

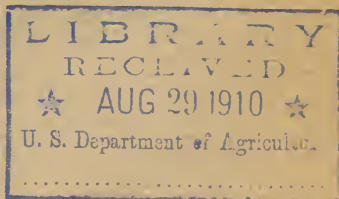
Issued August 27, 1910.

U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF SOILS—BULLETIN NO. 72.

MILTON WHITNEY, Chief.

BARIUM IN SOILS.



BY

G. H. FAILYER.



WASHINGTON:

GOVERNMENT PRINTING OFFICE.

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BUREAU OF SOILS.

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LETTER OF TRANSMITTAL.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF SOILS,
Washington, D. C., May 10, 1910.

SIR: I have the honor to transmit herewith the manuscript of an article on Barium in Soils, by G. H. Failyer, of this Bureau, and to recommend that it be published as Bulletin No. 72 of the Bureau of Soils.

Very respectfully,

MILTON WHITNEY,
Chief of Bureau.

HON. JAMES WILSON,
Secretary of Agriculture.

PREFACE.

There has been a marked tendency in the past to confine chemical investigation of the mineral constituents of the soil to those which are popularly recognized as of importance in fertilizer practice. It is coming to be recognized, however, that many elements other than those in the conventional essential plant foods are very widely if not universally distributed in the rocks, the soils, and the plants, and that it is of importance, both theoretically and practically, to trace the relationships between these substances, as shown by the passage of the elements from the rock to the plant, through the soil. Recently a very strong plea for more thorough examinations and complete analyses of rocks has been made from the laboratories of the United States Geological Survey, and a no less strong argument can be made in the case of soils and plants.

It no longer suffices to consider the soil merely as the source of a few mineral elements, needed in plant metabolism. We now know that the presence of a small amount of arsenic in certain animal organisms is essential to their proper functioning, and we also know that arsenic in small quantities is very widely distributed; yet no one thinks of arsenic as an animal food. Similarly we are learning that small amounts of various organic and inorganic substances can, and do, produce marked physiological changes in plants, and that some of these are to be found widely distributed in soils. That we yet know but little as to their theoretical importance and nothing as to their practical importance is no argument that they do not possess the latter.

One of the important lines of work which this Bureau now has in hand is a study of the distribution of the mineral elements (including the so-called rarer elements) and the minerals in the soils of the United States, and one publication (Bul. No. 54, Bureau of Soils) has already been issued. The work reported in the present bulletin, while considered primarily as a further contribution to knowledge in this field of the Bureau's investigations, has had an impetus from

and been guided in part by the interest of the Bureau of Plant Industry in the possibility that the presence of barium in the soils of certain regions might cause some kinds of plants characteristic of these regions to prove poisonous to stock. But the more important result of the investigation is the recognition of the wide distribution of barium throughout the soils of the United States, and the probability that it may be encountered in plants grown in any part of the country.

FRANK K. CAMERON,
In Charge Physical and Chemical Investigations.

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BARIUM IN SOILS.

INTRODUCTION.

The literature on the occurrence of barium in soils appears to be meager. Its occurrence in some of the feldspars, as hyalophane and celsian, where it is considered an essential constituent, is well known. It is found in a number of other silicates and would seem to be more widely distributed in rocks than has generally been recognized. Clarke^a and Hillebrand^b state that barium is usually present in igneous rocks. According to Dieulafait^c it is a constituent of all primordial rocks, the feldspars, micas, gneiss, granite, and syenite containing barium in sufficient quantity to be easily detected in one gram of substance. In the past it was customary to look upon rock and mineral constituents that are present in small amounts as accidental and unimportant. Therefore they were often ignored in analysis. But from the soil standpoint anything found in the original rocks is important since it is almost sure to remain to some extent in the soil formed from them. Barium is often found in nature in the form of the sulphate or barite, but this mineral is doubtless a secondary product always, the barium coming from the weathering of silicates bearing the element, the sulphur through the oxidation of sulphides, generally pyrite. In some cases this may have been a remote source of the sulphate, gypsum being an immediate one. On several occasions the author has collected barite crystals, both large and small, from broken-down concretions occurring in the plains regions. The concretions vary from a few inches to several feet in diameter. They are frequently coated with leaflike twin crystals of gypsum and contain crystals of calcite and barite in what once were interior crevices produced probably when the concretion was in its formative stage. This occurrence of barite has been noted by many collectors. Pyrite and gypsum occur through the shales in which the concretions are found and from which the greater portion of their mass came. In the section on the source of the barium of the plains soils (p. 18) reasons are given for believing that it came from the feldspar and

^a U. S. Geol. Survey Bul. No. 228, p. 13 (1904).

^b U. S. Geol. Survey Bul. No. 305, p. 18 (1907).

^c Compt. Rend., 87, 934 (1878).

similar minerals of the Tertiary rocks. These Tertiary rocks and their débris are abundant in the region about these huge barite-bearing concretions. It seems probable that the feldspars and the pyrite are the remote sources of the barite constituents, whatever transformations may have intervened.

No attempt is here made to give the bibliography of the occurrence of barium in rocks, but some references that seem to be of special interest from the standpoint of the soil are given. Barium sulphate has been observed as the main cementing material of sandstones near Nottingham, England, by Clowes.^a Delkeskamp^b mentions the occurrence of barite as the cementing material of sandstone in the Wetterau and Rheinhessen districts of Germany. Mackie^c found it in small nodules disseminated through sandstones of Elginshire, where it cemented the grains of sand together. Various other references to barite as a cementing material occur in the literature. In what have been called sand-barites, the forces of crystallization have controlled the form; but these are only remotely connected with barium in soils. Pogue^d goes into this subject in detail. Lutterkorth^e found barium in sandstones in the region of Göttingen. Since water failed to extract it and it was dissolved out by hydrochloric acid, he concluded that barium carbonate was a constituent of the stone. Lutterkorth was led to look for the barium from the fact that Eckard^f had found it in the ashes of beeches growing in the soil of the region. It does not appear that the soil itself was tested for barium. But the occurrence of the compounds of barium in such rocks as sandstones, that readily break down into soils, would render it probable that the latter would contain barium. The source of the barium of the rocks is not always obvious. Bischof^g mentions similar occurrences and suggests sources of the element. Many brines and some mine waters contain barium said to be in the form of chloride, derived probably from the weathering of more complex minerals, and the sulphate may result from double decomposition of the chloride and soluble sulphates. It is not impossible, however, that conditions may exist where the barium sulphate remains in solution for a time and is carried to the place of deposition. Some of the crystalline occurrences of barite and the stalactites in which it is sometimes found point to this strongly.

^a Proc. Roy. Soc., **46**, 363 (1889).

^b Notizbl. Ver. Erdkunde, **21**, 47 (1900).

^c Rept. Brit. Assoc. Adv. Sci., p. 649 (1901).

^d Proc. U. S. Nat'l Museum, **38**, 17-24 (1910).

^e Ann. der Chem. u. Pharm., n. s., **24**, 296 (1856).

^f Ann. der Chem. u. Pharm., n. s., **24**, 294 (1856).

^g Elements of Chem. and Phys. Geol., **1**, 432 (1854).

Knop^a and Dworzak^b found barium in the Nile mud. It was extracted by treating the Nile sediment with dilute hydrochloric acid, from which it was inferred that it was in the form of carbonate. It does not appear whether compounds of barium insoluble in the acid occur in the mud. Both mention the presence of flakes of mica visible to the naked eye. Nothing is said of other minerals. Hornberger^c having found barium in the ashes of beeches, examined the soils in which the trees grew. He was able to extract the element by treatment with dilute hydrochloric acid. By the same means he proved the presence of barium in the sandstone by the disintegration of which the soil was formed. Chatard^d found 0.05 per cent of BaO in a clay collected at New Ulm, Minn.

In studying the distribution of barium in the soils, there were two reasons for giving special attention to the soils of the Great Plains region. It has been suggested that there is a connection between the barium in the soil and the poisonous character of certain plants growing in that region;^e and the investigations of the U. S. Geological Survey have shown an apparent segregation of barium in the rocks of the Rocky Mountain regions.

Prior to this investigation the Bureau of Plant Industry had established a station for experiments upon the loco disease at Hugo, in the plains region of the State of Colorado. Hugo was made a headquarters for the collection of samples of soil and of such minerals and rocks as might throw light on the occurrence, distribution, and origin of barium in the soils.

In the immediate neighborhood of the station the soils were quite thoroughly sampled, but many samples were collected from the surrounding country. This sampling extended 25 miles from Hugo.

Outside of the Hugo region soil samples were taken at points widely separated over eastern Colorado, western Kansas, and southwestern Nebraska. Thus collections were made in the region of Woodland Park, Fountain, Pueblo, Huerfano, Raton Mesa, Thatcher, La Junta, Buchtel, Olney, Seibert, Fort Morgan, Akron, Wray, Sterling, Holyoke, Kit Carson, Cheyenne Wells, and Eads, all in Colorado. In Kansas soils were collected in the region of Goodland, Colby, Clayton, Phillipsburg, Winona, Wakeeney, Tribune, Scott City, Ness City, Heizer, Hutchinson, Belvidere, and Rago; in Nebraska around Benkelman, Culbertson, Imperial, and Grant. The territory including all these places is 225 miles north and south and 350 miles east and west, but no samples were obtained from the extreme northwest

^a Landw. Vers.-Stat., **17**, 65 (1874).

^b Landw. Vers.-Stat., **17**, 398 (1874).

^c Landw. Vers.-Stat., **51**, 473 (1898-99).

^d U. S. Geol. Survey Bul. No. 228, p. 359.

^e Bul. No. 129, Bureau of Plant Industry, U. S. Dept. of Agr.

and northeast and middle southern portions of this territory. For the most part this region lies in the Great Plains, but a few of the places mentioned are beyond the confines of the plains. Woodland Park is in the Rocky Mountains. It is northwest of Manitou Springs, about 25 miles up through Ute Pass. The rocks here are granite and the soil is full of fragments of the broken-up rocks, a red feldspar being a prominent constituent. Generally the sampling auger was stopped at the depth of a foot or two by the larger fragments, or even by the solid stone in some cases.

The Raton Mesa is a part of the Raton Mountains, and at the point where the samples were taken has an altitude of over 9,000 feet. The soil of the mesa at this point is largely made up of the débris of broken-down lava and contains much fragmental lava. Hutchinson and Rago, Kans., are too far east to be considered in the Great Plains. Aside from the two mountainous sections of the region in question, the surface is generally that of a plain, with occasional elevations left by the general erosion to which it has been subjected, and, of course, with eroded stream valleys. Geologically, rather diverse formations occur, as might be expected in so wide an area. In the extreme southeast, including Hutchinson and Rago, Kans., the rocks now remaining are largely Permian. Northwesterly, later formations are encountered—those of Cretaceous and Tertiary time. These deposits have been deeply eroded and extensively removed.

It is not necessary here to go into detail regarding the geology of the region, but from the foregoing it can be readily understood that the soils have been formed from very diverse rocks. The Dakota sandstone, the Pierre shale, and the Tertiary grit form very different soils by breaking down, but the erosion has been such that there has been much mixing of materials from one formation with that from another. This results in complexity of the soils, which has been greatly increased by the sands and loess carried by the winds. At various points in eastern Colorado and western Kansas there are bluffs and buttes capped by Tertiary grits and mortar beds. The latter, as the name implies, are composed of sand and gravel cemented by an excess of calcium carbonate. The gravel is composed of various materials. Feldspars and quartz are most abundant, but the pebbles may be rounded fragments of granite, gneiss, syenite, or lava. While these Tertiary rocks are found now in isolated areas, they seem to have once been much more nearly general over the area, for the characteristic gravel of the rocks is found widely distributed over the surface of the soil.

While the soils are evidently admixtures of materials of diverse source, as stated above, they often retain their distinct individuality.

The soils range from dune sand to the most plastic gumbo. Sandy loams and silt loams are very common types.

A 1½-inch auger was used in taking the samples. In general the soil was sampled to a depth of 4 feet in 1-foot sections. In some cases, owing to the difficulty of boring or other circumstance, sampling was to less depth, and in other than foot sections. When the soil was a sand or silt and air dry, as was often the case, it would run off the auger, and it became necessary to pour water down the hole to wet the soil so that it would be brought to the surface by the auger on drawing the latter out. For the most part distilled water, obtained at the station, was used for this purpose. When this was not available and it was absolutely necessary to use water, it was obtained from a well or stream in the vicinity, and records were kept of such facts. A soil sample as collected and sent in for analysis generally consisted of a composite made up of the borings from three to six holes put down within a space a few rods square.

METHODS OF EXAMINATION.

The laboratory examination of the material collected may be arranged under three heads. These are chemical, spectroscopical, mineralogical. The chemical examinations for the most part consisted in attempts to separate the whole of the barium from the soil, but in one series of tests the soils were treated with carbonated water to learn whether the barium could be extracted by this means. In the former, the soils were pulverized and treated with hydrofluoric acid, in some cases after previous ignition, in others without ignition. After digestion in hydrofluoric acid the mass was evaporated on the steam bath with an excess of sulphuric acid. When reduced to small volume by this means, the sulphuric acid was driven off on the hot plate. It was then taken up with dilute hydrochloric acid in the presence of a small amount of sulphuric acid. After digesting for some hours, the insoluble material was filtered off, dried, the filter burned, and the mass fused with sodium carbonate. After solution in water and filtration, the residue was dissolved in hydrochloric acid and any barium present precipitated by the addition of sulphuric acid.

It was realized that it is difficult to obtain a pure precipitate of barium sulphate without prolonged treatment, but the precipitate was generally weighed without further purifying, since the method of sampling would not give exact samples of the soil and it was considered very important to determine whether the element is present in the soils, but of minor consequence in what percentage, this always being small. The precipitate after being weighed was tested by the spectroscope for the presence of barium.

In taking up the analytical work, the samples were treated in the order in which they were collected. After a number had been analyzed in order, a portion of those collected in any locality were analyzed, often omitting the samples from the deeper subsoil. By this means the general occurrence of barium could be determined without the labor of working upon the great number of soil samples collected.

In making the spectroscopic examination a Hilger wave-length spectroscope was used. The precipitated barium sulphate was placed in an arc lamp especially constructed for the purpose, and the spectrum compared with that of pure barium sulphate from a comparison arc. The coincidence of the spectra proved that the precipitate contained barium. In some instances lines of calcium or other elements were visible. The carbons gave the sodium spectrum, and of course it was always present with that of barium in both arcs. For the most part nothing further could have been desired in the definiteness and positiveness of the spectroscopic test. In some cases only the more prominent lines of barium were positively discernible; but these are so characteristic, and coinciding as they did with the strong lines of the comparison spectrum, they prove the presence of barium even when other lines were not distinguished. The lines to which reference is here made are the red line, 6497; the orange, 6141.9; the green, 5535.7; the green, 4934.2; the blue, 4554.2.^a In this work, however, no attempt was made to read the values of the lines to more than four significant figures.

BARIUM IN THE SOILS OF THE GREAT PLAINS.

The table gives the location where samples were collected and the percentages of barium found by analysis. It will be observed that barium was found in all of these soils. While the percentages are somewhat variable, in no case are they large, 0.11 per cent being the greatest proportion for the purer precipitates. The average for these plains soils is about 0.06 per cent. According to the data of Clarke^b the average barium content of 617 igneous rocks analyzed by the United States Geological Survey would be about 0.10 per cent. This includes igneous rocks widely distributed over the United States, but according to Hillebrand^c the igneous rocks of the Rocky Mountain region contain a higher percentage of barium than those of the

^a Different observers might easily disagree as to the color limits, and the author himself would not in all cases assign the above colors to the lines designated. In the text he has followed the classification given by Listing; *Spectrum Analysis*. John Landauer (1907), p. 92, also *Ann. der Phys. u. Chem.*, **131**, 564 (1867).

^b U. S. Geol. Survey Bul. No. 228, p. 17.

^c U. S. Geol. Survey Bul. No. 305, p. 18.

eastern or the more western portion of the United States. No estimate can be made of the probable barium content of the original rocks from which the plains soils were formed, for we do not know enough of the sources of the soils nor have the rocks to the westward been sufficiently studied with this in view. But it would appear from what is known that there has been an appreciable loss of barium in the weathering processes to which the material has been subjected. This would be expected, of course, but the persistence with which substances existing in the rocks, even in small quantities, are retained in the soils resulting from them is shown by the almost universal presence of barium in these soils.

Apparently there is no characteristic relation between the depth of the samples and the barium content. Nor does there seem to be positive evidence of any geographic relation. The formations are such that one would expect a general similarity, for there are no sharp stratigraphic transitions. The differences in the soils are largely those of size of particles and produced mainly by the selective action of water and wind.

TABLE I.—Percentages of barium found in certain soils.

Location of soil.	Depth of soil sample.	Barium in soil sample.
	Inches.	
One-fourth mile southeast of experiment station, Hugo, Colo.....	0-12	0.02
	12-24	.02
	24-36	.05
	36-48	.03
Sand washed from soil from which samples 1-4 were taken.....		.06
One-fourth mile northwest of experiment station, Hugo, Colo., fine gravel.....		.08
One-fourth mile northwest of experiment station, Hugo, Colo.....	0-12	.02
	12-24	.01
	24-36	.07
	36-48	.03
Loco pasture northwest of experiment station, Hugo, Colo.....	0-12	.06
	12-24	.09
	24-36	.08
	36-48	.08
Three-eighths mile west of experiment station, Hugo, Colo.....	0-12	.05
	12-24	.08
	24-36	.06
	36-48	.08
Three-eighths mile west of experiment station, Hugo, Colo.....	12-24	.08
	24-36	.08
	36-48	.08
	0-12	.08
Unfenced pasture land southeast of experiment station, Hugo, Colo.....	12-24	.07
	24-36	.06
	36-48	.06
	0-12	.06
Unfenced pasture land southeast of experiment station, Hugo, Colo., south of preceding.....	12-24	.07
	24-36	.06
	36-48	.07
	0-12	.08
Unfenced pasture land southeast of experiment station, Hugo, Colo., south of preceding.....	12-24	.05
	24-36	.06
	36-48	.05
	0-12	.04
South slope of hill, three-fourths mile southeast of Hugo, Colo.....	18-36	.06
Schroeder's pasture, 3 miles southwest of Hugo, Colo.....	0-48	.06
	0-12	.05
	12-24	.06
Schroeder's pasture, 3 miles southwest of Hugo, Colo.....	24-36	.07
	36-48	.04
	0-18	.07
	18-36	.07
Flat 1 mile northwest of Hugo (Colo.) court-house.....	0-18	.07
	18-36	.07
	0-18	.07
One mile northwest of Hugo (Colo.) court-house.....	18-36	.07

TABLE I.—Percentages of barium found in certain soils—Continued.

Location of soil.	Depth of soil sam- ple.	Barium in soil sample.
	Inches.	Per cent.
Top and the north slope of hill, three-fourths mile southeast of Hugo, Colo.....	0-12	0.05
	12-24	.08
	24-36	.07
Richenberg's pasture, 6 miles southwest of Hugo, Colo., northwest of house	36-48	.07
	0-12	.05
	12-24	.07
Shale bluff, east of Laurie's house, 25 miles southwest of Hugo, Colo.....	24-36	.07
	36-48	.06
Draw northeast of Laurie's house.....	0-12	.08
	12-24	.07
	24-36	.08
Flat northeast of Laurie's house.....	36-48	.07
	0-12	.06
	12-24	.07
One-sixteenth mile west of Will's house, west of Mirage, Colo.....	24-36	.07
	36-48	.07
	0-12	.06
Swale southeast of experiment station, Hugo, Colo.....	12-24	.04
	0-12	.03
Near west end of lane, west of experiment station, Hugo, Colo.....	12-24	.06
	0-12	.05
Loco pasture, 4 miles west of Woodland Park, Colo.....	0-12	.11
	12-24	.04
Southeast hillside, loco pasture, 4 miles west of Woodland Park, Colo.....	0-12	.08
	12-24	.04
Hill north of road, one-half mile east of Edlow, Colo.....		.06
Hill north of road, one-half mile east of Edlow, Colo.....	0-12	.04
Grassy hill on Bald Mountain, Colo.....	0-12	.10
Grassy hill on Bald Mountain, Colo.....	0-12	.10
Wooded knoll on Bald Mountain, Colo.....	0-18	.03
Hillside on gulch east of Green Mountain Falls, Colo.....	0-12	.11
One-eighth mile south of Cheyenne Wells, Colo.....	0-18	.03
	18-36	.08
Flat about 2 miles east of north of Sheridan Buttes, Kans.....	36-54	.09
South of Winona, Kans.....	18-36	.09
East of McAllester, west of Sheridan Buttes, Kans.....	0-18	.03
One-eighth to one-fourth mile south of Wakeeney, Kans.....	0-18	.05
One-eighth to one-fourth mile south of Wakeeney, Kans.....	0-18	.03
Southwest corner pasture, northeast of Phillipsburg, Kans.....	0-18	.08
East side of same pasture, Phillipsburg, Kans.....	0-18	.06
Top of hill, one-half mile south of Clayton, Kans.....	0-18	.08
Swale, one-half mile south of Clayton, Kans.....	0-18	.09
Slopes of Beaver Creek, 10 miles northeast of Goodland, Kans.....	0-18	.08
Upland swale, one-fourth mile southwest of Seibert, Colo.....	0-18	.06
Slopes of draw, one-fourth mile northeast of Seibert, Colo.....	0-18	.05
South Bluff of Rig Sandy, 1½ miles southeast of Limon, Colo.....	0-12	.04
On hill north of Rock Island Railroad, one-fourth mile east of Limon, Colo.....	0-18	.08
Alfalfa field southwest of schoolhouse, Hugo, Colo.....	0-12	.05
	12-24	.05
	0-12	.05
150 yards southwest of Swan's house, 7 miles southwest of Hugo, Colo.....	12-24	.09
	30-48	.05
Northwest of Richenberg's house, 6 miles southwest of Hugo, Colo.....	0-12	.04

It was thought that a further study of these soils by simply separating the barium in sufficiently concentrated form for testing with the spectroscope, without purifying the precipitate for weighing, would give useful information regarding its distribution. Accordingly all further examinations were qualitative. The test consisted in obtaining a final precipitate by sulphuric acid in the presence of dilute hydrochloric acid after removal of the great bulk of the sample by treatment with hydrofluoric acid and fusion with sodium carbonate in the general manner as previously given, and the testing of this precipitate by the spectroscope. The following list gives the location and the depth in inches of samples tested in this qualitative way. All contain barium.

- Between Laurie's and Hamp's ranches, 20 miles southwest of Hugo, Colo., 0-12, 12-24.
- Hill northeast of Hamp's ranch house, 20 miles west of Hugo, Colo., 0-12, 12-24.
- Pasture northwest of McIntyre's house, 12 miles west of Hugo, Colo., 0-12, 12-24.
- One-fourth mile north of Mirage, Colo., 12-24.
- One-eighth mile northwest of Will's house, west of Mirage, Colo., 0-12, 12-24.
- Six miles southwest of Hugo, Colo., Richenberg's pasture, 12-24.
- Six miles northeast of Fountain, Colo., 0-12.
- Eight miles northeast of Pueblo, Colo., 0-12.
- On Apache Creek, northwest of Huerfano, Colo., 0-12.
- Lava, Raton mesa, compact.
- Lava, Raton mesa, honeycomb.
- Soil on Raton mesa, 0-12, 12-24.
- Sand and gravel, Threemile Creek, 6 miles northeast of Hugo, Colo.
- Nine miles northeast of Hugo, Colo., mortar-bed soil, 0-12.
- Seven miles northeast of Hugo, Colo., mortar-bed soil, 0-18.
- Dune sand, Wray, Colo.
- One mile north of Wray, Colo., 0-36.
- Two miles southeast of Wray, Colo., high land, 0-36.
- Four miles north of Holyoke, Colo., 0-24.
- Dune sand, $1\frac{1}{2}$ miles southwest of Sterling, Colo.
- Three-fourths mile southwest of Sterling, Colo., 0-36.
- Town site, Hugo, Colo., gumbo, 0-12.
- Station field, Eads, Colo., 0-18, 18-36.
- East Ephraim, Utah, 0-12.
- East Ephraim, Utah, 0-10.
- Half mile northwest of Benkelman, Nebr., 0-18.
- Shale, 1 mile east of Benkelman, Nebr., 0-18.
- Shale, $1\frac{1}{4}$ miles east of Benkelman, Nebr., 0-18; outcrop.
- Half mile northwest of Culbertson, Nebr., 0-18.
- Half mile southwest of Culbertson, Nebr., 0-18.
- Fair grounds, Imperial, Nebr., 0-18.
- High bluffs south of Imperial, Nebr., 0-18.
- Calcareous deposits south of Imperial, Nebr.; outcrop.
- Three-fourths mile northeast of Grant, Nebr., 0-24.
- Two miles northeast of Grant, Nebr., 0-24.
- Slopes of draws in pasture, one-fourth mile northeast of Colby, Kans., 0-18.
- Two miles north of Sheridan Buttes, Kans., 0-18.
- One mile southwest of Tribune, Kans., 0-18.
- Six miles southeast of Scott City, Kans., 0-18.
- One mile north of Ness City, Kans., 0-18.
- Bank of Walnut Creek, south of Ness City, Kans., 5 feet, 20 feet.
- One mile east of Heizer, Kans., 0-24.
- Five miles northwest of Hutchinson, Kans., 0-18.
- Dune sand, 8 miles northeast of Hutchinson, Kans.
- One mile east of Belvidere, Kans., 0-24, 24-48.
- Four miles south of Belvidere, Kans., 0-18.
- Two miles northwest of Rago, Kans., 0-36.
- Town site, Rago, Kans., 0-36.
- Twelve miles south of Manhattan, Kans., 0-18, 18-36.

SOURCES OF THE BARIUM IN THE SOILS OF THE GREAT PLAINS.

Very little has been done to determine the source of the barium of these soils. Clarke ^a states that although in many analyses of rocks, barium, like other minor ingredients, is ignored, it is almost universally diffused in igneous rocks in quite perceptible quantities. Hillebrand ^b states that the element barium "is an almost never-failing constituent of the igneous rocks of the United States and of many of their derivatives." He points out that igneous rocks of the Rocky Mountains appear to contain much larger percentages of barium than those of other sections of the United States. It can not be questioned that the soils of the plains have been formed in very large part if not wholly from the débris of the rocks of the Rocky Mountains. The sands and gravels plainly show the minerals of igneous rocks, and the finer portions would be expected to contain them also. If the feldspars, so abundant in the Tertiary sands and gravels, contain barium, wherever these sands and gravels are found barium will be found in the soils. The Tertiary gravel is found very widely distributed over the plains, even where the Tertiary rocks are not now found. A test for barium in this gravel would seem to be an easy way of deciding on its presence in the soils; conclusive if the element be found. It would also point out one of the original sources of the barium of the soils.

While collecting the soil samples, the gravel so frequently found on the surface was often collected also. Having found barium in the soils, the gravels were tested for the element. In any locality feldspar of many different colors and appearance is found. It would have added much to the work to analyze each of the pieces separately. Were the object to study the feldspar, this would have been justified certainly; but the desire was simply to learn whether the feldspar gravel could be a source of barium to the soils where it was found. It was therefore deemed wise to sort the gravel into groups according to color, and analyze the composite formed, thus reducing the analytical work materially. Thus the white and the gray sorts from any locality formed a composite; another one was composed of the pink feldspars; another of the red kinds. A few samples were made up of gravel other than those of pure feldspar. It was deemed that no useful purpose would be served by making quantitative determinations of the barium present in samples made up in this way; less care was taken therefore to secure all the barium and to insure the purity of the precipitate. The quantity of the latter, judged by its appearance in the beaker and by the brilliance of the spectrum,

^a U. S. Geol. Survey, Bul. No. 228, p. 13 (1904).

^b U. S. Geol. Survey, Bul. No. 305, p. 18.

was greater for the feldspars than from the same quantity of soil. The following specimens of this gravel all showed the presence of barium:

- White and gray feldspar, 12 miles northwest of Hugo, Colo.
- Pink feldspar, 12 miles northwest of Hugo, Colo.
- Red feldspar, 12 miles northwest of Hugo, Colo.
- Feldspar, 12 miles northwest of Hugo, Colo.
- Gneiss and syenite, 12 miles northwest of Hugo, Colo.
- Lava, 12 miles northwest of Hugo, Colo.
- White and gray feldspar, 9 miles northeast of Mirage, Colo.
- Reddish feldspar, 9 miles northeast of Mirage, Colo.
- White and gray feldspar, 4 miles north of La Junta, Colo.
- Pink feldspar, 4 miles north of La Junta, Colo.
- Red feldspar, 4 miles north of La Junta, Colo.
- Granite, syenite, lava, 4 miles north of La Junta, Colo.
- Red feldspar, 2 miles north of Sheridan Buttes, Kans.
- Lava and feldspar, top of the west Sheridan Butte.
- Hard conglomerate, top of the west Sheridan Butte.
- Various colored feldspar, 1 mile north of Wakeeney, Kans.
- Reddish feldspar, 2 miles east of Belvidere, Kans.
- Various colored feldspar, northwest of Rago, Kans.
- Gravel composed of mixtures of minerals, northwest of Rago, Kans.

The very general occurrence of barium in the gravel scattered over the plains region may be considered as proof that the element exists in the finer parts of the soil. The same minerals that form the gravel occur in smaller fragments, even down to fine sand, and the siltlike particles and decomposition products will necessarily be constituents of the soil.

After the chemical work upon the gravel, as given above, was completed, several of the samples, in bulk, were submitted to Mr. W. J. McCaughey, of this Bureau, for a mineralogical determination through their optical properties. In the samples from northwest of Hugo, he reports pebbles of quartz, feldspar, granite carrying a pink feldspar and a light green muscovite, and andesite the bubbles of which are filled with calcite. Minerals detected are microcline in greatest quantity, fair amounts of orthoclase and hornblende, smaller proportions of magnetite, epidote, muscovite, and rutile. In the material from northeast of Mirage, he found the pebbles to be very similar to those above, and recognized microcline, orthoclase, muscovite, biotite, hornblende, quartz, plagioclase, oligoclase, calcite, augite, epidote, magnetite, and tourmaline, the first named being most abundant. The samples from near Wakeeney contain microcline, quartz, biotite, phlogopite, calcite, and orthoclase. It was a common observation that the microcline was very little altered compared to the orthoclase. Micropertthitic structure was observed in some of the feldspar pebbles.

EXTRACTION OF BARIUM FROM THE SOILS BY WATER.

For barium to be absorbed from soils by plants, the element must be present in forms that would dissolve in the soil moisture or be rendered soluble by the growth of the plants themselves. It is extremely probable that all soil minerals are soluble to some extent in the fluid forming the soil moisture. But to determine whether barium could be detected in a solution comparable to the water in the soils, trials were made by treating 200 grams of the air-dry soils with 2 liters of distilled water, and, after shaking and standing twenty-four hours, charging the water with carbon dioxide. The stoppered bottles were shaken occasionally, and after a week more carbon dioxide was passed through the water with shaking. The material was allowed to stand two weeks longer, with occasional shaking. Then 500 cubic centimeters were drawn off, concentrated by evaporation, sulphuric acid added, and the liquid filtered. The residue was tested for barium by the spectroscope, using the arc as before. Soils that had been found relatively rich in barium were used in this trial. Of the 25 soils tested in this way, all but three gave evidence of barium in solution. The amounts of barium extracted being small and the residue of complex composition, the spectra of barium were weak and less satisfactory than when working with pure precipitates, but they proved that the element went into solution in appreciable amounts in the solvent used—water containing carbon dioxide.^a

OCCURRENCE OF BARIUM IN SOILS IN THE NEIGHBORHOOD OF BARITE MINES.

In this study the question arose whether soils in the vicinity of barite mines and plants growing upon such soils contain barium. To this end samples of soil were collected about the barite mines near Catlett, Evington, Pittsville, and Gardner, in the State of Virginia. The aim was to take soils so situated with reference to the barite outcrops that the débris of the rocks inclosing the vein might reasonably be expected to have contributed to forming the soil. It

^a A conclusive proof that barium exists in many soils and in a form at least somewhat soluble in soil water is afforded by the fact that the element is found in plants of widely separated sections. The author has found it in corn blades from southwestern Nebraska; in alfalfa from two fields near Hugo, Colo.; in rattleweed (white loco) collected in 12 different places in Colorado, Kansas, and Nebraska; in purple loco from nine localities in these States; and in six other leguminous plants from the plains region. The Bureau of Plant Industry has accumulated a large mass of data showing the frequent presence of barium in many kinds of plants from various regions. For the most part these data have not been published. For further information see Bul. No. 129, Bureau of Plant Industry, U. S. Dept. of Agr.

was realized that it would be strange indeed if barium were absent from these soils. While location with reference to the barite outcrop and the débris from the mines was the controlling factor in the selection of soils, the presence or absence of crops or other plant growth was considered. Thus cultivated fields, meadow, or pasture lands were selected when possible.

The following list gives the localities in Virginia in which soils were collected. The surface soil and the subsoil were examined separately. All of these soils gave comparatively strong reactions for barium.

Soils and subsoils from five spots within 200 yards of the Hewitt mine, Evington, Va.

Soil and subsoil from three spots in fields east of Pittsville.

Soil and subsoil from field near Tuck's mine, Pittsville.

Soil and subsoil from field southwest of Bennett's mine, Toshes.

Soils and subsoils from five spots in fields south of Gardner.

Soil and subsoil from spot near Harmon's barite mine.

Soil in field southwest of Harmon's mine.

Soils and subsoils from three spots in vicinity of barite mine 4 miles southeast of Catlett.

BARIUM AS A GENERAL CONSTITUENT OF SOILS.

Having found the element barium widely distributed in the regions of the Great Plains, a region to the soils of which the rocks of the Rocky Mountains have obviously contributed much material, these rocks being unusually rich in barium; having also found it in quite appreciable quantities in the soils in the vicinity of barite mines, it is of interest to learn whether soils in general contain barium.

Composite samples of soils which had been prepared for use in another investigation were available for the present work. They represent types of soils well distributed over the United States. The list below gives those soils in which barium was found, together with the States in which they were collected. Orangeburg sandy loam of Alabama, Collington sandy loam of New Jersey, and San Joaquin sandy loam of California gave faint but positive spectra of barium. With the Norfolk sand the brightest lines of the barium spectrum were barely perceptible. These are all Coastal Plains soils. A sample of the Orangeburg fine sandy loam of Texas, and one from the Houston clay of Alabama, a highly calcareous soil, failed to show barium. The absence of barium in the calcareous soil seems to be in line with the results on limestones given by Clarke,^a where it is stated that composites of 345 and of 498 limestones gave no evidence of the presence of barium. Further investigation of this point is necessary before a positive statement would be justified.

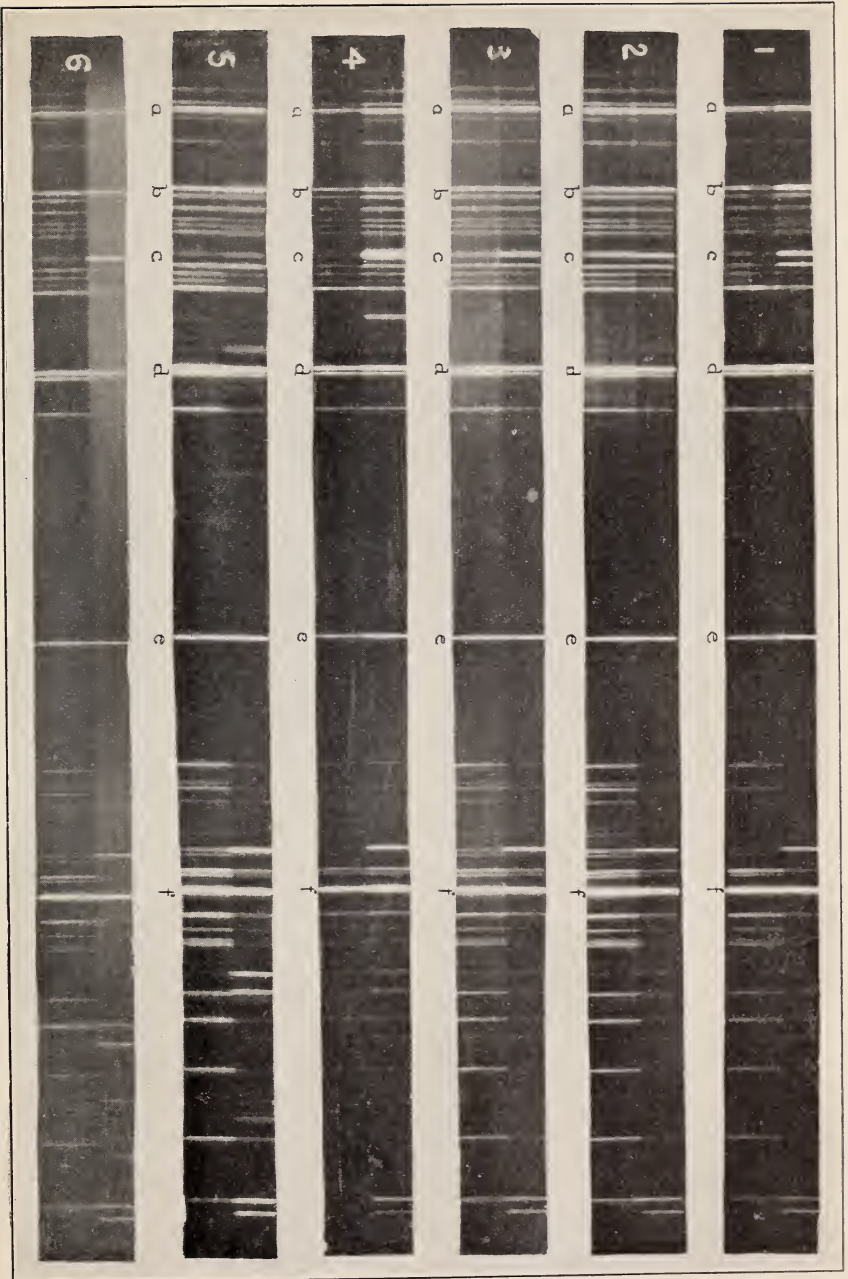
^a U. S. Geol. Survey Bul. No. 228, p. 21.

San Joaquin sandy loam, surface, California.
 Indio fine sandy loam, surface, California.
 Marshall silt loam, surface, eastern Nebraska.
 Marshall silt loam, subsurface, eastern Nebraska.
 Marshall silt loam, subsoil, eastern Nebraska.
 Marshall loam, surface, Minnesota.
 Marshall black clay loam, surface, Illinois.
 Miami silt loam, surface, Wisconsin.
 Wabash silt loam, surface, eastern Kansas.
 Wabash loam, surface, Ohio.
 Orangeburg sandy loam, surface, Alabama.
 Crowley silt loam, surface, Louisiana.
 Hagerstown loam, surface, Tennessee.
 Hagerstown clay, surface, Kentucky.
 Hagerstown shale loam, surface, Pennsylvania.
 Porters black loam, surface, Virginia.
 Norfolk sand, surface, Maryland.
 Leonardtown loam, surface, Maryland.
 Collington sandy loam, surface, New Jersey.

PHOTOGRAPHING THE SPECTRA OBTAINED IN TESTING FOR BARIUM.

Many of the precipitates obtained in separating the barium were too small to give spectra that would persist long enough for satisfactory photographing. It was, however, thought to be very desirable to obtain photographs of some of the spectra as a permanent record, and as a means of demonstrating the presence of barium to those not seeing the spectra themselves. Accordingly some of the larger precipitates were preserved for the purpose. Some of the photographs obtained are given in Plate I. In all cases the upper spectrum of a pair is that of the precipitate obtained from the soil; the lower, that of the barium sulphate used as a check. The coincidence of the lines is obvious. The lettering of the principal lines in the plate is purely arbitrary, and is for purpose of reference. The line *a* is in the red, wave length 6497; *b*, in the red (orange, Listing), 6142; *c*, the double sodium line; *d*, green, 5535.7; *e*, blue (green, Listing), 4934; *f*, indigo (blue, Listing), 4554. The other lines of the spectra may be approximately located by reference to these. The faint lines in the region of 4554 and beyond toward the violet were seldom visible to the writer and had no part in the detection of barium. It has not been determined whether they were produced by barium or are due to the carbons used for the arc.

In some cases the precipitates are apparently impure, since certain lines in their spectra are relatively stronger than the corresponding lines in the comparison spectrum, or are not found at all in the latter. If the foreign substance gives lines differing from those of barium, the latter condition would appear: if its lines have approximately the same wave length as those of barium, the former. The sodium line in the comparison spectrum is to be attributed to the



BARIUM SPECTRA.

presence of this element in the carbons. Other substances in the carbons may have affected the photographic plates, and carbon or its compounds may have produced some of the lines. But all of the continuously visible lines of the barium spectrum are reproduced in the photographs. In the upper portion of spectrum 4, the spectrum of the precipitate, the sodium line, *c*, is very prominent, presumably due to the precipitate containing a large percentage of sodium. The "light struck" appearance of some of the photographs is due to the arc being somewhat out of adjustment as to height. The adjustment was made by hand. Other imperfections will be observed, but the results of photographing the spectra substantiate the conclusions drawn from viewing them directly with the eye.

SUMMARY.

From the foregoing it appears that barium is a widely disseminated element and is present in most soils throughout the United States, and in larger quantities, as would be expected, in soils derived from masses carrying barite deposits and in the soils derived from the rocks of the Rocky Mountains.

The soil moisture may be expected to carry small amounts of barium. In all cases the feldspars of the igneous rocks from which the soil material has been derived seem to be an original source of the barium of soils.



