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BASE EXCHANGE IN GROUND WATER BY SILICATES
AS ILLUSTRATED IN MONTANA

BY

B. COLEMAN RENICK

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CONTENTS.

	Page.
Introduction.....	53
Acknowledgments.....	53
Geology.....	55
Lance formation.....	55
Fort Union formation.....	57
Leverrierite and related minerals, by Clarence S. Ross.....	60
Chemical character of the ground water.....	61
Base-exchange silicates.....	63
Origin of the soft waters.....	68
Summary.....	71

ILLUSTRATIONS.

	Page.
PLATE III. Photomicrographs of thin sections showing the texture and minerals of the rocks in the Lance formation.....	58
IV. Photomicrographs of thin sections showing the texture and minerals of the rocks in the Fort Union formation.....	59
V. A, Graphic representation of well depths and analyses of waters from the Lance formation, Rosebud County, Mont.; B, Graphic representation of well depths and analyses of waters from the Fort Union formation, Rosebud County, Mont.....	62
FIGURE 6. Topographic index map of Montana.....	54

BASE EXCHANGE IN GROUND WATER BY SILICATES AS ILLUSTRATED IN MONTANA.

By B. COLEMAN RENICK.

INTRODUCTION.

Changes in the chemical character of ground water with increase in depth have received considerable attention from students of ore deposits in connection with investigations of enrichment. These investigations have had to do mostly with reactions involving the heavy metals and their derivatives. The brines from deep levels in mines and oil fields have also been studied by numerous investigators.

In field studies of the geology and ground-water conditions in Rosebud County, Mont., which is in the Great Plains province (fig. 6), the writer encountered ground waters which appeared to show evidences of changes taking place in the ground different from those considered in various types of ore enrichment or in deep brines. All the samples discussed in this paper came from depths less than 600 feet.

The rocks of the Colorado and Montana groups (Upper Cretaceous) and the Lance (Tertiary?) and Fort Union (Tertiary) formations crop out in Rosebud County, and samples were obtained from all these formations, but the statements in succeeding paragraphs are made on the basis of data obtained from the Lance and Fort Union, unless otherwise specified, as these formations are the only aquifers that yield potable water of good quality over any considerable area, and as a result more samples were collected from these formations than from the others. The waters from the underlying Upper Cretaceous deposits are with local exceptions more highly mineralized, and many of them are not potable.

The conclusions contained in this paper were presented at the New York meeting of the Society of Economic Geologists May 24, 1924.

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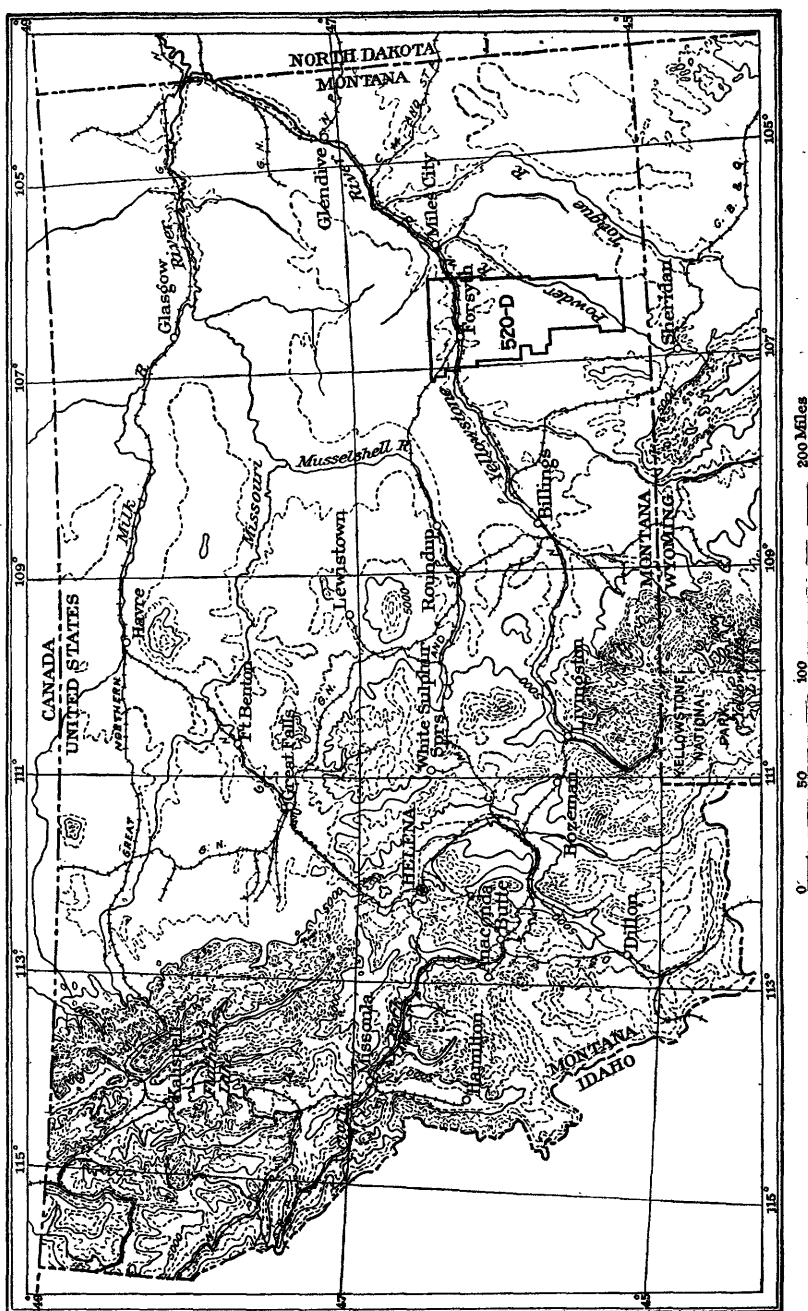


FIGURE 6.—Topographic index map of Montana. Contour interval 1,000 feet.

Collins, and D. F. Hewett. Special acknowledgments are due to H. B. Riffenburg for analyses of the water samples; to Clarence S. Ross, who has offered helpful suggestions and assistance in the petrologic determinations and who has kindly prepared the section of this paper which appears under his name; and to C. E. Dobbin and N. W. Bass for cooperation and courtesies extended in the course of the field work.

GEOLOGY.

For detailed geologic descriptions the reader is referred to the work of Bowen¹ in adjacent regions for the Upper Cretaceous rocks, and of Rogers and Lee² for the Lance and Fort Union formations. Thom and Dobbin³ in a recent paper have discussed in detail the stratigraphic correlations in this and adjacent regions, and a report by Dobbin and Bass⁴ embracing a portion of southern Rosebud County, confined for the most part to an area of Lance and Fort Union beds, is being prepared. A detailed report on the geology and ground-water conditions in central and southern Rosebud County is also in preparation.⁵ Only the most essential features of the geology are mentioned in the following paragraphs. The petrologic descriptions of the Lance and Fort Union formations are, however, based on thin sections cut from samples collected by the writer. The samples consisted of sandstone and sandy shale, because most of the material in the interbedded shale in these formations is so fine textured that in general individual mineral grains can not be identified, but in some places coarser mineral fragments could be identified within the fine-grained matrix of the shale. The samples were cut from outcrops and therefore presumably contain more calcite and secondary minerals than would be found in material from drill cuttings. No samples of drill cuttings could be obtained.

LANCE FORMATION.

The Lance formation is of fresh-water origin and is made up of two members.⁶ The lower member, known as the Hell Creek member, averages 675 feet in thickness and is made up of gray and buff

¹ Bowen, C. F., Gradations from continental to marine conditions of deposition in central Montana during the Eagle and Judith River epochs: U. S. Geol. Survey Prof. Paper 125, pp. 11-21, 1919.

² Rogers, G. S., and Lee, Wallace, Geology of the Tullock Creek coal field, Mont.: U. S. Geol. Survey Bull. 749, 1923.

³ Thom, W. T., jr., and Dobbin, C. E., Stratigraphy of the Cretaceous-Eocene transition beds in eastern Montana and the Dakotas: Geol. Soc. America Bull., vol. 35, pp. — (in press).

⁴ Dobbin, C. E., and Bass, N. W., Geology of the Forsyth coal field, Rosebud, Treasure, and Big Horn Counties, Mont.: U. S. Geol. Survey Bull. — (in preparation).

⁵ Renick, B. C., Geology and ground-water resources of central and southern Rosebud County, Mont.: U. S. Geol. Survey Water-Supply Paper — (in preparation).

⁶ Rogers, G. S., and Lee, Wallace, Geology of the Tullock Creek coal field, Mont.: U. S. Geol. Survey Bull. 749, p. 19, 1923. Dobbin, C. E., and Bass, N. W., op. cit.

sandstone and gray shale; in places the shale is calcareous. Thin seams of carbonaceous material are present locally. With the exception of the heavy sandstone at the base of this member, which is especially persistent and is believed to be in part the equivalent of the Lennep⁷ and Fox Hills⁸ sandstones, most of the sandstones in the Hell Creek member are lenticular and locally grade into shale.

The upper part of the Lance formation, which is known as the Tullock member, averages 250 feet in thickness in this region and is made up of yellow sandstone and shale, the shale in places somewhat calcareous. Unlike the Hell Creek member, the Tullock member contains a number of thin beds of coal and carbonaceous shale. A persistent sandstone, which gives rise to a rim rock throughout the region, defines the top of the Tullock member.

Thin sections⁹ from samples of so-called sandstone from the Lance formation show that it consists predominantly of angular and sub-angular grains of quartz and fragments of volcanic rock. Many of the rock fragments contain a glassy groundmass, which is considerably altered. (See Pl. III.) The quartz has been strained, undoubtedly before deposition, and appears biaxial, being therefore extremely difficult to distinguish from the orthoclase that is also present in these rocks. In thin section the quartz is seen to be generally more angular than the orthoclase, which is more altered than the quartz. Examination of the crushed fragments in index of refraction liquids shows that the orthoclase never exceeds 3 per cent of the sample and averages about 1 per cent. In many slides a chertlike material, which may represent altered rock grains of sedimentary (?) origin, is conspicuous (Pl. III, B). All slides of the Lance rocks also contain a few grains of plagioclase (Pl. III, B), muscovite, biotite, and detrital calcite. Glauconite grains were also identified. An examination by heavy solution of one sample of sandstone showed that the Lance rocks also contain garnet, pink and white zircon, and a pyroxene, probably augite.

The freshest material in the rock fragments consists of quartz and feldspar in a matrix of secondary material which is mostly leverrierite and an allied mineral. Leverrierite and the allied species are discussed by Clarence S. Ross on page 60. All thin sections contained some leverrierite, and in some sections as much as 10 per cent

⁷ Calvert, W. R., *Geology of certain lignite fields in eastern Montana*: U. S. Geol. Survey Bull. 471, pp. 187-201, 1910.

⁸ Stone, R. W., and Calvert, W. R., *Stratigraphic relations of the Livingston formation*, Mont.: Econ. Geology, vol. 5, pp. 551-557, 652-669, 741-764, 1910.

⁹ All the samples were first treated with bakelite in order to make them sufficiently coherent for grinding. Bakelite has a high index of refraction and appears isotropic through crossed nicols, as can be seen by observing the interstitial material in the thin sections shown in Plates III and IV. This method of hardening incoherent rock material with bakelite before grinding was devised by Clarence S. Ross and is described by him in a recent paper (*A method of preparing thin sections of friable rock*: Am. Jour. Sci., 5th ser., vol. 7, pp. 483-485, 1924).

was observed. Secondary claylike material and calcite are present in all slides, and chlorite was also noted. These secondary minerals are derived from the alteration of the feldspars and rock fragments. It is problematical just how much secondary material would be shown in thin sections made from drill cuttings.

FORT UNION FORMATION.

The Fort Union formation is divisible into two distinct lithologic units, a lower so-called somber member, known as the Lebo andesitic¹⁰ or shale¹¹ member, which averages 175 feet in thickness, and an upper light-colored coal-bearing member approximating 1,600 feet in thickness, which is known as the Tongue River member.¹² The preponderance of dark-gray and drab shale in the Lebo member makes it easy to distinguish in this region from the light-colored Lance below and the light-colored overlying beds of the Tongue River member. In general, the materials in the Tongue River member are better assorted than those of the Lebo member and the Lance formation.

The Lebo in this region, though made up largely of shale with numerous iron-stained calcareous and siliceous concretionary bands, everywhere contains well-developed sandstone lenses. The shale portions of this member are too fine textured for the identification of individual grains, but in the sandstone lenses quartz, rock fragments with glassy groundmass, chertlike fragments, orthoclase, plagioclase, calcite, chlorite, claylike material, and leverrierite and its allied iron mineral were found in approximately the same proportions and the same relations as in the Lance and the Tongue River member. (See Pl. IV, A.) Because of similar relations in the underlying and overlying beds it is somewhat doubtful whether these beds can be correlated by the petrologic methods suggested by Rogers.¹³

Five thin sections of the Lebo member were examined. The samples from which the sections were cut came from widely distributed regions and were selected as representative of the Lebo member in Rosebud County. Because of the fact that plagioclase is not more abundant in the Lebo member, as shown in these thin sections, than in the underlying Lance formation or in the overlying beds of the

¹⁰ Stone, R. W., and Calvert, W. R., *Stratigraphic relations of the Livingstone formation of Montana*: Econ. Geology, vol. 5, pp. 551-557, 652-669, 741-764, 1910. Woolsey, L. H., Richards, R. W., and Lupton, C. T., *The Bull Mountain coal field, Musselshell and Yellowstone counties, Mont.*: U. S. Geol. Survey Bull. 647, pp. 24-27, 1917.

¹¹ Rogers, G. S., *The Little Sheep Mountain coal field, Dawson, Custer, and Rosebud counties, Mont.*: U. S. Geol. Survey Bull. 531, pp. 159-172, 1913.

¹² Thom, W. T., and Dobbin, C. E., *Stratigraphy of Cretaceous-Eocene transition beds in eastern Montana and the Dakotas*: Geol. Soc. America Bull., vol. 35, pp. — (in press). Dobbin, C. E., and Bass, N. W., *op. cit.*

¹³ Rogers, G. S., *A study in the petrology of sedimentary rocks*: Jour. Geology, vol. 21, pp. 715-727, 1913.

PLATE III.

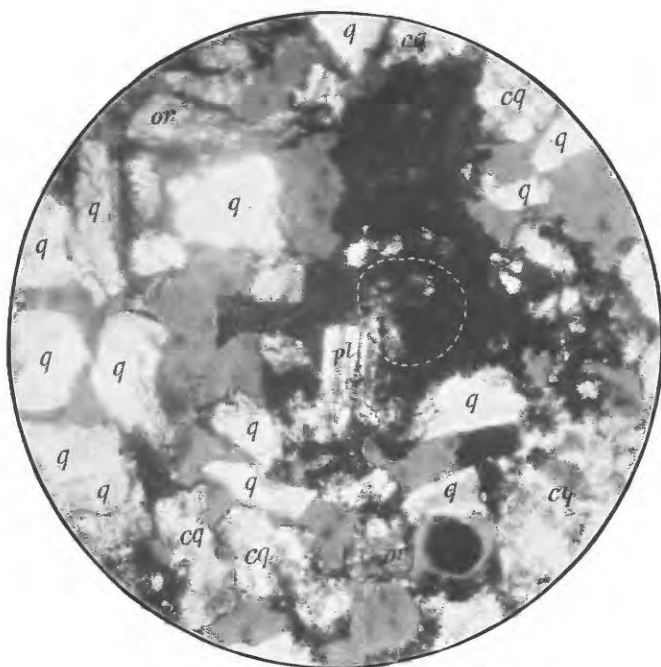
PHOTOMICROGRAPHS OF THIN SECTIONS SHOWING TEXTURE AND MINERALS OF ROCKS FROM LANCE FORMATION.

- A*, Sandstone from NE. $\frac{1}{4}$ sec. 7, T. 5 N., R. 41 E., nicols crossed.
- B*, Basal sandstone from NW. $\frac{1}{4}$ sec. 26, T. 6 N., R. 39 E., showing grains of altered igneous rock containing phenocrysts (also altered), nicols crossed.
- cq*, Chertlike material, in part possibly secondary, in part probably altered sedimentary rock grains; *f*, impure iron oxide, mostly limonite; *l*, leverrierite; *m*, colorless mica; *or*, altered mineral grains, probably orthoclase; *pl*, plagioclase; *q*, quartz; *x*, impure claylike interstitial material, in some places containing small amounts of disseminated calcite, probably in considerable part leverrierite.



1/2 mm.

A.



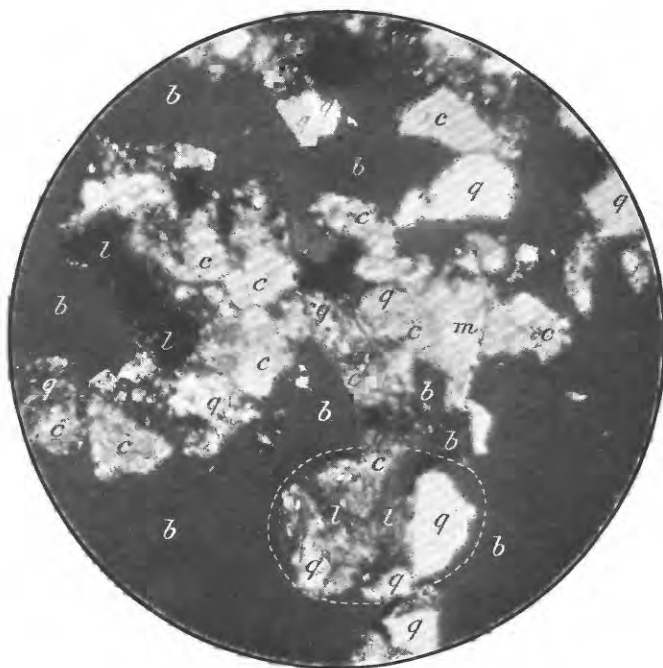
1/2 mm.

B.



1/2 mm.

A.



1/2 mm.

B.

PLATE IV.

PHOTOMICROGRAPHS OF THIN SECTIONS SHOWING THE TEXTURE AND MINERALS OF THE ROCKS IN THE FORT UNION FORMATION.

- A*, Lebo shale member, sandy facies, from NW. $\frac{1}{4}$ sec. 34, T. 8 N., R. 42 E.; one nicol.
- B*, Sandstone near base of lower light-colored member in NW. $\frac{1}{4}$ sec. 33, T. 2 N., R. 43 E.; nicols crossed. Section shows grains of altered igneous rock containing plates of leverrierite.
- a*, Air hole; *b*, bakelite mounting; *by*, claylike material stained with bakelite; *c*, calcite; *cq*, chertlike material, in part possibly secondary, in part probably altered sedimentary rock grains; *l*, leverrierite; *m*, colorless mica; *or*, altered mineral grains, probably orthoclase; *q*, quartz; *x*, impure claylike interstitial material, in some places containing small amounts of disseminated calcite, probably in considerable part leverrierite.

Fort Union, where it always amounts to less than 1 per cent, the descriptive term "andesitic" for this member is not applicable in Rosebud County.

The samples of waters from the Tongue River member discussed on page 62 were obtained within the lower 500 feet of this member. In many places the coals of the Tongue River member have been burned along the outcrop. This burning oxidizes the iron present and fuses and slags the overlying sandstone and shale, giving rise to beds of different hues of red rock above the ash of the burned coal.

Like the Lance formation, the Tongue River member of the Fort Union is made up of angular grains, predominantly strained quartz, rock fragments of igneous origin, and cherty quartzose fragments of probable sedimentary origin. The grains of igneous origin contain much glass, which has been highly altered. Orthoclase, plagioclase, muscovite, biotite, claylike material, and chlorite are also present. In general, sections of these rocks contain considerably more secondary calcite than those from the Lance beds. Leverrierite¹⁴ and its allied iron mineral (see p. 61), both secondary after the glassy material, are present in considerable amounts but on the whole are not so abundant as in the Lance formation. Most of the feldspar, especially the orthoclase, is greatly altered.

Rogers¹⁵ doubtless included leverrierite and its associated iron-bearing mineral when in describing the petrologic character of some Fort Union rocks in southeastern Montana he said: "There is usually much fine clayey interstitial material, commonly iron stained."

LEVERRIERITE AND RELATED MINERALS.

By CLARENCE S. ROSS.

In a recent description of leverrierite, by Larsen and Wherry,¹⁶ the following statements regarding the chemical and optical properties of this group of minerals are made:

¹⁴ Since this paper was written an article by Pierre Termier on the presence of leverrierite in the Tonstein of the Sarre coal formations has appeared (*Soc. franç. minéralogie Bull.*, vol. 46, pp. 18-20, 1923; *Chem. Abstracts*, vol. 18, p. 649, 1924). The leverrierite described by Termier occurs in small crystals in clay beds of the coal-bearing group of rocks, but the leverrierite referred to in the present paper is not confined to argillaceous beds but is plentiful in the sandstone—in fact, the petrographic descriptions in this paper are based on the leverrierite in the sandstones. It is interesting to note that in both localities the leverrierite is associated with coal-bearing rocks and that the leverrierite of the Sarre coal formations is associated with detrital quartz, carbonaceous vegetable débris, calcite, dolomite, siderite, and to a less extent with biotite, muscovite, and chlorite, a mineral association which is very similar to that found in the rocks of the Lance and Fort Union formations of Montana.

¹⁵ Rogers, G. S., Baked shale and slag formed by the burning of coal beds: *U. S. Geol. Survey Prof. Paper* 108, p. 5, 1917.

¹⁶ Larsen, E. S., and Wherry, E. T., Leverrierite from Colorado: *Washington Acad. Sci. Jour.*, vol. 7, pp. 208-217, 1917.

Chemically it differs from kaolinite chiefly in the fact that it retains only 7 per cent of its H_2O at 110° and very little at 350° , while kaolinite retains nearly all of its 14 per cent of H_2O up to 400° . Optically leverrierite has higher indices of refraction, much stronger birefringence, and much smaller axial angle than kaolinite, and it is commonly found in larger plates.

The leverrierite group includes, then, the micaceous hydrous silicates of aluminum with small amounts of Fe_2O_3 , RO , and R_2O , in which the ratio $Al_2O_3 : SiO_2$ varies at least from 1.85 to 3.95; the H_2O content under normal conditions is from 15 to 25 per cent, of which all but about 7 per cent is given off below 110° . In physical and optical properties leverrierite resembles muscovite, but its cleavage is less prominent, it is rather brittle when dry and very plastic when wet, and its axial angle is commonly very small.

The thin sections made from samples of sandstone from the Lance and Fort Union formations show that in many of the rock fragments the mineral grains have no characteristic outline and the nature of the original rock is not evident, but in others euhedral feldspar in a fine-grained groundmass indicates derivation from a volcanic rock. The groundmass in these rock grains is an aggregate of secondary material. Part of this is undoubtedly leverrierite, as it agrees in appearance and optical properties with that mineral. The same kind of material also forms a scant cement between mineral grains.

In the section from which Plate III, *A*, was made, a pale-brown material with a silvery luster forms rather definite masses between other grains. In thin section it is seen that these masses have a micaceous structure, but instead of being plates, many of them are made up of groups of plates with random orientation, or of fan-shaped or rudely radial aggregates of plates. The best of these plates give a negative optical figure with a small axial angle. The indices are 1.60 to 1.70, and the birefringence is about 0.03. In habit and general appearance and in all optical properties but the indices of refraction this brown material resembles the leverrierite that occurs in the same rock. The ferric iron content of this brown mineral is high, and in consequence the indices of refraction are high. The nature of this material is not entirely clear, but it is probably related to the hydrous ferric iron silicate nontronite, or possibly it is an iron-bearing leverrierite. Nontronite and leverrierite are probably related, as the former is a hydrous ferric iron silicate and the latter a hydrous aluminum silicate. Therefore, a mineral near nontronite in chemical composition but with the habit and relations of leverrierite is not at all improbable.

CHEMICAL CHARACTER OF THE GROUND WATER.

Twenty analyses of waters from the Lance formation are shown in Plate V, *A*, and ten analyses from the Fort Union formation are shown in Plate V, *B*. These analyses are platted graphically by

reacting values or milligram equivalents¹⁷ in both figures.¹⁸ All samples were collected from wells that begin in the formation from which they obtain their water. Well No. 28, which obtains water from the Lebo member, begins in the upper light-colored Tongue River member of the Fort Union formation. In wells reaching a depth of 100 feet or more and in many shallower wells the upper water is cased off, and it is reasonably certain that the waters discussed come from depths approximating those shown in Plate V.

The analyses represented in these diagrams show that on the whole the waters from the Lance formation are more highly mineralized than those from the Fort Union formation. The maximum total dissolved solids in the Lance waters shown in Plate V, *A*, is 2,911 parts per million (No. 12), and the maximum in the Fort Union waters shown in Plate V, *B*, is 1,231 parts per million (No. 3), but locally a Fort Union bed yields water that contains as much dissolved mineral matter as any of the waters from the Lance formation.

Of the waters from the Lance formation platted in Plate V, *A*, those from wells less than 125 feet deep contain from 43 to 162 parts per million of calcium and magnesium, and those from wells more than 125 feet deep contain from 5.2 to 18.1 parts per million. Of the waters from the Fort Union formation (including at the base the Lebo member) platted in Plate V, *B*, those from wells less than 80 feet deep contain from 99 to 212 parts per million of calcium and magnesium, and those from wells more than 80 feet deep contain from 5.2 to 23 parts per million. These statements, exemplified on Plate V, indicate clearly that the waters from the shallow wells are relatively high in calcium and magnesium and that those from the deeper wells contain little calcium and magnesium but are relatively high in sodium—that is, the water in the shallow wells is hard and that in the deeper wells is soft.

After averaging the analyses of the shallow hard waters and the deeper soft waters in both the Lance and Fort Union formations it is clear that there is no noteworthy difference in the total quantity of dissolved salts in these two types of waters. In the Lance forma-

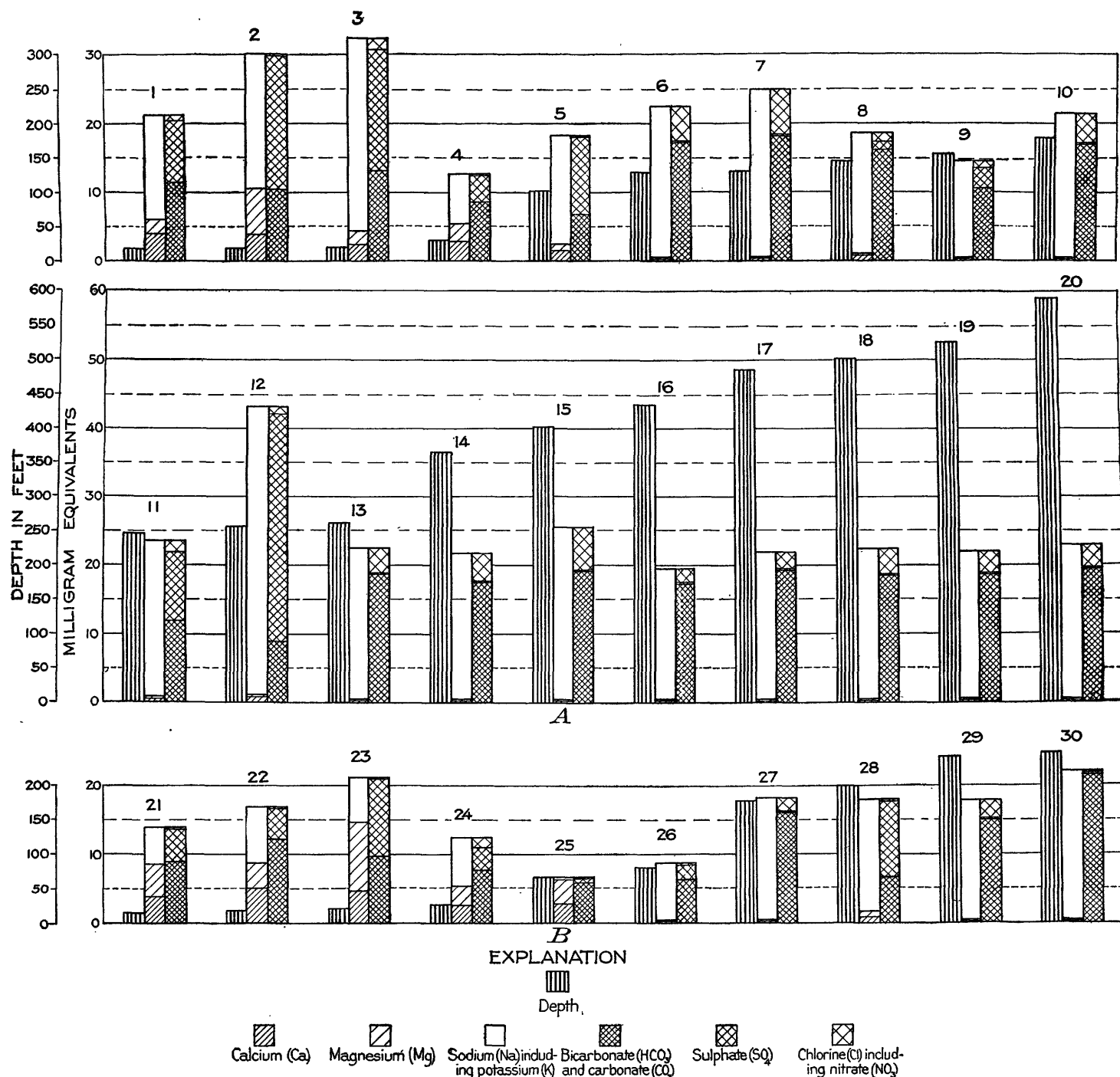
¹⁷ Palmer, Chase, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, 1911. Rogers, G. S., The interpretation of water analyses by the geologist: Econ. Geology, vol. 12, pp. 56-88, 1917. The milligram equivalents are calculated as follows:

$$\text{Combining weight of radicle} = \frac{\text{atomic weight or sum of the atomic weights}}{\text{valence of the radicle}}$$

$$\text{Number of milligram equivalents} = \frac{\text{parts per million}}{\text{combining weight of the radicle}}$$

In the diagrams 1 milligram equivalent=23 parts per million Na, 39 K, 20 Ca, 12 Mg, 61 HCO₃, 30 CO₃, 48 SO₄, 35 Cl.

¹⁸ The legend used in Plate V has been adapted from that suggested by W. D. Collins (Graphic representation of water analyses: Ind. and Eng. Chemistry, vol. 15, No. 4, p. 394, 1923).



GRAPHIC REPRESENTATION OF WELL DEPTHS AND ANALYSES OF WATERS FROM ROSEBUD COUNTY, MONT.

A, Waters from Lance formation; B, waters from Fort Union formation. See text for explanation.

tion the average total dissolved solids in the shallow well waters (Nos. 1 to 5) is 1,416 parts per million and in the deeper well waters (Nos. 6 to 20) 1,362 parts per million. In the Fort Union formation, where the waters are less mineralized, the average total dissolved solids in the shallow well waters (Nos. 21 to 25) is 792 parts per million and in the deeper well waters (Nos. 26 to 30) 961 parts per million.

Potassium is comparatively low in all these waters. Nine potassium determinations in the 30 analyses were made by Mr. Riffenburg; the maximum amount of potassium determined was 24 parts per million (Nos. 12 and 15), as compared with a maximum of 957 parts per million of sodium (No. 12). This small amount of potassium, though not referred to in the following discussion, is included with the sodium.

Considerable tracts of alluvial land along Yellowstone River are irrigated, and the waters from shallow wells in the alluvium in these tracts are in general more highly mineralized than they would be under natural conditions. These waters are not typical or representative of the shallow wells in other parts of the region and are therefore eliminated from consideration in this paper.

BASE-EXCHANGE SILICATES.

On the basis of some experiments carried on in 1845 Thompson¹⁹ pointed out that certain soils possess the power of decomposing and retaining the salts of ammonia. He stated that he had not studied the reaction sufficiently to account for the manner in which it was accomplished. About the same time Way,²⁰ an English investigator, observed that this power of soils is not confined to ammonium salts but that the bases of different alkaline salts may be separated from solution and retained by ordinary soils. Summarizing his previous work in a later paper²¹ he made the following pertinent statements:

But further, this power of the soil was found not to extend to the whole salt of ammonia or potash, but only to the alkali itself. If, for instance, sulphate of ammonia were the compound used in the experiments, the ammonia would be removed from solution, but the filtered liquid would contain sulphuric acid in abundance—not in the free or unconfined form, but united to lime; instead of sulphate of ammonia we would find after the experiment sulphate of lime in solution; and this result was obtained whatever the acid of the salt experimented on might be. * * * It was satisfactorily proved that the quantity of lime acquired by solution corresponded exactly to that of ammonia removed from it; the action was therefore a true chemical decomposi-

¹⁹ Thompson, H. S., On the absorbent power of soils: Roy. Agr. Soc. Jour., vol. 11, pp. 68–74, 1850.

²⁰ Way, J. T., The power of soils to absorb manure: Roy. Agr. Soc. Jour., vol. 11, pp. 313–379, 1850.

²¹ Way, J. T., Roy. Agr. Soc. Jour., vol. 13, pp. 123–143, 1852.

tion. * * * It was found that the process of filtration was by no means necessary; by the mere mixing of an alkaline solution with a proper quantity of soil, as by shaking them together in a bottle and allowing the soil to subside, the same result was obtained; the action, therefore, was in no way referable to any physical law brought into operation by the process of filtration.

Again it was found that the combination between soil and alkaline substance was rapid, if not instantaneous. * * * It was shown that the power to absorb alkaline substances did not exist in sand; that the organic matter of the soil had nothing to do with it; that the addition of carbonate of lime to a soil did not increase its absorptive power for these salts; and indeed that a soil in which carbonate of lime did not occur might still possess in a high degree the power of removing ammonia or potash from solution, and it was evident that the active ingredient in all these cases was clay. * * * The stiffest and most tenacious clays taken from considerable depths, which had never since their deposition been exposed to atmospheric influences, and which also were absolutely free from organic matter, or carbonate of lime, possessed to the fullest extent the absorptive property. By these experiments the subject was so far narrowed that the origin of the power in question had been traced to the clay existing in all soils. * * * It soon became evident that the idea of the clay as a whole being the cause of the absorptive property was inconsistent with all the ascertained laws of chemical combination. * * *

I was, indeed, convinced at a very early period of this inquiry that the absorptive property was due to a small quantity of some definite chemical compound existing in the clay and possibly not constituting more than 4 or 5 per cent of its whole weight. I had hoped that, although I might not be able to separate this substance from clay—for of that there was little prospect—it might yet be possible to form it artificially from other sources at the disposal of the chemist, and by producing a compound, or compounds, having the same properties as those shown to be possessed by clay to prove their identity with the active principles of clay itself and thus indirectly establish its real nature.

After eliminating lime (CaO), lime carbonate, sulphate, nitrate, and other simple salts of lime from consideration as the material that gave to soils this reactive power, Way concluded that it must be due to some silicate. After preparing a simple lime silicate, which he found did not possess this property, he turned his attention to the preparation of double silicates of alumina with the alkalies and alkaline earths. He observed that these silicates possessed the property of exchanging their bases and concluded that the base-exchange material in soil was similar in chemical composition but that it was not feldspar or other undecomposed minerals from granitic rocks. Way furthermore brought out the important point that these silicates contain water of combination and that if it is driven off by strong heating the base-exchange property is destroyed, the silicate being no longer reactive.

From the foregoing description of the work of Way it is evident that much was known about base-exchange silicates at a relatively early date. It has long been known that the mineral zeolites are capable of readily exchanging their bases, and after Way's discovery of base-exchange silicates in soils many agriculturists came to regard

the reactive material as zeolites. This base-exchange material in soils is referred to as the zeolitic portion of soils even to the present time, though ordinary soils almost certainly do not contain zeolites.

Sullivan,²² in addition to summarizing the work of earlier investigators on base exchange in natural and artificial silicates, made a noteworthy contribution to the subject. He effected numerous base-exchange reactions between natural silicates and the base of numerous salts in solution. Some of his conclusions follow:

The fact of prime significance geologically seems to be that by a process of simple chemical exchange the metal may be removed from solution and fixed in a solid state and thus concentrated, by contact with even the most stable of the silicates. The changes under consideration involve the action of the alkali or alkaline-earth salt of a weak acid (silicic or aluminosilicic) and are thus analogous to the more familiar behavior of sodium carbonate with solutions of salts of the metals. Owing to hydrolysis the precipitates caused by sodium carbonate tend to split up into the acid and base (carbonic acid and metal oxide or hydroxide), and the weaker the base the more marked is this action. The precipitate from solutions of salts of strong bases, such as calcium chloride, is the normal carbonate; a weaker base, such as nickel, is precipitated as basic carbonate or a mixture of the normal carbonate with hydroxide or oxide; while the very weak bases, as iron in ferric salts, are precipitated as hydroxide or oxide containing little or no carbonate, and the corresponding quantity of carbon dioxide is set free.²³

Sullivan discussed the mechanics of the reaction and by way of summary said:

The natural silicates precipitate the metals from solutions of salts, while at the same time the bases of the silicates are dissolved in quantities nearly equivalent to the precipitated metals. The bases most commonly replacing the metals in these processes are potassium, sodium, magnesium, and calcium. Where exact equivalence is wanting, it is attributable either to solubility of the mineral in pure water or to the precipitation of basic salts.

The specific materials on which work was done are albite, amphibole, augite, biotite, enstatite, garnet, clay gouge, kaolin, microcline, muscovite, olivine, orthoclase, prehnite, shale, talc, tourmaline, and vesuvianite, with cupric sulphate solution; and orthoclase with salts of sodium, potassium, magnesium, calcium, strontium, barium, manganese, iron, nickel, copper, zinc, silver, gold, and lead. Experiments were also made on the action of kaolin on solutions of salts of zinc and iron, and of glass, fluorite, and pyrite on cupric sulphate and of carbonic and sulphuric acids on orthoclase.²⁴

Sullivan's conclusions differ somewhat from those previously arrived at by Lemberg,²⁵ who says:

In addition to these [the zeolites] I have experimented with the various feldspars, hornblende, cordierite, serpentine, and scapolite, but up to the

²² Sullivan, E. C., Interaction of minerals and water solutions: U. S. Geol. Survey Bull. 312, 1907. Also an earlier shorter paper, The chemistry of ore deposition—precipitation of copper by natural silicates: Econ. Geology, vol. 1, pp. 67-73, 1905.

²³ Sullivan, E. C., op. cit. (Bull. 312), pp. 61-62.

²⁴ Sullivan, E. C., op. cit., p. 64.

²⁵ Lemberg, J., Deutsch. geol. Gesell. Zeitschr., vol. 22, p. 335, 1870; vol. 24, p. 187, 1872; vol. 28, p. 591, 1876. Cited by E. C. Sullivan, U. S. Geol. Survey Bull. 312, p. 23, 1907.

present only in the case of hornblende could an exchange of substance be proved with certainty.

This conflict in statement may be due to a difference in viewpoint—that is, Lemberg might not have regarded an exchange as taking place unless it was fairly complete, while Sullivan regarded an experiment as highly successful and demonstrative of base exchange if only a very small part of the silicate was exchanged.

Although these base-exchange silicates had been prepared and most of their properties understood for over half a century, Gans, by publishing two papers²⁶ in 1905 and 1906, aroused considerable interest in them. He apparently was the first one to conceive of the idea of utilizing artificially prepared sodium base-exchange silicates for softening water by allowing hard water containing salts of calcium and magnesium to flow over it, the calcium and magnesium being removed by exchange with the sodium to give a mixed calcium, magnesium, and sodium base-exchange silicate and soft water. This artificial water softener, which he considered must contain the essential molecules soda, alumina, silica, and water of combination, he named permutite and patented.

When the sodium capable of exchange has been exhausted the base-exchange silicate is regenerated by passing a strong solution of a sodium salt, preferably chloride, through it. Regarding the ability of these double silicates to be regenerated by reversing the reaction Way²⁷ erred when he wrote, "Of course, the reverse of this action can not occur."

In 1907 Feldoff²⁸ reported on the success of this method of softening water for use in boilers, and furthermore showed that permutite could be used to remove iron and manganese quantitatively from drinking water. Gedroiz²⁹ has since stated that this exchange may take place between the base of any metallic salt and a base-exchange silicate. As pointed out in a recent thesis by Baker,³⁰ artificial softeners have been patented which substitute the oxides of zinc, tin, lead, titanium, zirconium, chromium, and iron for alumina, and boric acid has been used in place of silica.

Since 1907 the use of so-called artificial zeolites has become of considerable economic importance in municipal and industrial water-

²⁶ Gans, Robert, Zeolites and similar compounds, their constitution and their importance for technology and agriculture: Preuss. geol. Landesanstalt Berlin Jahrb., Band 26, Heft 2, pp. 179-211, 1905; The constitution of zeolites, processes of obtaining and technical importance: Idem, Band 27, Heft 1, p. 63, 1906.

²⁷ Way, J. T., Power of soils to absorb manure: Roy. Agr. Soc. Jour., vol. 13, p. 132, 1852.

²⁸ Feldoff, A., Natural and artificial zeolites (permutite) and their technical application: Centralbl. Zuckerindustrie, vol. 15, pp. 1307-1310, 1907; Chem. Abstracts, vol. 1, p. 2755, 1907.

²⁹ Gedroiz, K. K., Colloidal chemistry as related to soil science: Russia Bur. Agr. and Soil Sci. Communication 8, p. 25, 1912 (U. S. Dept. Agr. translation, p. 18). Recent papers of Dr. Gedroiz, of Petrograd, published between 1912 and 1923, have been translated into English by Dr. S. A. Waksman and mimeographed by the United States Department of Agriculture in order that they may be available to American investigators.

³⁰ Baker, G. C., Water softening by base exchange: Am. Waterworks Assoc. Jour., vol. 11, pp. 128-149, 1924.

softening plants. Many investigators in Europe and America have studied the permutite reaction, but in spite of much detailed work, different investigators have arrived at different conclusions with regard to the mechanics of the reaction, some contending that this exchange is ionic, and others that it is a phenomenon of adsorption.³¹ Rideal,³² in referring to the reaction of carbonate of lime with natural mineral zeolites, said, "The reaction suggests another way by which nearly pure alkali may originate in nature." Numerous papers by Gedroiz are especially noteworthy, as they contain not only much valuable original work but also discussions of the papers of earlier workers. The mechanics of the reaction has also been discussed by numerous investigators, including Wiegner,³³ Don,³⁴ Raumann, Marz, Biesenberger, and Spengel,³⁵ Rothmund and Kornfeld,³⁶ and Raumann and Junk.³⁷

Gans, like his predecessors, assumed that the soil contains mineral zeolites. Since Gans's papers appeared many writers on this subject have referred to these complex aluminum silicates capable of base exchange found in the soil as "zeolites." As ordinary soil does not contain mineral zeolites, it seems that the usurping of a definite mineralogic term to describe any complex hydrated aluminum silicate capable of base exchange gives an erroneous concept. For such material the term "base-exchange silicates" instead of zeolite seems appropriate.

Gedroiz³⁸ concludes that this exchange is ionic and states that

The zeolitic (and humic) part of every soil contains a well-defined quantity of zeolitic cations. These cations can be replaced by any cation or mixture of any cations. The replacement takes place as a result of the reaction of mutual exchange of the cations between the zeolitic (and humic) part of the soil and the solution of the salt or acid taken. As a reaction of double exchange, the replacement takes place in equivalent concentrations.

Besides artificial base-exchange silicates, many of which utilize kaolin, quartz, and feldspar, there are certain natural minerals and rock materials that will soften water and have been used for that purpose. These natural materials are rendered more efficient by

³¹ Gedroiz prefers the use of the word absorption. Some writers include both phenomena under the general term sorption.

³² Rideal, S., Origin of carbonate of soda in natural waters and mineral deposits: *Chem. World*, vol. 1, p. 16, 1912.

³³ Wiegner, George, The exchange of bases in cultivated soil: *Jour. Landw.*, vol. 60, pp. 197-222, 1912; *Chem. Abstracts*, vol. 6, pp. 2477, 3304, 1912.

³⁴ Don, J., The use of permutit and polarit in water purification: *Glasgow Kolloid Zeitschr.*, vol. 15, pp. 132-134, 1914; *Chem. Abstracts*, vol. 9, p. 676, 1915.

³⁵ Raumann, E., Marz, S., Biesenberger, K., and Spengel, A., The exchange of bases of silicates—Exchange of alkalies and ammonium by hydrous aluminum-alkali silicates permutites: *Zeitschr. anorg. allgem. Chemie*, vol. 95, pp. 115-128, 1916; *Soc. Chem. Industry Jour.*, vol. 35, p. 1129, 1916; *Chem. Abstracts*, vol. 11, p. 2174, 1917.

³⁶ Rothmund, V., and Kornfeld, G., Basic exchange in permutit: *Zeitschr. anorg. allgem. Chemie*, vol. 103, pp. 129-163, 1918; *Chem. Abstracts*, vol. 13, p. 2828, 1919.

³⁷ Raumann, E., and Junk, H., Basic exchange in silicates—III: *Zeitschr. anorg. allgem. Chemie*, vol. 114, pp. 90-104, 1920; *Chem. Abstracts*, vol. 15, p. 2592, 1921.

³⁸ Gedroiz, K. K., op. cit., p. 26 (U. S. Dept. Agr. translation, p. 19).

various treatments, many of which are relatively simple. The most useful of these minerals are greensand or glauconite, bentonite, and clay or kaolin. Bentonite, though containing more than one mineral, always consists chiefly of leverrierite, or one of the group of micaceous clay minerals which includes the mineral commonly known as leverrierite. This group possesses the property of readily exchanging its bases and is considerably more reactive than the ordinary natural clays. The bentonite from Ardmore, S. Dak., consists mostly of leverrierite but contains a considerable quantity of disseminated carbonate (probably calcite) and a few grains of biotite and muscovite. This leverrierite-bearing material from Ardmore after being treated to render it more reactive and to prevent it from swelling (a characteristic property of leverrierite) is used as a commercial water softener.

ORIGIN OF THE SOFT WATERS.

It is believed that the difference in the composition of water in deep and shallow wells in this area of Lance and Fort Union rocks can be explained as the result of natural softening. This exchange of the calcium and magnesium in the water for sodium can be accounted for by the minerals of the leverrierite group, which exchange their bases easily and which are plentiful in these formations. The hypothetical reactions might be written as follows:

- (1) $\text{Na (or K) base-exchange silicate} + \text{Ca (HCO}_3)_2 \text{ (or Mg (HCO}_3)_2) = \text{Ca (or Mg) base-exchange silicate} + 2\text{NaHCO}_3 \text{ (or } 2\text{KHCO}_3\text{)}.$
- (2) $\text{Na (or K) base-exchange silicate} + \text{CaSO}_4 \text{ (or MgSO}_4\text{)} = \text{Ca (or Mg) base-exchange silicate} + \text{Na}_2\text{SO}_4 \text{ (or K}_2\text{SO}_4\text{)}.$

Analyses of minerals of the leverrierite group.^a

	1	2	3	3a	4	5	6	7	8
SiO ₂	47.28	47.84	47.56	789	47.95	49.90	50.55	49.4	48.43
Al ₂ O ₃	20.27	20.88	20.57	256	32.67	37.02	19.15	45.1	41.63
Fe ₂ O ₃	8.68	8.48	8.58		.23	3.65			
MnO.....		.24	.24				4.40		
CaO.....	2.75	2.52	2.52	89	.41	Tr.	.63		2.13
MgO.....	.70	.91	.80		.46	.30			2.13
Na ₂ O.....	.97	1.58	1.28		2.47				
K ₂ O.....	Tr.	Tr.			.24	1.13			
H ₂ O+.....		6.65	6.65		7.03	8.65		5.6	7.70
H ₂ O+.....	19.72	10.95	12.01		8.56	(?)	24.05	(?)	(?)
Al ₂ O ₃ :SiO ₂	100.37	100.05	100.21		99.36	100.65	98.78	100.1	99.89
			1:2.76		1:2.34	1:2.11	1:3.95	1:1.86	1:1.94

^aLarsen, E. S., and Wherry, E. T., *Leverrierite from Colorado*: Washington Acad. Sci. Jour., vol. 7, No. 8, p. 213, 1917.

1 and 2. Material from Beidell, Colo. New analyses by E. T. Wherry.

3. Average of 1 and 2.

3a. Molecular proportions of 3.

4. Average of two analyses of "rectorite," Garland County, Ark. Brackett, R. N., and Williams, J. F., *Am. Jour. Sci.*, 3d ser., vol. 42, p. 16, 1891.

5. *Leverrierite*, Rochelle, France. Termier, P., *Soc. min. Bull.*, vol. 22, p. 29, 1899. Analysis made on material dried at 110°-130°. Older analyses show 13.21 and 13.0 per cent of total water.

6. "Montmorillonite, var. delanouite," Millac, France. Quoted from Lacroix, A., *Minéralogie de la France*.

7. "Batchelorite," Tasmania. H₂O stated as "combined H₂O." Gregory, J. W., *Australian Inst. Min. Eng. Trans.*, vol. 16, p. 137, 1905.

8. *Kryptotile*. Quoted from Dana. The original article reports H₂O without a statement as to whether it represents total water or water above 100°.

These analyses of minerals of the leverrierite group show that there is considerable variation in the quantity of bases in different species and thus suggest easy base exchange among the leverrierite minerals.

Although it is believed that leverrierite is the principal mineral that brings about this natural softening of the water in the area here considered, it is recognized that other hydrated aluminum silicates, such as kaolin, feldspars, and mica, are also capable of exchanging wholly or in part their sodium and potassium for other bases.

An inspection of Plate V shows that the calcium and magnesium have been essentially removed by exchange for sodium by the time the water reaches a depth of 125 feet and in some localities before it reaches 80 feet. The diagrams might convey the impression that the calcium and magnesium are more readily exchanged in the Fort Union rocks than in those of the Lance formation. This may or may not be the case, for this apparent difference may be accounted for by the fact that no analyses of samples of water from wells in the Lance formation between the depths of 30 and 100 feet are at hand.

It is not intended to convey the idea that the hard near-surface ground water is softened by direct downward percolation through a given number of feet of these leverrierite-bearing strata, because most of the deeper soft water has moved laterally through many feet and even miles, and it is impossible to say just how necessary or important this lateral movement may be. But owing to the facts that these reactions between dissolved salts and base-exchange silicates are rapid and that the exchange has been accomplished in all waters beyond a given depth, the conclusion seems justified that ground water will have its calcium and magnesium essentially removed by percolating through relatively few feet of rock containing leverrierite.

It is apparent from Plate V that there are notable differences in the acid radicles in the Lance and Fort Union waters. The most striking feature is that some of the waters contain sulphate and others do not. It is not within the scope of this paper to discuss the acid radicles in these waters. The cause of the elimination of the sulphate, which, on the whole, is less abundant in the waters from the deeper wells, is considered in another paper.³⁹ Bicarbonate and carbonate are usually the most abundant acid radicles, especially in the waters from the deeper wells.

The noteworthy fact that the mineral content of these waters from the Lance and Fort Union formations does not appreciably

³⁹ Renick, B. C., Some geochemical relations of ground water and associated natural gas in the Lance formation, Montana (to be published in Jour. Geology).

increase with increasing depth indicates that the amount of dissolved salts is determined relatively near the surface, and that any subsequent change that the basic radicles suffer is in the nature of an exchange. This exchange is probably not of the nature of an absorption phenomenon but is more likely an ionic exchange, as contended by Gedroiz.⁴⁰

The possibility of the removal of calcium and magnesium by means of a reaction between calcium bicarbonate and magnesium sulphate dissolved in the ground water, with the consequent deposition of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), has been considered, but because of the relatively slight concentrations existing in these waters such a reaction seems improbable. If calcium and magnesium had been removed in this way, the total solids in the deeper waters would be less (calcium and magnesium having been removed), and, as pointed out on page 62, there is no essential difference in the amount of total solids in the shallow and in the deep waters.

The dissolved salts in the upper hard waters are derived from the soluble materials resulting from the decomposition of minerals in the sedimentary beds and also to some extent from soluble salts deposited in the interstices between mineral grains. The distance through which it is necessary for these hard waters to percolate before they are softened depends upon the quantity of leverrierite and related mineral species in the rocks, and these minerals; although distributed throughout the Lance and Fort Union section in this area, are more abundant in some places than in others. It is probable that the distance may also depend somewhat on the character of the material—that is, whether it is rock in place or alluvium—because aggregates of leverrierite swell and go to pieces when wet, and this would happen when the Lance and Fort Union beds are converted into soil and alluvium. The leverrierite might thereby lose its effectiveness by being disintegrated and decomposed when the Lance and Fort Union beds are converted into alluvium, while that in the Lance and Fort Union beds would be prevented from being disintegrated when wet by the containing walls formed by adjacent mineral grains.

The rate of erosion would, no doubt, be another factor influencing the depth necessary for softening. Where the land was being rapidly degraded it would probably not be necessary for the water to pass through as great a distance as in a region where degradation was relatively slow, for in the region of rapid erosion the base-exchange material would be removed at a rate somewhat proportional to the rate at which its property to exchange alkali for alkaline-earth bases was exhausted, whereas in the region of rela-

⁴⁰ Gedroiz, K. K., op. cit., p. 26 (U. S. Dept. Agr. translation, p. 19).

tively slow erosion there would accumulate a considerable thickness of rock *débris* whose base-exchange material had exhausted its property to exchange alkali for alkaline-earth bases, and under these conditions unsoftened water would be encountered at a somewhat greater depth. In this connection it is interesting to note that Way (see p. 64) long ago found that the deeper clays which had not been exposed to weathering were the most effective in producing base exchanges.

Other factors that affect the depth requisite for softening include the structure of the rocks, which would influence the rate of lateral flow underground, and the texture and porosity of the strata, which would influence the rate of downward and lateral percolation.

The discussion of the origin of the soft waters given in this paper is based entirely on data obtained from the Lance (Tertiary?) and Fort Union (Tertiary) formations. It seems very probable that this exchange of bases has also taken place in the underlying Upper Cretaceous beds in this region, but complete data to establish this point are not yet available.

Soft sodium bicarbonate or carbonate and sodium sulphate waters at depths comparable to those of the waters described above are known to occur at many places in the United States, but their origin and their depth relations have not been explained. It is likely that they originated in much the same way as the soft waters in the Lance and Fort Union formations in central Montana and that the natural softening was effected by some mineral having base-exchange properties, not necessarily of the leverrierite group but very probably closely related to it.

SUMMARY.

Studies of ground water in an area of Lance (Tertiary?) and Fort Union (Tertiary) formations in east-central Montana, in the Great Plains province, show that near the surface the water is relatively high in calcium and magnesium, which, with increasing depth, are exchanged for sodium (and potassium?), the result being a natural softening. The minerals of the leverrierite group, which are plentiful though disseminated in these formations and are believed to be derived from the decomposition in place of the glassy constituents of rock fragments, are considered the principal agents in effecting this exchange of bases, though the exchange may be aided by such minerals as kaolinite, feldspar, and mica, which are also present in these rocks. This exchange of bases is accomplished by the time a depth of 125 feet or less is reached. There is no tendency for the water to acquire more dissolved material with increasing depth. The amount of total dissolved solids is therefore determined relatively near the surface.

In this paper the discussion of base exchange by silicates is confined to reactions involving the alkalies and alkaline earths, but similar exchange reactions take place between the most resistant mineral silicates and the bases of salt solutions of the heavy metals. Perhaps the data presented will be of assistance in estimating the number of feet through which it is necessary for ground water carrying salts of the heavy metals in solution to percolate under natural conditions in order to deposit the bases of the metals by exchange with the bases of silicates.

