Since the selenium content of a plant species varies with the stage of growth, some of the plants listed above would have contained much more selenium in their earlier stages of growth than is indicated by the values shown. Because of the high content of water-soluble selenium in the tuffs, even the plants not classified as selenium indicators were found to be highly seleniferous.

Perhaps it should be pointed out that the selenium in grasses, cereals, and farm crops is considered high if present in amounts exceeding 25 ppm. These foodstuffs would be toxic to livestock if much less selenium were present, possibly as little as 5 ppm. The selenium-indicator plants have the capacity to absorb selenium in much greater quantities than grasses and cereals. In an indicator plant, such as *Astragalus bisulcatus*, a selenium content of 200 to 300 ppm. would be considered low, 500 to 1000 ppm. a moderate amount, and 1000 to several thousand ppm. would be high.

SELENIFEROUS SANDSTONE

For many years a localized range (T. 12 N., R. 93 W.) in southwestern Carbon County, Wyoming, has been referred to by livestock operators as the Poison Butte area. Suspected vegetation was examined in 1933 and selenium was positively identified as the principal toxicant in the plants at that time. The kind of rock supporting the highly toxic vegetation was not studied critically until 1945. In general, all the rocks in the area are of Tertiary age. Specimens from the various outcrops which were analyzed show that the selenium is dominant in a fine-grained buff sandstone.

Thin sections of the rock were examined microscopically. It was found to consist principally of subrounded quartz grains in a cement of carbonate, muscovite, and limonite. The quartz grains range in size from very small up to 1/4 mm. across, the average being approximately 1/8 mm. Minor minerals include microcline, orthoclase, plagioclase, muscovite, chlorite, epidote, tourmaline, and magnetite. The feldspars and quartz are partly replaced by the carbonate and muscovite of the cement, and magnetite is slightly altered to limonite. In addition to the above-mentioned minerals, numerous grains are present which are now chalcedonic quartz and limonite. It was not possible to determine the original nature of these grains but they may be highly altered lithic fragments.

For the purpose of determining water soluble selenium in the siltstone, a sample was taken from each location that represented the maximum selenium concentration. Only a small portion of the total is soluble in water. At location I the soluble selenium amounts to 3.2 percent of the total, and at location II, 4.5 percent is soluble. In both samples the selenate form is the only one recognized in the water extracts. Usually one or two distillations with hydrobromic acid and bromine are sufficient to remove the selenium, quantitatively, from a soil or rock, but the vanadiferous siltstone proved to be an exception. At least five separate distillations had to be made before all the selenium was recovered from the sample. To avoid so many distillations the process was simplified by first oxidizing the ore with a mixture of sulphuric and nitric acids, and then distilling in the usual manner with hydrobromic acid and bromine.

FORM OF SELENIUM IN PHOSPHATE ROCK

Phosphatic rock from the Phosphoria formation of western Wyoming was investigated as to its seleniferous status by Beath et al., (5) in 1937. Variations were found from a few ppm. to 212 ppm. for the total selenium. Upon re-examination of a high grade phosphate rock for available selenium, it was found that very little of the total was water soluble. The particular specimen examined yielded 95.0 ppm. in total selenium. Selenate selenium was 5.5 ppm., and no selenite or organic selenium was detected. No attempt was made to determine the composition of the insoluble portion.

FORM OF SELENIUM IN URANIUM-VANADIUM ROCKS AND ORES, UTAH

Beath (10) in 1943 described the seleniferous character of some rocks, ores, and vegetation in southeastern Utah. Some alluvial deposits (Sec. 33, T. 22 S., R. 22 E.) were also sampled and reported on at that time. Because of the abundance of indicator plants associated with the uranium-vanadium deposits, a re-examination has been made of type rocks, ores, and soils as to the form of selenium present. The principal ore horizon occurs in the persistent sandstone bed that marks the top of the Salt Wash member of the Morrison formation. Alluvial wash overlying the uranium-vanadium ore beds is mineralized, indicating that it was derived, in part at least, from the ore-bearing rocks. Two samples of alluvium were selected from a representative deposit for analysis. One sample was taken from the surface to a depth of 24 inches; the other was taken from 24 to 36 inches in depth. The analyses are tabulated to show total selenium, selenate, and selenite:

Table 4

Sample No.	Depth (inches)	Total Se (ppm.)	Selenate Se (ppm.)	Selenite Se (ppm.)
1	0 - 24	82.0	55.4	0.6
2	24 - 36	45.2	25.4	2.6

It will be observed that a very appreciable amount of total selenium in the alluvium is soluble in water and that the dominant form is selenate.

A low grade ferruginous ore specimen taken from a point below the alluvium yielded 2630 ppm. selenium. It was not possible to detect selenate or selenite in this material. A high grade uranium-vanadium ore specimen from another bed yielded 563.0 ppm. selenium. A water extract prepared from an aliquot of the same ore yielded 40.7 ppm. selenate and 35.3 ppm. selenite. This is the only known instance where a naturally occurring rock or ore has yielded nearly as much selenite as selenate.

FORM OF SELENIUM IN SHALE, PROVO CANYON, UTAH

A certain shale formation in Provo Canyon, Utah, of late Mississippian or early Pennsylvanian age was examined for selenium by Beath et al. (6), in 1939. A critical analysis was made of material from Canyon Glen Camp Grounds, Provo Canyon. At the time the first report was made, only the total selenium in the various beds was determined. Recently a sample of carbonaceous shale from Provo Canyon was re-examined. Total selenium was 96.3 ppm. and the amount extractable with water was 16.0 ppm., occurring entirely as selenate. Shale from this particular bed would be capable of supporting highly toxic vegetation.

FORM OF SELENIUM IN CARBONACEOUS SHALE, ALBANY COUNTY, WYOMING

In 1936, Beath and Gilbert (3) reported on the high selenium concentration of a shale carrying fossil leaves in the Medicine Bow formation (Upper Cretaceous) in Albany County, southeastern Wyoming (Sec. 7, T. 16 N., R. 77 W.). Some specimens assayed over 150 ppm. selenium. When the finely-powdered shale was placed in greenhouse boxes, however, and sown to grains and forages, the resulting crops were non-toxic. This negative result led to the preparation of a water extract from a channel sample of the leaf-bearing shale which contained 22.6 ppm. total selenium. No inorganic or organic selenium was detected in the water solution. The stability of selenium in this shale was similar to that encountered in some ores and related deposits.

FORM OF SELENIUM IN A NATURALLY OCCURRING TOXIC SOIL, WYOMING

A toxic soil area in northeastern Niobrara County (Sec. 1, T. 38 N., R. 61 W.), Wyoming has received special study by the writers. A sample of green *Astragalus racemosus* was found in 1937 to carry 14,920 ppm. selenium Beath et al. (4). Toxic grains and forages are prevalent in the same soils. This toxic area was originally reported to be loam derived from the Pierre shale but subsequent geological study has shown that the shale and loam are clearly of Niobrara age. At the location selected for taking samples, it was found that the top 6 to 8 inches is disintegrated Niobrara shale. Below this point typical shale was encountered for the remaining depth (40 in.). Two

samples were taken, the first from 0-20 inches and the second from 20 to 40 inches. Gypsum crystals were discernable throughout the material. Results of the chemical analyses are as follows:

Table 5

Sample No.	Depth (inches)	Total Se (ppm.)	Selenate Se (ppm.)	Selenite Se (ppm.)	Organic Se (ppm.)
1	0 - 20	21.9	2.6	0	6.0
2	20 - 40	32.0	9.5	0	3.4

In a toxic area such as this the influence of converter plants is recognized by the amount of organic selenium, especially in the upper part of the soil profile. The inorganic selenium is entirely in the selenate form.

SELENIUM-SUPPLYING POWER OF SOILS

Absorption of selenium by a plant depends upon selenium-supplying power of the soil and selenium-accumulating power of the plants. The selenate form of selenium is the dominant inorganic source in most naturally occurring toxic areas in the western states. The selenite form is believed to be of minor significance. Data presented by Byers (1935) and other investigators show little, if any, correlation between selenium content of any given species of plants and the total selenium content of the soil on which it grows. This absence of a direct correlation probably has resulted from differences in availability of the selenium in various soils and from failure to obtain samples that adequately represented the soil actually surrounding the plant roots. Other contributing factors may have been differences in non-seleniferous soil constituents, in age of the plants or their physiological condition, or in various unknown conditions.

The selenium accumulator plants native to western ranges are stimulated by soil selenium in any form (Fig. 5). It has not been possible, by means of artificial cultures (sand, solution, or garden plot), to produce accumulator plants having a selenium concentration as high as those occurring on the ranges. Tests have been carried out by Beath with high concentrations of selenate, selenite, and organic selenium in soil plots, using various *Astragalus* indicator species. It is concluded that other factors prevail under natural range, soil, and moisture conditions favorable to selenium absorption that are not understood.

In culture solutions the presence of sulphate is known to reduce the absorption of selenate, but has little or no effect on absorption of either selenite or organic selenium compounds derived from native plant sources. Sulphates are known to occur in association with practically all the toxic soil areas in the western states. Even though the selenate form of selenium is indicated to be the dominant inorganic source, toxic grasses, forages and farm crops do occur in highly sulphated soils. So far as the selenium-accumulators are concerned, sulphates have no bearing on their absorbing powers. This is best illustrated by the growth of *Astragalus pattersoni* and *Stanleya pinnata* on the Paradox formation which is largely gypsum (Beath, 10).

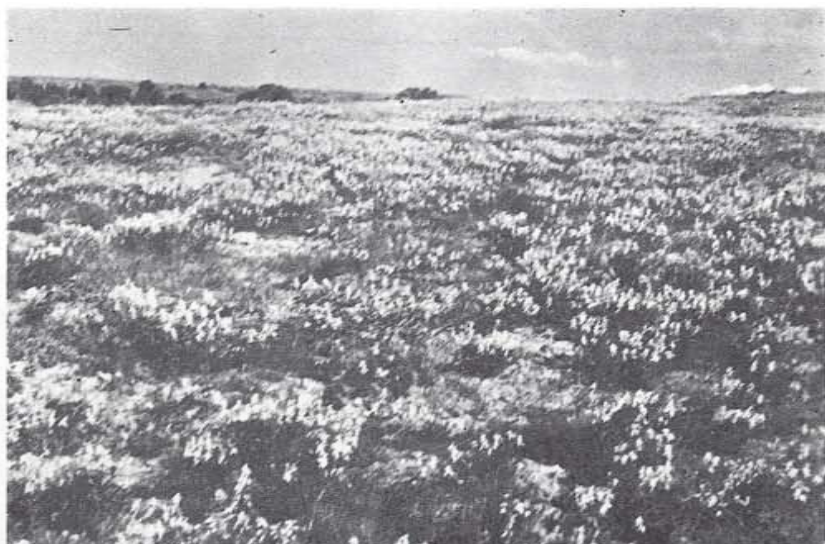


Figure 5. Dense stand of *Astragalus pattersoni* Gray. Appears to be stimulated by selenium. Near Thompson, Utah.



Figure 6. Available selenium determines whether or not a grass is toxic. Near Laramie, Wyoming.

The highly toxic rocks and soils discussed in this paper show that the available form of selenium is largely in the selenate form. Where exposures of these rocks and soils accommodate plant growth, chemical analyses indicate that practically all the plants are toxic (Fig. 6). Consequently, grazing livestock utilizing the forage of these highly poisonous areas soon succumb to acute selenosis. Since some plants remain succulent throughout the winter months and others retain some potency in their dried-out condition, the hazard to livestock may be considered present at any season of the year.

SELENIFEROUS VEGETATION AS AN AID IN MINERAL EXPLORATION

It is believed that the analysis of selenium-bearing vegetation may be of aid in locating certain mineralized areas. Lundberg (20) has suggested such a possibility in connection with heavy-metal content of vegetable matter, and Goldschmidt (15, 16) and Vernadsky (28) have done considerable work on the distribution of heavy metals in vegetation.

Indicator and accumulator plants can be used in locating areas high in selenium. Although this paper treats primarily with selenium content, it is known that certain toxic vegetation also carries relatively high rare-metal values such as molybdenum. Geologic mapping and the use of geochemical exploration methods (17, 21) may lead to the discovery of mineralized areas, in particular those with which selenium and its compounds are associated (Clarke, 14).

SUMMARY

Geologically, the highly seleniferous rocks and soils in the western states are not restricted to any one system or formation. Volcanic tuff (Tertiary) in Fremont County, Wyoming is particularly significant because of its large amount of water soluble selenium, attaining a maximum of 187 ppm. Two representative specimens of tuff, from different beds, were analyzed. Thin section study confirmed the identity of the tuff.

A specimen of seleniferous rock from an outcrop of uranium-vanadium ore contains water soluble selenium that is about equally divided into selenate and selenite. A specimen of low grade vanadium ore nearby yielded 2,650 ppm. selenium, but none was water soluble. Vanadiferous siltstones from western Wyoming are seleniferous and show a parallel trend in their selenium-vanadium content.

Selenate selenium is the dominant water soluble form in the toxic areas investigated by the writers. This form is more toxic to non-accumulator plants than is the organic form. Selenium accumulator plants are stimulated in their selenium absorption by all naturally occurring forms. The extremely toxic range areas in the western states are hazardous to grazing livestock because all the indigenous vegetation is seleniferous. Furthermore, the accumulator plants absorb unusually large amounts of selenium in these areas.

Analysis of seleniferous vegetation may aid in the location of certain mineralized areas, in particular those with which selenium is associated.

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REFERENCES

- (1) BEATH, O. A., et al. 1934. Certain poisonous plants of Wyoming activated by selenium and their association with respect to soil types: *Jour. Amer. Pharm. Assoc.*, 23, 94-97.
- (2) BEATH, O. A., EPPSON, H. F., AND GILBERT, C. S. 1935. Selenium and other toxic minerals in soils and vegetation: *Wyo. Agr. Exper. Sta. Bull.* 206.
- (3) BEATH, O. A., AND GILBERT, C. S. 1936. Selenium-bearing vegetation during late Cretaceous time: *Science*, 84, 484-485.
- (4) BEATH, O. A., EPPSON, H. F., AND GILBERT, C. S. 1937. Selenium distribution in and seasonal variation of type vegetation occurring on seleniferous soils: *Jour. Amer. Pharm. Assoc.*, 26, 394-405.
- (5) 1937. Selenium in soils and vegetation associated with rocks of Permian and Triassic Age: *Amer. Jour. Bot.*, 24, 96-101.
- (6) 1939. The use of indicator plants in locating seleniferous areas in western United States: I. General. *Amer. Jour. Bot.*, 26, 257-269.
- (7) 1939. The use of indicator plants in locating seleniferous areas in western United States: II. Correlation studies by states. *Amer. Jour. Bot.*, 26, 296-315.
- (8) 1940. The use of indicator plants in locating seleniferous areas in western United States: III. Further studies. *Amer. Jour. Bot.*, 27, 564-573.
- (9) 1941. The use of indicator plants in locating seleniferous areas in western United States: IV. Progress report. *Amer. Jour. Bot.*, 28, 887-900.
- (10) BEATH, O. A. 1943. Toxic vegetation growing on the Salt Wash sandstone member of the Morrison formation: *Amer. Jour. Bot.*, 30, 698-707.
- (11) BYERS, H. G. 1935. Selenium occurrence in certain soils in the United States, with a discussion of related topics: *U. S. Dept. Agr. Tech. Bull.* 482.
- (12) 1936. Selenium occurrence in certain soils in the United States, with a discussion of related topics: II. *U. S. Dept. Agr. Tech. Bull.* 530.
- (13) BYERS, H. G., et al. 1938. Selenium occurrence in certain soils in the United States, with a discussion of related topics: III. *U. S. Dept. Agr. Tech. Bull.* 601.
- (14) CLARKE, F. W. 1924. The data of geochemistry: *U. S. Geol. Survey Bull.* 770, p. 19.

- (15) GOLDSCHMIDT, V. M. 1937. The principles of distribution of chemical elements in minerals and rocks: Jour. Chem. Soc., London, Pt. 1, 655-673.
- (16) 1938. Geochemische Verteilungsgesetze der Elemente: Oslo.
- (17) 1938. De senere års utvikling av vart kjemmskap til geokjemien; Luftens, havets og jordens mengdevisse opbygning av elementene; Naturen arg. 62, no. 11, p. 321-334, no. 12, p. 353-362, N. D. (In G. S. A. Bibl. & Index of Geol. Exclusive of N. A., 1940).
- (18) HERSHEY, A. L. 1945. Some poisonous plant problems of New Mexico: Agr. Exper. Sta. Bull. 322.
- (19) LAKIN, H. W. AND HERMANN, F. J. *Astragalus artemisiarum* Jones as a selenium absorber: Amer. Jour. Bot., 27, 245-246.
- (20) LUNDBERG, H. 1940. The future of geophysics in the light of new developments: Can. Min. Jour., 61, 225-227.
- (21) 1941. New techniques in geoexploration: Mining & Metallurgy, 22, 256-257.
- (22) MOXON, A. L., OLSON, O. E. AND SEARIGHT, W. V. 1939. Selenium in rocks, soils, and plants: S. D. Agr. Exper. Sta. Tech. Bull. 2.
- (23) MOXON, A. L. AND SEARIGHT, W. V. 1945. Selenium in glacial and associated deposits: S. D. Agr. Exper. Sta. Tech. Bull. 5.
- (24) OLSON, O. F. et al., 1942. Field studies on methods for determining availability of selenium to plants: Soil Sci. 53, 365-368.
- (25) TOURTELOT, H. A., AND NACE, H. L. 1946. Tertiary stratigraphy of the northeastern part of the Wind River Basin, Wyoming: U. S. G. S. Oil and Gas Investigations, Prelim. Chart 22.
- (26) TRELEASE, S. F. AND MARTIN, A. L. 1936. Plants made poisonous by selenium absorbed from the soil: Bot. Rev. 2, 373-396.
- (27) TRELEASE, S. F. 1942. Identification of selenium indicator species of *Astragalus* by germination tests: Science 95, 656-657.
- (28) VERNADSKI, V. I. 1938. On some problems of biogeochemistry: Acad. Sci. URSS, B. Ser. Geol. No. 1, 19-34 (English summary).
- (29) WILLIAMS, K. T., LAKIN, H. W., AND BYERS, H. G. 1940. Selenium occurrence in certain soils in the United States, with a discussion of related topics: IV. U. S. Dept. Agr. Tech. Bull. 702.
- (30) WILLIAMS, K. T., LAKIN, H. W., AND BYERS, H. G. 1941. Selenium occurrence in certain soils in the United States, with a discussion of related topics: V. U. S. Dept. Agr. Tech. Bull. 758.

