

1) COLORADO

3) 4)
Bulletin 277

May, 1922

2)
The Agricultural Experiment Station
OF THE
Colorado Agricultural College

FIXATION OF NITROGEN
IN COLORADO SOILS

OCCURRENCE OF
NITRATES ON ROCKS

By W. P. HEADDEN



PUBLISHED BY THE EXPERIMENT STATION
FORT COLLINS, COLORADO
1922

The Colorado Agricultural College

FORT COLLINS, COLORADO

THE STATE BOARD OF AGRICULTURE

	Term Expires
HON. H. D. PARKER	Greeley, 1923
MRS. AGNES L. RIDDLE	Denver, 1923
HON. J. C. BELL	Montrose, 1925
HON. E. M. AMMONS	Denver, 1925
HON. W. I. GIFFORD	Hesperus, 1927
HON. J. B. RYAN	Rocky Ford, 1927
HON. A. A. EDWARDS, President of the Board	Fort Collins, 1929
HON. J. S. CALKINS	Westminster, 1929
GOVERNOR OLIVER H. SHOUP	{ Ex-Officio
PRESIDENT CHAS. A. LORY	
L. M. TAYLOR, Secreretary	G. A. WEBB, Treasurer

EXECUTIVE COMMITTEE

E. M. AMMONS	A. A. EDWARDS, Chairman	H. D. PARKER
--------------	-------------------------	--------------

OFFICERS OF THE EXPERIMENT STATION

CHAS. A. LORY, M.S., LL.D., D.Sc.	President
C. P. GILLETTE, M.S., D.Sc.	Director
LD CRAIN, B.M.E., M.M.E.	Vice-Director
L. M. TAYLOR	Secretary
ANNA T. BAKER	Executive Clerk

STATION STAFF

Agricultural Division

C. P. GILLETTE, M.S., D.Sc.	Director	Entomologist
W. P. HEADDEN, A.M., Ph.D., D.Sc.		Chemist
G. H. GLOVER, M.S., D.V.M.		Veterinarian
W. G. SACKETT, Ph. D.		Bacteriologist
ALVIN KEZER, A.M.		Agronomist
G. E. MORTON, B.S.A., M.S.		Animal Husbandman
E. P. SANDSTEN, M.S., Ph.D.		Horticulturist
B. O. LONGYEAR, B.S.		Forestry Investigations
I. E. NEWSOM, B.S., D.V.S.		Veterinary Pathologist
A. K. PEITERTSEN, B.S., M.S., Ph.D.		Botanist
R. E. TRIMBLE, B.S.	Assistant in Irrigation Investigations	
EARL DOUGLASS, M.S.	Assistant in Chemistry	
P. K. BLINN, B.S., Rocky Ford	Alfalfa Investigations	
MIRIAM A. PALMER, M.A.	Delineator	
J. W. ADAMS, B.S., Cheyenne Wells	Assistant in Agronomy, Dry Farming	
RALPH L. PARSHALL, B.S., U. S. Irrigation Engineer	Irrigation Investigation	
CHARLES R. JONES, B.S., M.S.	Assistant in Entomology	
GEORGE M. LIST, B.S.	Assistant in Entomology	
CARL ROHWER, B.S., C.E.	Assistant in Irrigation Investigations	
CHAS. I. BRAY, B.S.A., M.S.	Assistant to Animal Husbandman	
EA J. MAYNARD, B.S.A., M.S.	Specialist in Animal Investigations	
W. L. BURNETT	Rodent Investigations	
FLOYD CROSS, D.V.M.	Assistant Veterinary Pathologist	
WM. H. FELDMAN, D.V.M.	Assistant Veterinary Pathologist	
N. E. GOLDTHWAITE, Ph.D.	Home Economics Investigations	
CAROLINE PRESTON	Artist	
J. H. NEWTON, B.S.	Assistant Entomologist	
J. L. HOERNER, B.S.	Assistant in Entomology	
J. W. TORISKA, P.S., M.A.	Assistant in Chemistry	
C. E. VAIL, B.S., M.A.	Assistant in Chemistry	
C. D. LEARN, B.S., M.A.	Assistant in Botany	
DAVID W. ROBERTSON, B.S., M.S.	Assistant in Agronomy	
LEON R. QUINLAN, B.S.	Assistant in High Altitude Horticulture	
I. G. KINGHORN	Editor	
B. MILDRED BROWN, B.S.	Assistant in Bacteriology	
C. M. TOMPKINS, B.S.	Assistant in Horticulture	

Engineering Division

LD CRAIN, B.M.E., M.M.E., Chairman	Vice-Director
E. B. HOUSE, B.S. (E.E.) M.S.	Civil and Irrigation Engineering
O. V. ADAMS, B.S.	Testing Engineering
G. A. CUMMINGS, B.S.	Assistant in Mechanical Engineering

OCCURRENCE OF NITRATES ON ROCKS

By William P. Headden.

This bulletin is an extension of the subject presented under the general project, "The Study of the Occurrence of Nitrates in Our Soils". Two phases of the question have been presented in the soil studies; First, The fact of the occurrence of large quantities of nitrates in certain soils up to a maximum of 14.0 per cent of the air-dried soil; Second, The source of the nitrogen contained in these nitrates, which is attributed to the nitrogen-fixing flora of the soil. In the present bulletin I shall attempt to present the same questions as they apply to rock surfaces, and for this reason I retain the general title, Fixation of Nitrogen in Colorado Soils, as I consider the Occurrence of Nitrates on Rocks as only a special case.

OCCURRENCE AND DISTRIBUTION OF NITRATES

The occurrence of nitrates in cavities in the surface of rocks, in caves and in crevices in rocks forming veinlets, all near or at the surface, has been known for a long time and many records of it made; yet almost nothing satisfactory is to be found relative to this subject. The most satisfactory information that I have found has been gathered by Mr. Hoyt S. Gale and recorded in U. S. Geol. Sur. Bul. 523. There are older statements relative to such occurrences in many places,—India, Ceylon, Spain and elsewhere,—but the information conveyed is very small indeed and consequently altogether unsatisfactory.

Nitre, including potassic, sodic, calcic, magnesian and other nitrates, occurring in surface soils and on rocks, has been noted from Alabama, Arizona, Arkansas, Georgia, Indiana, Illinois, Idaho, Kentucky, Missouri, Nevada, California, Colorado, New Mexico, Oregon, Utah, Texas, Tennessee, West Virginia, Virginia, Wyoming, Montana and British Columbia.

These occurrences, while prevalent in limestone caves, are not confined to any particular class of rocks. They may occur in sedimentary or eruptive, and are present on metamorphic rocks. The base combined with the nitric acid may be wholly or largely determined by the character of the rock with which the nitrate is associated. If we have an eruptive, rich in potash, the nitrate associated with it will probably be wholly or largely potassic nitrate. If in a soil carrying large quantities of calcic or sodic carbonate, the corresponding nitrate will probably be found present.

In former publications concerning the occurrence of nitrates in Colorado soils, we have been compelled by

analytical results to assume the presence of calcic, magnesian, and sodic nitrates and have considered it purely a matter of convenience as to which base was used, the important fact being the presence of nitric acid. In some instances one or another of these bases was present in such large percentage that it was necessary to combine it with nitric acid. It seems rarely the case that a single nitrate is present to the exclusion of others. They are usually mixed, but the statement of an analysis is usually only a convenient manner of expression and not in every case a faithful representation of the composition of the material analyzed—a fact which I think is universally understood and accepted.

NITRATES THAT OCCUR IN OUR SOILS

It is to be expected that the nitrates found in Colorado should be those of calcium, magnesium, and sodium. The general conditions are plain. Our soils are made up largely of the disintegration products of mica schists, gneisses, and granites. Many of our sandstones even show fragments of feldspar and flakes of mica. The first line of decomposition products of these is calcic, magnesian, and sodic carbonates. The potash appears more slowly, always in smaller quantities, and usually in forms insoluble in water. Our soils are rich in the so-called alkalis, simply because the products of this first phase of weathering have not been removed. These alkalis consist largely of sulfates at the present time, usually mixed with a little sodic carbonate, in a few instances consisting largely of sodic carbonate, but the rule is to find a mixture of calcic, magnesian, and sodic sulfates. Under these conditions it would be surprising if our soils did not carry liberal proportions of calcic carbonate and our rocks frequently be incrustated with it, which is the case.

These are the bases existing everywhere in more than sufficient quantities to unite with any nitric acid that may be formed and these are the nitrates that should be found in our rocks and in our soils, which is in harmony with the fact.

MAGNESIC NITRATE ABUNDANT

I have no desire to pass over in this, or any other connection, some difficulties of minor importance; for instance, why should we, as in fact we do, find magnesian nitrate very predominant in some instances and not in others? This particular question does not appertain to the nitrate alone; it is quite as pertinent to the sulfate as to the nitrate. If the particular soil in which these magnesium compounds occur more largely than elsewhere were actually richer in magnesian carbonate, for instance, than the others, one could explain it, perhaps justly, by such a fact, but, so far as I know, such a fact, however convenient it might be, does not exist. Still

we have ground-waters and alkalies, as well as soil-extracts, that are strikingly rich in magnesium salts. Sulfates and nitrates are here had in view.

This peculiarity in the composition of certain ground-waters, alkalies, and soil-extracts is mentioned to show that we are neither ignorant of it nor wish in any way to evade it. We are, however, concerned with the occurrence of the nitric acid, and in a lesser measure only with the bases with which it is combined. If any real difficulty exists in explaining why we find magnesian nitrate in one place and calcic nitrate in another, it does not affect the general statement that the nitrates to be expected in our soils and on our rocks are the calcic, magnesian, and sodic nitrates, just as we would have reason to expect to find the corresponding sulfates in our alkalies, even if we did not know that these salts make up the great bulk of them.

ORIGIN OF THE NITRATES.

There is apparently a certain unanimity of opinion regarding the origin of the nitric acid in these nitrates, to wit: The oxidation of organic nitrogen which formerly existed, as some assert, predominantly in the excrements and remains of various living beings, using this term in its common acceptance not including micro-organisms. The fact that nitrates are frequently found in caves associated with bat droppings has led to the assumption of this source for many of the occurrences.

In this connection I may cite Mr. Hoyt S. Gale, who formulates this view clearly in U. S. Geol. Sur. Bul. 523, p. 30, where he says, "No generally accepted or satisfactory explanation for the origin of the South American nitrates appears yet to have been found." On page 35 he says, regarding reported occurrences of these salts, "The frequently reported deposits of nitrate salts in caves or overhanging ledges in this country as well as elsewhere probably constitutes a well-defined type. Field observations have led the writer to the belief that a considerable number, probably a majority of such deposits, are derived from the decomposition of bat or similar guano. It happens that these nest-building animals select for their habitation, sites favorable to the accumulation and preservation of the soluble nitrate salts."

If the nitrate should be found under a ledge of rock, it is assumed that it may have been the lodging place of insects or the nesting place of birds. We further know that certain animals have dunging places; mountain rats, for instance, often have. The material from such places has been brought to me quite frequently under the impression that it was a mineral of some value. This habit of animals has been

appealed to to account for the formation of nitrates on a large scale.

It is certain that caves are frequently occupied by large numbers of bats and that cave earth may be rich in nitrates due to their droppings, but to extend this excremental theory to almost all the occurrences of nitrates is laying a heavy burden on it. I have referred to the fact that mountain rats have dunging places, and I know of a cave that was, some years ago, the abode of large numbers of these animals, and any nitrates found in the earth of that cave might justly be associated with its occupancy by these animals, but to apply this explanation to the origin of nitrates found in other caves in the mountains of that section would be wholly gratuitous. It would be simply extending an explanation probably applicable in one case to others because we thought that we had no better one to apply.

EXCREMENTAL THEORY NOT SATISFACTORY

Even in this and in similar cases, it is by no means proved that the animal droppings are the exclusive source of the nitrogen in the nitrates. The occurrences of nitrates are very widely distributed, not only in caves but in the surface portions of land and of rocks. The ordinary occurrence of nitrates in soils up to 8 p. p. m., or even a little more, is not considered in this statement. Such occurrence is universal and its origin is considered as satisfactorily accounted for by the presence of organic matter in the form of plant residues, etc. The fact that such quantities are so good as always present is accepted without any question in regard to its origin, simply because it is always so. The case is different, however, when this quantity increases locally by a hundred fold and exterminates vegetation. The same is even more striking when a surface rock is found to carry nitric acid equivalent to more than two thousand pounds of sodic nitrate to each million pounds of rock. The latter statement is a simple, demonstrated fact, and not one made for illustrative purposes. In these cases we naturally seek for some satisfying, if not demonstrable reason. The surface of a perpendicular rock face or even a bare, horizontal one is not readily accepted as impregnated with plant residues in sufficient quantities to furnish the nitrogen found, nor can one find any satisfaction in the theory that it has been furnished by excrementitious material.

FUMAROLIC GASES NOT SATISFACTORY

In the case of certain rocks, volcanic gases, among them ammonia, have been suggested as possible sources of the nitrogen. The rocks in or on which nitrates are found are not by any means all of igneous origin, nor are they of such recent geological date that one can well conceive of either

the ammonia, ammonium salts or even nitrates having endured from the time when these rocks were young. Besides there are no reasons, except the desire to furnish an explanation for the presence of the nitrates, for assuming the action of fumarolic gases, even in the case of igneous rocks, for instance our rhyolites.

Concerning certain shales, one correspondent suggests that the nitrates may be connate. The suggestion was made sincerely enough, but with no appreciation of the conditions which such an assumption would presuppose.

There are a few outstanding facts in connection with the occurrence of nitrates.

1. These salts are not primary components of any rocks.
2. Their distribution is very wide, but confined in humid countries to protected places, and always to the surface of either soils or rocks. Their solubility is assumed as known to everyone.
3. They are always present in small quantities in fertile soils.
4. They are almost universally present in the surface of rocks.

NITRATES UNIFORMLY PRESENT ON ROCK SURFACES

This latter fact has heretofore been wholly overlooked. I do not know how this might appear if the tests were made in the field in a country with a humid climate, but in Colorado and in Montana the application of a solution of diphenylamine in sulfuric acid will quite uniformly give the blue color due to nitric acid. This statement applies to limestones, sandstones, and gneisses. The few specimens that I have had from Nevada, apparently of a decomposed rhyolite, give this reaction strongly. Also two pieces of rhyolite, labelled Caldwell, Idaho, which I am sure came from Succor Creek, Oregon, and samples which I gathered myself in the canyon of Succor Creek gave this reaction, even samples which were not gathered as samples carrying nitrates. It is much more difficult to obtain a negative result by applying this test to exposed surfaces of sandstones, limestones or gneisses outcropping in the foothills west of Fort Collins, than it is to obtain positive results,—I would say 10 to 1, including all varieties, white, gray, red, etc. Some of the sandstones, mostly shades of red, with an abundant calcareous cement, react very strongly. Unquestionably it will be asked whether organic matter, lichens, mosses, etc., may not give reactions which may be mistaken for that of nitric acid. My observation is that they will not. When they produce any interfer-

ing color it is usually yellow or some off-color not mistakable for the nitric acid reaction. This reaction is positive for practically all of our rocks.

This statement is true only when an old exposed surface is understood. It frequently happens that the interior portions of even small, freshly broken pieces will give no reaction. I have seen this very clearly shown by limestones. In these cases, the reagent could be applied to the freshly exposed surface and allowed to flow across it without coloration till it reached the old exposed edge when it would produce a strongly blue, thin streak, showing that the nitrate existed on the surface only and had not penetrated to any appreciable depth. I have seen the same thing in sandstones, but limestones have furnished the best examples of this. Limestones have not furnished the best samples of nitre-bearing rock but simply the best examples of this reaction. So far as my observation goes, certain sandstones with a calcareous cement have furnished the best samples of nitre-bearing rock, while those with siliceous cements are not usually favorable material.

It is evident that while the excremental origin of nitrates may be true of some caves and of isolated spots, such as the dunging places of mountain rats, it does not apply to perpendicular or even overhanging, smooth, rock surfaces. The very general, almost, if not altogether, universal occurrence of nitrates on such surfaces precludes such an origin.

NITRATES IN RECESSES OR SMALL CAVES IN CLIFFS

No one hesitates to account for the salts, alkalies, found in the small cavities frequently occurring in the face of sandstone cliffs by the washing from the face of the cliffs. The origin of the salts is found in the changes in the constituent minerals or weathering of the rocks. Such deposits frequently carry small, sometimes larger quantities of nitrates. The explanations offered for their presence are either that they have been washed out of the rocks in which they are assumed to have existed as an integral part, or recourse is had to the explanation furnished by the extremes and remains of animals. This theory of animal origin for the nitrogen of these nitrates has been applied as accounting for both small and large deposits of nitrates, those in Chile and Peru, as well as those in caves and cavities in rocks.

ORIGIN OF SOUTH AMERICAN NITRATES

Concerning the source of the nitrogen now forming the nitrates of Chile and Peru, Hilgard, Soils, page 67, says, "The latest and apparently the most reasonable suggestion is that of Kuntze who calls attention to the fact that the vacuynas and llamas which are at home in this portion of the

Andes, and are known to have roamed over that region in countless herds, have the curious habit of always depositing their manure in one and the same place whenever at liberty. Each herd of these animals has its definite dunging place at some convenient point. That such herds have existed in the region from time immemorial is evident from historical as well as collateral evidence, and, as their manure accumulated, its nitrification would progress rapidly under the prevailing arid conditions. The common salt would naturally be derived from the urine and excrements and the alkaline salts which exist throughout the region, as the products of soil decomposition, would be quite sufficient to account for the alkaline bases in the caliche."

Others, while espousing the excremental source of the nitrogen, attribute it to excrements of a little different nature. For instance, R. A. F. Penrose, Jr., *Journal of Geology*, Vol. 18, 1910, p. 16, says, "The discussion of the origin of the nitrates of Chile involves chiefly the source of the nitrogen and many suggestions have been advanced to explain its presence, but its derivation from organic matter, and especially from guano, seems the most probable hypothesis."

In further discussion of this subject by the same author, it is said, "Incidentally it may be stated that in many parts of the world, especially in warm regions, nitrates are found in small deposits in caves, in association with bat guano, and that the source of the nitrogen from this guano is very generally recognized."

A. Muntz and V. Marcano, *Compt. Rend. Acad. Sci.*, Vol. 101, 1885, p. 65, attribute the formation of these nitrates to the action of nitrifying organisms on bat and other excrements. They speak of deposits in various parts of Venezuela, the subordinate ranges of the Cordilleras, the valleys and basins of the Orinoco and the sea coasts of the Antilles. They continue, "These nitre-earths are very abundant in this region where they cover extensive areas. Their composition is very variable, but one finds in all of them calcic carbonate, calcic phosphate, and nitrogenous organic matter. The nitrate always occurs as calcic nitrate."

"These nitrates are especially abundant about caverns, some of which have been described by Al. von Humboldt, and others, which serve as a refuge for birds and bats. The droppings of these animals, as well as their bodies, accumulate in these caverns and form a veritable deposit of guano or bird dung, which overflows and spreads to the surroundings, and which, wherever it comes in contact with calcareous rocks, and the access of the air is sufficient, nitrifies rapidly under the influence of the high temperature of these climates." Again they say, "The nitrification is affected by

micro-organisms." ***Further, they state, "The coexistence of the nitrate and phosphate, upon which we have principally relied for the proof of the animal origin of the nitrate, furnishes a means of judging whether the latter has been formed in place. In fact, if the nitre has been carried away by water and concentrated by evaporation in another place, it is separated from the phosphate that originally accompanied it. We shall apply this fact to the theory of the formation of deposits of nitrate of soda."

This application is made by one of the authors, A. Muntz, *Compt. Rend. Acad. Sci.*, Vol. 101, 1885, p. 1267. On the west coast, the large deposits of nitrates are not accompanied by phosphates, and the author argues that they have been dissolved out of nitrified guanos, gathered in salt marshes, and have been subsequently concentrated by evaporation. This discussion lies beyond the limits of my present purpose, but I shall give his principal argument.

The author points out that the nitrate is associated with salt and the iodate and bromate of soda. These three salts are assumed to be derived from sea water which found its way into the salt marshes. The iodate and bromate of soda occurring in these nitrate beds are the only oxidized compounds of iodine and bromine found in nature. The iodine and bromine exist in sea water as iodides and bromides, but it is held as proven that these salts may be converted into iodates and bromates by the same organisms that convert the nitrogen of organic compounds into nitrates, and further, that this process may go on in sea water.

The association of sodic nitrate and chlorid and the absence of calcic nitrate, which is the first nitrate formed by the oxidation of the guano and which was brought into the marshes in solution, is accounted for by the action of the salt of the marsh water upon this calcic nitrate, whereby sodic nitrate and calcic chlorid was formed. The source of the nitrogen is held to be guano, deposited at some distant place where the phosphate remained.

The object of the above theory is to meet the fact that the big deposits of nitrates are not associated with phosphates, and the phosphates have not been accounted for so far as I know.

FIXATION SOURCE OF NITROGEN IN MOST NITRATE

This excremental theory has been applied to the soil-nitrates only indirectly. These are generally attributed to a vegetable origin. A vegetable origin has also been assigned as the source of the nitrogen now found as nitrates in Chile and Peru.

The variety of sources suggested for the nitrogen of the South American nitrates, the dung of vast herds of animals,

the droppings of birds, guano, great masses of marine vegetation, the concentration of soil nitrates, W. Newton, Soc., Chem. Ind., Vol. 19, 1900, p. 418, the direct oxidation of atmospheric nitrogen by electrical discharge, by the action of ferric hydrate or the carbonates of the alkalies or alkaline earths, and volcanic gases, may indicate how unsatisfactory is our knowledge of this subject. The difficulty lies in accounting for the supply of nitrogen. There is unanimity of opinion in regard to the adequacy of known agencies to effect the conversion of nitrogen, given in either vegetable or animal compounds, into nitrates. This nitrifying action of certain organisms is accepted as universal and adequate to produce all of the nitrates occurring in our lands and even in our great deposits. I have elsewhere, Col. Exp. Sta. Bul., 155, p. 47, suggested that other organisms capable of using atmospheric nitrogen in building up their tissues may be quite adequate to furnish the nitrogen for the nitrifying organisms to convert into nitric acid or nitrates. While the adequacy of these latter organisms to accomplish the conversion of the nitrogen formerly existing as vegetable or animal compounds into the nitrates now found is acknowledged, the adequacy of the other group, consisting of organisms capable of taking their needed nitrogen from the air, is not generally accepted.

EXCREMENTAL THEORY GENERALLY ACCEPTED

I have failed to find any definite statements similar to these just made, but we find the excremental theory of the source of nitrogen constantly put forward or fallen back upon as a final solution of the question. Mr. Hoyt S. Gale, in U. S. Geol. Sur. Bul., 523, p. 13, quotes Dr. Whitman' Cross's* description of the occurrence of potassic nitrate in the Lencite Hills, Wyo., and of sodic nitrate in the breccia forming the Boars' Tusk. In this description Dr. Cross states, "As far as known there is nothing to indicate the derivation of the niter from organic substances of any kind, yet such an origin is either evident or assumed as probable for all other occurrences of natural nitrates of which I find mentioned in manuals of mineralogy." After suggesting several considerations bearing upon the origin of this nitre and describing the occurrences of sodic nitrate at the Boars' Tusk, he continues, "The discovery of soda niter in anything resembling this occurrence has not been announced before, as far as I can ascertain. The similarity in the conditions of occurrence of the two nitrates described above adds to the strength of the hypothesis that both are immediately related in origin to the peculiar magma of this region. Yet it is possible that organic matter from clefts above inhabited by birds or small animals might have furnished the nitrogen for this niter."

Dr. Cross states plainly in the first sentence quoted that there is nothing to indicate that the potassic nitrate found owes its origin to organic substances of any kind. We are evidently justified in assuming that he referred to visible accumulations of organic matter such as he later refers to in the last sentence quoted.

I think that Dr. Cross's attitude represents very fairly that of most persons who have any attitude at all toward the question. He finally admits the possibility of the excremental theory in the case.

Mr. Gale in an article published in the Mining and Scientific Press, of 10, November, 1917, is much more positive in his views in regard to the origin of nitrates. As Mr. Gale has had excellent opportunities for studying the occurrences of nitrates and its literature, his conclusions are of more than usual interest. Mr. Gale, after describing the general manner of obtaining saltpetre in India, continues, "The same thing that is being done artificially in India is going on in many natural accumulations of compost, either manure or general refuse of animal life where animals are herded together. Cave-earths were worked as a source of saltpetre during the Civil War, and at other times in the history of the United States. There is no doubt that the nitrates in the caves originated in an exactly similar way. Caves and cavernous ledges are the natural refuge of all sorts of animal life, including insects, birds, reptiles and many of the larger animals. In these recesses they leave not only excrementa but bits of their food, hair, bones, flesh and even grains mixed in a soil that is often light and porous and may be filled with twigs and dead leaves. This is probably stirred by the coming and going of the cave denizens. Parts of these recesses are often damp with ground-moisture or with wind-blown storm water or mist, and when damp and at the same time warm, they are in an ideal condition to promote the activity of the nitrate-forming bacteria. Thus it is easy to account for the accumulation of saltpetre or nitrate salts in caves or in the cavernous recesses of rock ledges."

Concerning these nitrifying bacteria Mr. Gale states in a preceding paragraph, that they "Are present almost everywhere that the conditions are favorable. They are found in practically all soils and nearly everywhere on the surface of the earth. They have been found on rock masses high in the mountains."

"There are many variations which will lead the prospector to think that his case is different from the type described. For instance, how is one to account for the fact that a test for nitrate may often be obtained in a barren hillslope, in a soil just below the surface layer, especially in certain

puccular clay soils? The explanation, however, is the same as in the more definite cases cited above. Even these apparently barren soils contain much organic matter especially at the surface. Bits of animal refuse and vegetation are sufficient to show fixed nitrogen almost anywhere that a sample may be taken.*** "The foregoing is an adequate explanation for most of the occurrences of nitrate salts that have been reported from many parts of the United States."

These quotations are given because they are the most satisfactorily definite ones that I have found presenting this theory; also to show how firmly the theory seems to be fixed in the literature of the subject and the minds of investigators. I take it that the quotation from Mr. Gale stands for much more than the results of his study of the literature on the subject, as it includes his personal convictions based on observations made on many occurrences of nitrates. The quotation from Dr. Cross shows the influence of this same teaching in the literature, for while his language indicates a doubt as to the actual origin or source of the nitrogen found as nitrate, he is not satisfied that it may not have been furnished by organic matter from clefts inhabited by birds and animals.

EXCREMENTAL THEORY PARTIALLY APPLICABLE

In some cases the most reasonable explanation to account for the nitrates, especially in some caves, is unquestionably the oxidation of the nitrogen contained in bat droppings, just as it would be to assign rat droppings as the origin of the nitrogen in any nitrates that might be found on a ledge of gneiss or granite recently used as a dunging place by mountain rats, but we are not justified in assuming a similar source for all the occurrences that we find wherever they may occur, or even for most of these occurrences. In fact it applies to only a few.

There are two things assumed in this theory that are evident: First, The previous existence of the nitrogen now found as nitrate in the form of organic or ammoniacal nitrogen; Second, The oxidizing agency of certain organisms. These two things, together with the conditions necessary in order that the nitrifying organisms shall carry on their life processes, are undoubtedly the prerequisites for the formation of the nitrates found in soils and on rocks. That some nitrate may be formed in other ways, for instance ammonium nitrate during thunderstorms, is also certain, but these quantities are wholly negligible compared with the quantities with which we have to deal.

*Whitman Cross "Igneous rocks of the Lencite Hills and Pilot Butte, Wyo., Am. Jour. of Sci. 4 Ser., Vol. 4, 1897, pp. 115-144.

OUR APPROACH TO THIS STUDY

We have approached this subject in trying to find a sufficient source of nitrogen for the formation of the nitrates found in our soils in excessive quantities up to 14 per cent of the air-dried soil.

The basal observations were the condition of barrenness, due to the presence of excessive nitrates, and the fact that this condition is not a fixed one but has both a beginning and an end. In other words, it is not a permanent condition but comes and may pass away, though this latter feature of it has taken place too seldom.

The maximum of nitrates found in a surface soil up to the present time is 14 per cent of the air-dried weight of the soil. The area was comparatively small. In three years after this sample was taken the occurrence had almost entirely disappeared. In another instance the amount of nitrate found in a surface soil was 5.6 per cent; this has entirely disappeared. Another sample contained 6.5 per cent. This represented a larger area, probably eight acres, and the bad conditions still existed the last time that I visited that section of the State. Much of the land affected in this way was only a few years, perhaps one or two years, previous to the time of this development, good, productive land, apparently desirable from every standpoint. But in these spots, sometimes acres in extent, the accumulation of the nitrates exceeded the limit of endurance of the plants and the result was disaster.

THE USUAL EXPLANATIONS FOR SOURCES OF NITRATE NOT APPLICABLE

That the nitrates were the cause of this was easily established experimentally. The answer to the question relative to the origin of these nitrates was not evident. On the contrary it was difficult to find a reasonable and sufficient explanation, not for their presence, but of the source whence their nitrogen came. The facts known concerning the history of these lands precluded all of the sources usually suggested in this connection, and yet we had the facts that these lands had changed from fertile to wholly unproductive ones; well established healthy trees and other vegetation were totally destroyed. The land outside of these areas, which was as productive as heretofore, contained no unusual amount of nitrogen or nitrates. These areas contained an excess of both nitrogen and nitrates, but most markedly of nitrogen as nitrates. All of the sources usually suggested for these nitrates were patently irrelevant. There had been no accumulation of plant residues, and none of dung from any source to distinguish these spots from the surrounding land. There was no visible cause. In the case of the first few small

spots that I had to deal with, I tried to attribute it to animal remains, but this cause was wholly unsatisfactory, for I could in no instance establish the former presence of such with any degree of probability, and wholly inadequate as well as contrary to the known facts when these spots began to involve 5 to 40 or more acres. Transportation and concentration will account for veinlets filled with crystallized potassic or sodic nitrate, but not to a half acre spot in the middle of a flat field carrying from 500 to 4,000 parts per million of sodic, calcic or magnesian nitrate. I sought to apply this theory and to account for the spots by solutions rising from below due to hydrostatic pressure, but our ground-waters do not carry nitrates except under conditions exactly the opposite of those that we need to establish this point.

THE ADDITION OF MANURE WITHOUT EFFECT

Manure was in some cases applied in the hope that it would ameliorate the existing condition, but it did neither good nor harm. It did not mitigate the trouble and it did not increase the crops.

This was not a surprising result under the circumstances; it neither removed the nitrates nor added anything that would act promptly enough to meet the situation. It is a well known fact that the formation of nitrates in farmyard manure or compost corresponds to an advanced stage of alteration, so it could do no harm by increasing the nitrates, and there was nothing of a corrective nature present, so it did not mitigate the action of the nitrates already present.

THEORY OF CONCENTRATION FAILS

The theory of concentration apparently gained a little support from the fact that some waters that seeped from beneath mesas along the outcrop of the underlying shales were found to carry nitrates. The explanation offered for this condition was that this water is none other than the water applied to the mesas as irrigation water, returning to the water courses, and had derived its content of nitrate from the surface soils of the mesas which were at that time dotted with nitre-areas. In one of the instances these conditions grew much worse in succeeding years, so bad, in fact, that portions of the mesa became wholly unproductive, corroborating our view in the strongest possible manner.

The preceding statement would have no force whatever if the water applied carried even small amounts of nitrates, but such is not the case. The waters used for irrigation are free from nitrates and whatever nitrates the return waters may carry have been derived from the soil or the underlying rocks through which they have passed. If ours were an old country that had been heavily fertilized for a long series of years and were still being so fertilized, a case might be

made that these nitrates owed their origin to this source as the water supply in our country is inadequate to wash them out except as we add it in irrigating. Our country is not old and it is not our habit to fertilize, or the practice is so limited that it may be disregarded.

CHARACTERISTICS OF NITRE-AREAS

These nitre-areas can usually be recognized with certainty without the aid of chemical tests, especially in an advanced stage of development. There are several criteria by which one may judge. They are the structure of the surface soil and its color. Sometimes the soil has a slight crust and beneath this a loose mass of soil impregnated with crystals of various sorts; sometimes the whole surface of the soil is fluffy, mealy and velvety underfoot; sometimes it has a uniform, shining, dark crust, and sometimes it is simply a dark brown, without a crust. Land corresponding to any of these characteristics, whether it is a perpendicular surface, such as the land-side of a furrow, or a bank, or a flat surface, almost always contain nitrates in very easily detected quantities. There are a few conditions under which this may not be the case; land may be actually moist, due to the presence of calcic chlorid, it may also be dark, due to humus in solution and perhaps to other causes. I have met the former, i. e., the presence of calcic chlorid, more often than the others. The color of humus solutions is darker than the color peculiar to the nitre-spots, and would not often be mistaken for the latter.

When we consider the characteristics of these occurrences, i. e., that we not only failed to find any proof even tending to establish a process of concentration which might account for these spots but have adduced conclusive proof that they have not been produced by such a process, that they are often very limited and sharply defined, that they may contain two, three or even seven thousand parts per million of nitric nitrogen whereas land only twenty feet from the margin of such a spot may contain only from two to ten parts per million, that they appear in land that has been cultivated for five, ten or twenty-five years, or perhaps in virgin soil, that they often increase, coalesce and ultimately occupy areas of many acres in extent and persist for years, or that they may entirely disappear, it is evident that none of the explanations to account for the nitrogen existing as nitrates, either in soil or on rocks is applicable in these cases. These things begin, run their course and disappear and we know that none of the explanations offered applies to them even in a small measure, except one, to wit, the activity of micro-organisms, living agents, which may increase in the intensity of their development, or perish wholly, and

which in their varied forms and associations are everywhere present, ready under favorable conditions to develop vigorously.

THE FIXING POWER OF THESE SOILS

That these soils possess the power of fixing the atmospheric nitrogen is not an assumption, but a repeatedly proven fact. Under field conditions an ordinary soil has been shown to fix 36 parts of nitrogen per million of soil, or to build up 225 pounds of proteid matter in thirty days, while a soil from the edge of one of these nitre spots built up 3,812 pounds in forty days. While the latter experiment was made in the laboratory, no conditions were changed except the temperature. The soil was simply brought to the laboratory and the moisture content brought up to 15.0 per cent by the addition of ammonia-free distilled water and left undisturbed for forty days, when the total proteid matter was found to have increased by the amount stated above, i. e., 3,812 pounds for each millin pounds of soil. This proteid matter was built up from the nitrogen of the atmosphere and added to that which was already present in the soil when the experiment was begun.

At best ordinary plants, insects, birds and beasts contribute no increase to the store of nitrogen; they are simply agents contributing to the cycle of changes through which the nitrogen of the nitrates are converted into proteids to pass back again into nitrates, always with a loss of nitrogen. The excremental theory of the origin of nitrates, including residues of both plants and animals, does not apply to these soils for it is a fact, well known, that no accumulation of this sort has existed at these spots which for years of cultivation have shown no visible differences to distinguish them from the surrounding lands. The soil of these spots pass through a series of changes which do not vary much from a definite order, and ultimately become so enriched in nitrates that all vegetation is exterminated, even the micro-organisms themselves.

No one doubts that Indian saltpetre is derived from the nitrogen carried in the house drains, or that the urine and refuse added to saltpetre plantations is oxidized by micro-organisms to nitric acid, or that these same processes go on in the case of bat dung voided in caves. These are all limited, specific instances of nitrification. It is, however, conceded that the process is universal, not wholly eliminated by extreme cold or by the exclusion of air, but it everywhere requires proteid matter or its decomposition products, ammonia or ammonium salts. This proteid matter is all that is necessary to furnish under our existing conditions to bring about the formation of nitrates. In these soils this proteid matter does not exist as excrementitious material nor as the remains

of the ordinary, living things with which we are acquainted, but is produced by living organisms, some of them microscopic but others not, which either alone or in association with each other are capable of building this proteid matter using partly or wholly the free nitrogen of the atmosphere, or, as it is expressed, of fixing it. This is what happened when the soil from the edge of a nitre-area increased its content of nitrogen by 610 pounds of nitrogen corresponding to 3,812 pounds of proteid matter in 40 days. During these 40 days the other process of breaking down the proteids and converting the nitrogen into nitric acid was going on and that quite vigorously. The nitrogen present as nitric acid increased by 74 pounds in each million pounds of soil in this time. This increase was 120 percent of the quantity present at the beginning. These two processes go on simultaneously and on a scale of sufficient magnitude to account for all of the facts that we have observed.

The minor questions such as: To what extent this accumulation may go before it inhibits itself, The distribution of the products formed, The optimum conditions for fixation and nitrification, and the like, are problems which present themselves for solution in any theory that may attempt to account for the origin of the nitrogen in the nitrates found universally. The only way to escape them is to ignore the source of the nitrogen and assume it as given, which clearly fails to meet all cases, in fact, to meet the cases which are perplexing, such cases as we have observed to begin, grow and disappear, and for which we could not account by assuming the existence of animal remains or excremental material, for we knew that these had not existed in these cases.

CONCENTRATION THEORY INCONSISTENT WITH FACTS

It would be exceedingly difficult to account for these areas on the supposition that the nitrates had previously existed at some other locality and had been transported to these spots. They do not, as a rule, present instances of collecting basins where the nitrates diffused through the soil have been collected and concentrated by the evaporation of the carrying water. We met so many difficulties in trying to harmonize this idea with the facts that we abandoned it. Two statements will suffice to show the force of these difficulties. Underground waters, drain- and well-waters, outside of nitre-areas, do not carry these nitrates. The second statement is akin to the former. Depressions outside of these areas in which water does collect and evaporate to dryness are sometimes entirely free from nitrates, even in sections where nitrates are of common occurrence.

Notwithstanding these considerations, the fact that waters issuing from certain shale beds already referred to

led to the investigation of many waters. We stated that we held the explanation of the presence of nitrates in these waters issuing from the shales to be the fact, that they were really waters issuing from beneath areas already affected by these nitre-spots. The alternative conclusion would be that the shales or other rocks through which these waters found their way contained nitrates that had not been derived from the surface but existed in the rock as an integral part of it.

NITRATES NOT CONTAINED IN MASS OF ROCKS

We attacked this problem in two ways, by the examination of waters from deep wells and from mines. There was little need of examining deep well-waters for the record of water investigations show that it is seldom that such waters contain nitrates. G. S. Rogers in U. S. Geo. Sur. Bul., 653, Chemical Relations of the Oilfield Waters in San Joaquin Valley, Calif., p. 47, says, that nitrates were sought in 27 waters and found present in five waters. Four of these were surface waters. I do not know that he discusses the fifth one at all. It is known that artesian waters seldom carry nitrates but may carry them in small quantities, a few parts per million, up to 11 p. p. m. if I am not mistaken.

It happens that the shales from which one of the nitre-bearing waters mentioned in the preceding paragraph issues is near to a coal mine, but if I recall the stratigraphical relations correctly it is lower than the coal mine by 300 or more feet, but I do not think it is more than 400 feet and is surmounted by a large cultivated mesa, a portion of which is rich in nitre-spots. The coal mine stratum is covered by stratified rocks and an uncultivated mountainous country. The breast of the coal mine is in about 2,700 feet and a stream of water issues near this point. The roof is slate overlaid by sandstone. This water is so good as entirely free from nitrates (0.1 p. p. m.), whereas that from beneath the cultivated area carried 66.0 p. p. m. of nitric nitrogen. A second mine water was examined. This was also a coal mine fourteen or eighteen miles north of the former and in the same geological horizon. This water also issued from the shale and carried no nitric nitrogen (0.3 p. p. m.). Whenever we have had an opportunity to examine waters from deep wells, we have availed ourselves of it and determined the nitric nitrogen in them. I shall give only a few of the results. In one case the water from a well forty feet deep carried 147 p. p. m. of nitric nitrogen, in the adjoining section of land a well 160 feet deep yielded water free from nitrates. In another instance a surface well yielded water carrying 309 p. p. m. nitric nitrogen, and a well 280 feet deep in the same piece of ground, within 50 feet of the former well, yielded water carrying no nitric nitrogen. In a third instance a surface well-

water carried 132 p. p. m., and the water of a 400 foot well, perhaps 450 feet away, carried none. The deepest well, the water of which we have examined for nitric nitrogen, was 700 feet deep and we found none. Perhaps the most striking proof that the nitrates are confined to the surface and do not come from the shale underlying the land is furnished by a case in which the water at a depth of 6 or 7 feet carried approximately 880 grains of sodic nitrate in an imperial gallon, but at the depth of sixteen feet the water issued from the shales and was much richer in total solids but was free from nitrates.

The deep wells examined all penetrate the shales which I suppose furnish the water in every case. The wells were probably cased for a portion of their depth in order to cut off all surface water.

I give these cases to show that our deep well-waters are not exceptions to the rule that such waters are free from nitrates, and hold it as conclusive proof that the rock through which these waters have passed contains no nitrates, whereas surface wells may be very rich in nitrates. The object had in view in giving the surface waters is to show that there is no connection between the presence of nitrates in the surface waters and the underlying rocks, as shown by the waters contained in them. The presence of nitrates in these waters depends wholly upon surface conditions. The deepest well-water in which I have found nitrates is 65 feet, and the deepest issuing seepage water was about 80 feet.

NITRATES OCCUR AT THE SURFACE OF SOILS

Others have called attention to the fact that the occurrence of nitrates is confined to the surface portions, even those of Chile and Peru attain no considerable depth, usually less than 20 feet and rarely more than 25 or 27 feet. Even in this case there is no question but that the origin of the nitrates is a surface one. In fact, of the many descriptions and discussions of the Chilean surface nitrates no author suggests any other than a surface origin, nor do they suggest any relation of the origin to the ground-water. Ralph Abercromby, *Nature*, Vol. 40, 1889, p. 188, says, "The well-water from the center of the Pampa contains too great a proportion of salts to be considered drinkable, and that from the western margin of the plain and not from the niter beds belongs to the Calcareous-Magnesian class which is totally unfit for domestic or culinary purposes. The following examples will make this very clear and also the further remarkable fact **that the underground waters of the Pampa do not contain the slightest trace of either nitrate of soda or of iodine.**"

In soils, the very surface is usually the richest, provided that rains or the application or irrigating water has not removed them. I have collected many samples of soil and I

can now recall but one instance in which the nitrates proved to have been moved downward so that the second foot was richer in nitrates than the top or first foot. This would, of course, not be the case in a humid climate. The seasonal movement of the nitrates in the soil will evidently depend upon the soil and the amount of water received, either in the form of irrigations or as rain-fall.

NITRATES OCCUR IN SURFACE PORTIONS OF ROCKS

These facts pertain to the rock surfaces just as they apply to the soils. It is well known that all cultivated soils contain small amounts of nitrates. It is also true that the surface portions of rocks contain small amounts of these salts, not simply the underside of a ledge but the face of the rock, provided it is not exposed too directly to the weather and washing by rain storms.

I have previously stated that a sulfuric acid solution of diphenylamine applied to rocks, especially those in place, will give a very large percentage of positive results, showing the presence of nitric acid. I have applied this test to limestones, sandstones, granites, gneisses and rhyolites. Certain light red sandstones have given the most striking results, but all of these classes of rocks have usually given clear indications of the presence of nitrates. We have stated that these nitrates do not belong to the rocks. This is an accepted fact, but I have presented the absence of nitrates from deep wells as a proof of this. Nitrates are unquestionably present on and, if the surface portions of the rocks is not compact, as the limestones usually are, but open, like sandstones with more or less porous cementing material, it permeates them to a slight depth. The superficial character of these occurrences would seem almost self-evident. I have, however, tried to obtain samples from the surface and interior of rocks to show that while the one carries nitrates, the other does not, or carries them in much smaller quantities. It has proved a difficult matter to obtain satisfactory samples for this purpose, because there is no active stone quarry in our section at the present time. This industry, at one time quite a flourishing one in this section, is dead. The only quarrying that I have known of in this section in the last twenty years is that of limestone for use in the sugar factories. Limestone is by no means a desirable substance for this experiment and reacts with sulfuric acid and diphenylamine, so clearly, showing the presence of nitric acid on the exposed surface, and is absent in the interior, that to make other tests would scarcely be free from the charge of choosing material that we have good reason to believe would give favorable results. While it is legitimate to use the knowledge of this fact, it is scarcely legitimate investigation to make ex-

periments whose results are foreknown. The interior of a comparatively small piece of a compact limestone will give no reaction for nitric acid, while the old, weathered exterior surface usually reacts with satisfactory intensity.

Almost any piece of compact limestone with an old, weather surface on it will show this reaction. With granular limestones, this probably is not the case. I have examined but one granular limestone and this was very rich in nitric nitrogen, 270 p. p. m. This sample was sent to me from Montana by Professor Edmund Burke. We have found it so good as impossible to obtain satisfactory rock material to demonstrate this point, i. e., to obtain a series of rock samples to show that the exterior portions of the rocks alone contain nitrates and that they penetrate even fairly porous rocks only to very moderate depths. It has not been feasible for us to open up ledges for this purpose, which it would have been necessary for us to do. Handicapped in this particular, as we have found ourselves, we have been compelled to use such samples as we could obtain by breaking larger rocks into pieces. This is the reason that our samples to demonstrate this point are not so satisfactory as I could wish.

The following samples were gathered at a point about 250 or 300 feet above the neighboring valley. The shales at this point are overlaid by a series of sandstones. The cliffs are so steep that we could not scale them. We obtained two samples of sandstones above the shale, surface samples only; one contained 2.0 and the other 48.0 p. p. m. of nitric nitrogen. Loose material gathered at the base of the shale carried 8.0 p. p. m., and alkali gathered from sandstone below the shale carried 64.0 p. p. m. of nitric nitrogen. A tunnel was being driven into this shale and we were able to get a sample of freshly broken material about fifty feet under cover. This carried 0.017 p. p. m. of nitric nitrogen. The water that issued from this shale at about 2,000 feet from the entrance of an old tunnel carried 0.1 p. p. m. of nitric nitrogen as it was delivered to the people in the valley for domestic use. Another pair of samples obtained from a sandstone ledge, broken out as best we could with pick and sledge, gave for the exterior portion total nitrogen 367.0 p. p. m., nitric nitrogen 3.2 p. p. m. The interior portion gave for total nitrogen 262.0, and for nitric nitrogen 1.5 p. p. m. Another pair of samples obtained in the same manner gave for the exterior samples total nitrogen 110.0 p. p. m., nitric nitrogen 6.0 p. p. m.; the interior sample, two inches deeper, gave total nitrogen 100.0 p. p. m. and nitric nitrogen 1.0 p. p. m. A pair of rhyolite samples were collected at Del Norte. These samples were the best that we could collect with the means that we had for taking them, but were altogether unsatisfactory to us at the time. The surface sample

contained total nitrogen 375.0 p. p. m. and nitric nitrogen 12.5 p. p. m. A sample broken from a recently made opening 18 inches below the surface contained total nitrogen 107.0 p. p. m. and nitric nitrogen 8.5 p. p. m.

These pairs of samples are from widely separated localities, but they agree in showing that both the total and nitric nitrogen content fall very rapidly as we penetrate the rock. Only one of the samples can be claimed to fully represent the interior of the respective rock masses, i. e., the sample of shale broken fifty feet from the entrance of the tunnel that was just being driven. This sample carried 0.017 p. p. m. of nitric nitrogen. The other samples were all relatively near the surface, and yet we find in the case of a fairly compact sandstone a falling off in the amount of nitric nitrogen present from 6 p. p. m. to 1.0 p. p. m. in the second two inches of rock. This pair of samples was taken in the vicinity of Fort Collins. Another pair of samples was taken in a different manner, one being taken from the face of a stratum just as it has been weathered, the other being broken out of a big block of rock where the same stratum had been opened as a quarry twenty years or more ago. The two points are close together. The sample from the face of the bluff carried total nitrogen 310.3 p. p. m., nitric nitrogen 233.8 p. p. m.; that broken out of the rock in the old quarry carried total nitrogen 100.0 p. p. m., nitric nitrogen 1.0 p. p. m. Samples broken from the face of another outcropping stratum carried even more nitric nitrogen, viz. 395 and 590 p. p. m.

These samples are from the same locality. These strata dip quite strongly at the point of outcrop. The only water that can reach these rocks is storm-water. Our rainfall is less than 15 inches, so the amount of washing is very moderate. I do not know the average moisture content of these rocks; at times it must be quite low near the surface, especially where exposed to direct sunshine, but where protected I imagine that it is not especially low.

While these results are not wholly satisfactory, because of the difficulty in obtaining entirely competent samples, there is no question but that the surface portion of rocks contain both organic and nitric nitrogen often in very significant quantities, while in the deeper portions, even at the moderate depth of two inches in a fairly compact sandstone, both classes of nitrogen compounds fall off rapidly. In the last case cited the total nitrogen in the sample from the face of the outcrop was 310.3 p. p. m. and in the second two inches of a large block that had been broken some years before for commercial stone, it was only 100 p. p. m., and the nitric nitrogen fell from 233 to 1.0 p. p. m. In the first case given the exterior portion of the sandstone above the shale

carried 48.0 p. p. m. nitric nitrogen, and the shale fifty feet from the surface carried only 0.017 p. p. m., and the water issuing from it carried 0.1 p. p. m. as delivered for domestic uses.

I hold that the existence of nitrogen in the surface portions of rocks in much larger quantities than in those lying only a little deeper is demonstrated; also that nitrogen in the form of nitrates occurs generally and often abundantly in the surface portions of rocks, but is absent from the interior portions.

NITRATES ON SURFACE OF ROCKS IS GENERAL

I have stated that diphenylamine in sulfuric acid gives the reaction for nitrates in almost every case when applied to the weathered surface of a rock, which is not the case when applied to the surface of a freshly broken rock representing an interior portion. This reaction for nitrates is given by all rocks to which we have applied the test; some rocks give the test more strongly than others, but they all give it, indicating that the nitrates are nearly always present on the surface of rocks.

It is practically universal under our conditions. A few instances follow. The samples are from different localities and represent the general conditions existing on the rocks, in other words, they may be duplicated by samples from any locality.

Nitric Nitrogen in Surface Portions of Rocks		
Rock	State	Nitric Nitrogen Parts per Million
Sandstone	Colorado	334.6
Sandstone	Colorado	395.0
Sandstone	Colorado	590.0
Sandstone	Colorado	73.0
Sandstone	Colorado	9.8
Sandstone	Colorado	233.8
Sandstone	Colorado	2.0
Sandstone	Colorado	12.0
Rhyolite	Montana	29.4
Gneiss	Montana	5.6
Gneiss	Montana	11.2
Sandstone	Montana	6.8
Sandstone	Montana	40.6
Sandstone	Montana	39.2
Sandstone	Montana	281.4
Sandstone	Montana	9.8
Limestone	Montana	9.3
Limestone	Montana	4.2
Limestone	Montana	270.0

These are general surface samples such as can be obtained on any exposed rock surface. These samples were gathered from steeply inclined or vertical faces with one exception, that of the rhyolite, which was from the strongly weathered upper surface of a mass of this rock. I had the excremental theory in mind when collecting these samples, and while its applicability in the case of caves where bats or other animals void their excrements so that there is an accumulation of them, may be accepted as partly true and certainly convenient, it is extending the application too far

if we apply it to the face of whole mountains and perpendicular cliffs, where we have no observable justification for assuming it to apply. It cannot be justly claimed that a sufficient amount of excrementitious matter can accumulate to account for the universal occurrence of nitrates on the surface of rocks and in the positions that we find them. To make such an assumption is simply finding an explanation for an unexplained fact by analogy in default of knowledge concerning it.

EXCREMENTAL THEORY NOT APPLICABLE TO ROCKS

When the small return in the form of nitrates from excrementitious matter, even under artificially produced and favorable conditions is considered, and also the further facts, which the compost heap teaches us, i. e., that there are losses and that nitrification occurs only as a late phase of the changes, the amount of excrementitious matter required to produce the quantities of nitrates found universally diffused, one cannot believe that the necessary quantity exist as a fact. In the case of the soils, we know that the facts in the case preclude the theory of excrementitious matter, and also any assumption of a previous accumulation of animal remains. I was forced by the large areas involved, by the rapidity of the increase in the size of the areas, and by the rapid increase in the quantity of nitrates present in the areas in question, also by my failure to find a single small occurrence for which I could find any proof, that it owed its origin to either animal excrements or remains, to abandon any such theory and was compelled to seek a more general cause, one both adequate and continuously active. I find myself in the same position in regard to the occurrence of nitrates on the rocks.

The following are the facts in the case: The nitrates are not permanent, original, and integral constituents of rocks, but exposed, weathered rock faces contain nitrates in determinable quantities; surface rocks sometimes contain them in large quantities. We have found of these nitrates, calculated as sodic nitrate, as much as 0.35 per cent of the weight of the rock. The occurrence in the surface portions is not confined to any certain class of rocks, but is universal. The excremental theory of the origin of these nitrates is not applicable to such a general occurrence. The excrements are assumed to be the source of nitrogen found in the nitrates, and it is in this sense that they are considered the source of the nitrates. The question is really to account for the nitrogenous matter which the nitrifying organisms require for the production of nitrates. These organisms are supposed to be universally present in sufficient numbers to account for all of the nitrates found, if only they are furnished with the nitrogenous material without regard to whence it came, from

excrements, dead bodies, vegetable or animal, or ammoniac salts from volcanic exhalations. They are ubiquitous, sufficient in numbers and can adapt themselves to very wide ranges of temperature; such is our common belief concerning these organisms. It is also true that there are insects and animals everywhere, but the conception of their numbers and distribution is a wholly different one from that of the numbers and distribution of these micro-organisms. We can only imagine the numbers of insects, reptiles, birds and animals as distributed everywhere and in sufficient numbers to furnish droppings and dead bodies as the nitrogenous material from which these nitrates are formed. There is no question but that such residues fall a prey to micro-organisms wherever they may be dropped, and that a part of their nitrogen is changed into nitrates. The total of droppings and dead bodies necessary to meet the requirements of the facts pertaining to the occurrence of nitrates would be exceedingly great and the supply a continuous one. We have no knowledge of any such conditions as actually existing. Such considerations led us in the case of the soils to seek for a more generally diffused, continuously acting, and yet sufficient production of nitrogenous material to account for the nitrates.

NITRATES IN WALLS, ETC.

The facts relative to the occurrence of calcic nitrate in the walls of stables, especially in the mortar of such walls, has been known for a very long time. I am not conversant enough with the history of this subject to know when mention was first made of this. The explanation was found in the oxidation of the ammonia present in the atmosphere of the stable arising from the decomposition of urine and other excrementitious matter present in such places. This is probably a correct explanation, at least in the main, for the formation of this particular occurrence. It, at least, is a cause easily apprehended as being the actual one in this case, and it can be accepted as sufficient to account for all of the nitrate found under such conditions. Old mortar or limy material from old buildings is recognized as good fertilizing material, not only for its lime content but also because of its nitrogen content. In this case, too, it is possible that the ammonia of the atmosphere may play a part, but it is not evident that this is the case, nor that it alone is sufficient to account for the facts.

The amount of ammonia salts present in the atmosphere even of cities is not very great, scarcely enough to play a part in impregnating old mortar with nitrates. There is, it is true, an abundance of calcic carbonate and hydrate to furnish an alkaline medium, which has been suggested, even as an oxidant for the nitrogen of the atmosphere. Both processes may take place in this old mortar, nitrification of

ammonia salts and direct oxidation of nitrogen under the joint action of the carbonate and oxid of calcium. I do not know that either of these processes has been established by experiment, nor do I know that either has been disproved. It is not difficult to conceive that the plastering of an old building occupied for many years should have absorbed a great quantity of ammoniac salts directly from the atmosphere, and also much other organic matter, enough perhaps to account for all of the nitrates that may have ever been found in old plaster or other limy material of such buildings. It may be accepted that these patent sources of nitrogen are sufficient to account for the nitrate present on the walls of stables and in old mortar or other limy debris of old houses, but not in the free walls of rock cliffs or the outside walls of brick or stone of modern buildings.

I have stated that the application of a solution of diphenylamine in sulfuric acid will show, practically always, the presence of nitrates in the surface of rocks of all sorts. The same is true of rocks and bricks in buildings. I have applied this test a number of times, but only to a comparatively few buildings. The building in which the chemical section of the Experiment Station is now quartered was constructed twenty-three years ago. The stone of which it is built was quarried in the neighboring foothills. It is perfectly safe to assume that the large pieces used in the construction of the porch were broken from solid interior rock at the quarry and were poor in total nitrogen and free from nitric nitrogen. The exterior portion of these rocks is now very rich in nitric nitrogen. The Mechanical Engineering laboratory was constructed twenty-two or twenty-three years ago. The foundation of this building is also a local stone. The same assumptions regarding the presence of nitric nitrogen in these rocks are justified and for the same reasons, namely, they were freshly dressed rocks and were from the interior of the ledge. A sample chipped from this foundation 12" to 18" from the groundline is now rich in nitric nitrogen.

Objection might be urged that the front porch of a chemical building was not a proper place to collect a sample for the purpose had in view. The objection in this case has no force, but it cannot in any way be urged against the Mechanical Engineering Laboratory where we took the sample on the north side, at a point where the protection from accidents is as great as we can in any case obtain. This sample reacted strongly for nitric acid. A second sample was taken from the west side of the porch of the chemical building. This sample was taken because I succeeded in breaking out a piece of the stone varying from $1\frac{3}{4}$ to over $2\frac{1}{2}$ inches in thickness. The exterior portion of this piece

reacted strongly for nitric acid. I found on trial that I could rasp this stone quite easily, so I removed from $1/32$ to $1/16$ of an inch from the exposed weathered portion of the piece to see whether this would cause a diminution in the amount of nitric nitrogen present, which it did. I realize that it is not proven that this sample is identical, even in its outer portions, with the sample taken to represent the outer portion of this rock in general, but the outer portion of this piece reacts strongly for nitric acid and the stone from which the sample was broken lies next to the others from which smaller fragments were broken and included in the general sample; hence I do not see that I am making any unjustified assumption in considering this sample as fairly representative of the rock in the porch taken to this depth, with the exterior, weathered portion rasped off. Another sample was made by rasping the outside portions of several rocks.

THE PART PLAYED BY MOISTURE

The importance of a good and constant moisture supply in the fixation of nitrogen and development of these nitrates has been insisted upon throughout the discussion of it, not as a matter of theory but simply as an observed fact. This relation of moisture was so evident that it could not escape observation. I recall stating that the outside of a ditch bank, irrigation ditch or canal, was a favorable place for the development of the brown color and of the nitrates because of the constancy and abundance of the moisture. For a like reason the base of a wall, especially on the north side of a building, our porch for instance, presents a favorable condition for this development. The total effect of this moisture is very frequently most clearly shown near the base of brick walls where an undulating line, often marked by the presence of a slight efflorescence, marks its effect. The brick, some or all of them in this zone, often show the weathering effects of these conditions. The general impression is that this is the effect of our alkalies. For our present purpose there is no need of considering the action of our alkalies in either brick or stone, for many of our sandstone foundations show the same tendency to decomposition. The simple fact is as stated, viz., that there is a zone at the foot of brick walls in which the brick, especially in old walls, shows various degrees of decomposition. The same is true of sandstone foundations.

NITRATES IN DECOMPOSED BRICKS

The brick in older walls, made of ordinary brick, whether they show any decomposition or not, usually respond to the test for nitric acid, though some may not, especially if they are very hard or partially glazed. To ascertain whether

brick from higher portions of the wall would give the reaction, I chipped off some flakes of a brick alongside of the casing of a second story window, also two samples from the outside of the tower of our oldest building, and one from the inside. The sample broken at the second story window showed the presence of nitric acid, one from the outside of the tower failed to give any reaction, and the second one gave it very faintly. The sample broken from the inside of the tower-wall reacted very strongly.

Even near the ground within five or six feet of it, some brick may fail to give the test while others give it strongly. This may be due to the different hardness of the brick or to slight glazing. These facts raise the question of absorption from the ground and a gradual concentration of these salts. Absorption of some salts takes place at the ground line, but to what extent the nitrates may be concentrated is an open question. I think that it cannot be denied that sodic sulfate will rise higher than calcic or magnesian nitrate. Direct experiments with soils to ascertain the capillary rise of these latter salts have led me to believe that it is very doubtful indeed whether any concentration of these salts would be effected above the ground line in a brick wall, even if the amount of calcic or magnesian nitrate in the soil were very much greater than in the soil of the college campus. The fact, however, is that the strongest weathering is just above the line of efflorescent salts or alkalies. Even if we admit that there is a probability of concentration in the zone next to the ground line, due to the capillary movement of the salts, it will not apply to points six or more feet up the wall. I do not believe that it is a case of concentration in any part of the wall but a case of formation.

SOME OBJECTIONS TO SAMPLES AND TESTS

I am aware that a rather specious objection to the samples taken on the inside of the tower might be made, to wit: that this is the same as taking a sample of plastering from any old wall and detecting nitric acid in it, the presence of which has been explained by assuming the oxidation of ammonia salts and other organic compounds present in the atmosphere of occupied buildings. As this tower is entirely outside of the building and open, I do not believe that the objection would be applicable, even if we accept the explanation offered for the presence of nitrates in limy material from old buildings. I do not believe, however, that we are under any necessity to accept this in any case as more than a partial explanation of the facts. A much more serious matter would be the objection to the test applied: First, that it is so delicate that it indicates quantities so small that they are not entitled to much weight in a question involving such

quantities as we have to deal with in the nitre question, but more particularly that other oxidizing agents may also give a blue color with diphenylamine and surfuric acid. This double objection would have a good deal of force if this reaction alone were really intended to have any quantitative value futher than may be suggested by the notation of a strong or weak reaction. In regard to its being subject to misinterpretation, there is but little or no danger, for while it is true that other oxidizing agents give a blue color with the reagent, the only one that might interfere in the case of either sandstones or brick is ferric oxid. A comparative test, using ignited oxid of iron, shows that only in case that a very small amount of nitric acid were indicated, would a mistake be likely to be made for the reaction was very weak. It is correct that when the sample is powdered and moistened, the ferric oxid is in a favorable condition to give the blue color but the amount of the ferric oxid is very small and acts somewhat slowly compared with nitrate. The same is true in the case of the binoxid of manganese, which often occurs on sandstones as dendrites. These are sources of error so patent that they are easily avoided and misinterpretation is very improbable. Moreover in event of misinterpretation, it would occur only where small quantities were involved and would not constitute a case for discussion in the problem that we have under consideration.

PRESSED BRICK NO EXCEPTION

The ordinary brick is very porous and presents very favorable conditions for all of the processes, either of living organisms or of chemical reactions and the sandstones also. This consideration led to the examination of pressed brick, these being denser, to see if they too would show the presence of nitrates. As it is customary to lay pressed brick on a foundation of some sort, it has been impossible to find a pressed brick wall without a concrete or stone foundation, so that the pressed brick are not in actual contact with the soil and the weathering noted in common brick is not present.

The best conditions that I have found for observing the pressed brick is at the Hydraulic Laboratory. I chipped three samples from the walls of this building. One of the three samples was in contact with the soil, owing to a slight fill. This fact has kept the brick moist for a number of years, about twelve years. One of the others was from the side of a window casing several fee above the ground, and the third was from the corner of the building, three courses above the foundation. These all reacted satisfactorily for nitric acid. The one that had been in contact with the soil and had been moist for years showed the presence of much more nitric acid than the others. Mr. Rohwer had noticed that the concrete

was crumbling a little just back of and above his office table. This was just about even with the ground on the outside. Mr. Rohwer gathered a small sample of this which I found to be relatively rich in nitric acid. This decomposed concrete and the brick that has been in contact with the soil, which also shows that decomposition is progressing, due, as I believe, not so much to the salts in the soil as to the moisture and the activity of organisms whose development is favored by it, are far richer in nitrates than the other two, but the sample by the window reacts more strongly than the one only three courses above the foundation and neither of these have absorbed any salts from the soil. These pressed brick are shale brick.

I have given these instances of nitrates in our sandstone foundations, ordinary brick foundations, ordinary and pressed brick in walls, to show the prevalence of nitrates under conditions both as to time and place, which preclude the accumulation of nitrogenous excremental material or the gregariousness of insects, birds or animals. The conditions of occurrence in these cases also go far toward precluding any theory of translocation or absorption.

QUALITATIVE REACTIONS ALONE NOT DEPENDENT ON

It may appear that we have depended upon our judgment of the intensity of the diphenylamine reaction for forming an opinion relative to the amount of nitric acid present. In part this is correct. We have to depend upon qualitative reactions in most cases, but we have also made quantitative determinations of the total and also of the nitric nitrogen in samples of brick and sandstones from these foundations, which will be given presently.

The sandstones have been partially described in a preceding paragraph stating the general features of the occurrence. Sample No. 1 in the following table represents the interior portion of the stone in the porch of the chemical building, two feet above the ground line; No. 2 was made up of small chips chiseled off of several (seven) stones 2½ to 3 feet above ground. These chips were rather too large for our purpose; they were too thick. No. 3 was obtained by rasping off the surface 3½ to 4 feet above the ground. Some of the stones rasped had also been chipped, but not all of them. No. 4 was chipped off of the foundation of the Mechanical Engineering Laboratory, twelve to eighteen inches above ground. No. 5 represents decayed brick in the back wall of the Electrical Engineering Building, No. 6 decayed brick in the north wall of the Mechanics Building eighteen to thirty inches above ground. No. 7 represents decayed brick from the rear wall of the Mechanics Building. The front wall of this building has a foundation, the rear wall only a

footing. No. 8 is the softened portion of the silica-lime blocks forming the outside wall of the basement of the Civil and Irrigation Engineering Building.

Sample No. 1 was a big flake from $1\frac{3}{4}$ to $2\frac{1}{2}$ inches thick after I had rasped off the outside, weathered portion. The stone from which the piece was broken lies next to and below one of the stones which were chipped in collecting the general chipped sample. The partially weathered-out brick in the walls of these buildings are fair imitations of cavities in sandstone strata exposed in the faces of bluffs.

No.	Total and Nitric Nitrogen in Material from Weathered Walls	
	Total Nitrogen parts per million	Nitric Nitrogen parts per million
1—Red sandstone, west side of Chemical Bldg., outer portion rasped off	21.00	12.25
2—Chips off of outside portion of porch wall	336.00	242.50
3—Outside portion of porch wall, rasped off	3360.00	2632.00
4—Red sandstone chips, foundation of Mechanical Engineering Laboratory....	870.00	621.25
5—Decayed brick, rear wall, Electric Engineering Building	1855.00	600.25
6—Decayed brick, north wall, Mechanical Engineering Building, old part	203.00	94.50
7—Decayed brick, south wall, Mechanical Engineering Building, old part	2026.00	686.00
8—Silica-lime blocks, C. & I. Eng. Bldg.	262.50	92.40

These samples were probably all free from both forms of nitrogen when laid in the walls. Number 1 represents the interior portion of the stone in the porch of the Chemical Building at the present time. It was a big flake $1\frac{3}{4}$ to $2\frac{1}{2}$ inches thick, with the weathered, outside portion rasped off. Number two represents the outside of the rocks in the porch wall removed by chipping off small pieces with a chisel. Number 3 represents the outside of the same rocks, obtained by rasping off the sample.

The interior of these rocks is even now poor in nitrogen, whereas the rasped off sample is very rich, ten times as rich as the chips that we obtained and 160 times as rich as the interior portion. The ratio of nitric to the total nitrogen in the chips and raspings is almost the same. It is evident that both the total and nitric nitrogen are almost wholly on the very outside of the rocks and are not in the rocks as an impregnation. Sample Number 4 was chipped off of the stone foundation of the Mechanical Engineering Laboratory and is more than twice as rich as the corresponding sample off of the porch of the Chemical Building. There is no sample of raspings corresponding to this. The reason is that the stone is quite firm and presents no good place to rasp off a sample. Samples 5, 6, and 7 are samples of decayed brick as they stand in the respective walls. In some cases the face of the brick is entirely weathered off and a recess is formed but not to the depth of the brick. In such cases the brick is soft and some of it can be easily scraped out. In other cases the face of the brick is still intact, but softened so that a

portion of it can be prized off easily. In the case of Number 5 there is a slight efflorescence on the lower portion of the wall, but there is none in the other cases. In this case there is no stone foundation, only a stone footing several feet below the surface of the ground.

Number 8 represents silica-lime blocks forming a veneer in the basement wall of the Civil and Irrigation Engineering Building. The building is about thirteen years old. The face of these blocks is now somewhat discolored, but not badly, except in a few streaks. In this case there can be no question that these blocks are too porous and unsuited for this portion of the structure. In no event can I believe that either the weather or biological factors is the principal cause of this rapid deterioration, though both of these have contributed materially. The decay is so far advanced in places that the blocks have scaled off to a depth of more than an inch. A general sample representing this basement wall showed the presence 154.0 p. p. m. of total nitrogen. The raspings from the southwest corner of the wall contained 262.5 p. p. m. total nitrogen. The method of manufacture probably rendered the original blocks entirely free from nitrogen or reduced the amount to a very small quantity.

NITROGEN IN SANDSTONES AND BRICK AS USED IN BUILDINGS

As this subject of original content of nitrogen has presented itself repeatedly, and as we were not entirely satisfied with the representative character of the samples of the interior portions of the rocks, we obtained one sample each of a gray sandstone from Fort Collins, one of Turkey Creek sandstone, one of a red shale brick and one of the so-called manganese brick in which we determined the total nitrogen. These samples represent material being put into a building. The sandstones carried 24.0 p. p. m. each, the red shale brick 14.0 p. p. m. and the manganese brick 24.0 p. p. m. of total nitrogen. If we assume that these silica-lime blocks carried 24.0 p. p. m. as placed in the wall, the exterior portion of the blocks as represented by the raspings have increased by 238.5 p. p. m. in the thirteen years that they have been in the wall. It is probable that much nitrogen has been lost in the meantime, so that the actual gain of 238.5 p. p. m. represents only the present residual nitrogen. Each of the sandstones and bricks contains a minute trace of nirtic nitrogen. Thirty grams of the pulverized samples when extracted with hot, dilute sodic carbonate solution and the solution evaporated to a drop or two, gave with diphenylamine and sulfuric acid from a faint to a moderate reaction for nitric acid. This quantity is negligible. The silica-lime blocks carry 92.4 p. p. m. in their surface portions. The sandstones given in the preceding tabular statement carry

242.0, 621.0, and 2632.0 p. p. m. of nitric nitrogen and the bricks carry 94.0, 600.0, and 686.0 p. p. m. There can be no question but that these stones and bricks have acquired the nitrogen as they stand in the walls. The total nitrogen now present attaining to 0.2 per cent in the brick and 0.33 per cent on the surface portions of the stones against a maximum of 0.0024 per cent for comparatively fresh stone and brick.

The ratio of the nitric to the total nitrogen in the outer portion of the sandstone is, in round numbers, 70, 72 and 78 per cent. In the decomposed brick the nitrogen present in other forms than nitrates predominates strongly, and we find the maximum ratio for the nitric nitrogen less than 47 per cent. In the other cases it is essentially 33 per cent. In the silica-lime blocks it is 35 per cent.

The total nitrogen, when the manner of collecting the samples is considered, is much higher in the brick than in the sandstones. The rasped samples of the sandstone cannot justly be compared with the samples of decomposed brick, for the latter represents a mass sample rather than a selected one, and yet it is very high in total nitrogen, 0.1855 and 0.2026 per cent against 0.3360 per cent for the very surface of the sandstones.

The sandstones have stood in their respective walls about 23 years, and the brick about 38 years. The chipped sample of sandstone shows the presence of 0.0336 per cent of total nitrogen, and the brick about six times as much. My interpretation is that the brick have proven more favorable for the accumulation of nitrogen than the sandstones, i. e., the nitrogen fixing flora has found a better habitat on the brick than on the sandstone, but that the nitrifying flora has found the sandstone more favorable. There is no doubt but that washing by storm-water, and in the case of our buildings by irrigating with the hose has played some part both in bringing about the present conditions and in determining the amount of nitrates now present. But we have no means of making even a poor guess as to the importance of this part; the presence of moisture favors development of the flora, but an excess may wash out the nitrates. We can only accept the results of all of the factors that have contributed to the present conditions as we actually find them.

Two things stand out prominently in these cases; that a relatively large accumulation of nitrogen has taken place in a very few years and that no theory of nitrogen supply except that of fixation by biological agents is in any measure applicable.

The amount of nitric nitrogen found in the case of these building materials and also in those of some sandstones and limestones is sufficient to give rise to deposits of crystallized nitrates of sodium or potassium under proper conditions.

CORRELATION BETWEEN NITROGEN CONTENT AND DISINTEGRATION OF SANDSTONES AND BRICKS

There is a close correlation between the process of disintegration of both sandstones and brick and the amount of total and of nitric nitrogen present. The activity of the organisms that have accumulated this nitrogen and converted part of it into nitric acid, respectively nitrates, is closely related to the disintegration of the brick. The same factors are active on the surface of the sandstones in our walls and probably constitute important ones in their weathering.

In the case of the soils these nitrates occur in spots which show a greater total nitrogen content than the immediately surrounding land. These spots increase and are sharply defined. The question was to account for the difference between these spots and the immediately adjacent land, also to account for their increase in size. No theory that has been advanced in attempting to account for the origin of the nitrates except that of micro-organisms comports at all with the facts as they have been ascertained. Several questions arose in this connection, among these the first one was, Does the nitrogen content of these soils actually increase? This question was not new. It had been shown that soils do increase in their nitrogen content, and that this is a very general fact. Experiment proved that our soils increase in their nitrogen content when kept moist and at a moderate temperature, even more rapidly than most soils. The next question was, Do these spots increase in their nitrogen more rapidly than adjacent soil? The answer found to this was affirmative, especially at the margins of these areas. Our ordinary soil gains, according to experiments made, from about 30 to 100 parts per million in thirty days; some soils will gain even more. At the edges of these spots it is higher. We have gotten a gain as high as 610 p. p. m. in forty days.

We do not know whether there are areas on the rocks corresponding to those observed on the soils where these nitrates occur more abundantly than on adjacent portions, but we have found that these nitrates occur on the surface of the rocks generally, and in as generous quantities as are general found in arable soils. We have further found that the surface portions of some rocks rival some nitre-spots in their richness in nitrates. In a preceding table we find for a sandstone 2950 p. p. m. of nitric nitrogen, which corresponds to sodic nitrate equal to 1.57 per cent of the weight of the rock; we found in a granular limestone 270 p. p. m. equivalent to 0.16 per cent of its weight of sodic nitrate. Nitrates occur as generally on rock surfaces as in arable soils and frequently in our climate attain a marked degree of concentration.

SANDSTONES FIX NITROGEN

Soils increase in their nitrogen content when placed under proper conditions of moisture and temperature without the addition of anything except water to make the soil moist, but this water, of course, must be free from nitrogen. If these surface rocks be treated in the same manner, they increase in their nitrogen content too. In this case we cannot take, as would be best, just the surface but simply pieces of our surface rock of some size and pulverize them, supposing that there is old, weathered surface enough to inoculate the whole mass. In the experiments that we made, we used sandstones which differed a great deal in character. One was light colored and compact, with a relatively small portion soluble in hydrochloric acid; two were red, varying a great deal in texture, and one was very dark red and shaly. These samples were ground on a buckboard which was thoroly flamed before the sample was rubbed down, and the rubber was also flamed. Twelve hundred grams of each were taken, the moisture made up to 15 per cent and incubated to see if any change would take place in the amount of nitrogen present.

Results of Incubating Sandstones

	Nitrogen at beginning Total p. p. m.	Nitrogen after 30 days		Nitrogen after 40 days	
		Total parts	Nitric per million	Total parts	Nitric per million
White from Stout	25	135	8	155	15
Red from Spring Canyon	31	315	69	328	88
Shaly from Dixon Canyon	12	250	25	211	28
Red from Dixon Canyon	310	370	93	364	100

The object of this experiment was to establish the fact that these sandstones, including the shaly one, really a red shale, actually possess the property of increasing in the amount of nitrogen contained in them under conditions identical with those existing on the cliffs where we took the samples, except the factors of an optimum temperature and degree of moisture. We added ammonia-free distilled water, avoiding the addition of any source of energy. The results are an imitation of what may take place on the face of these cliffs during any equal period of time. They all show an increase at the end of both periods, 30 and 40 days. The minimum increase at the end of 40 days is 54 p. p. m., the maximum is 297 p. p. m. The ascertainment of the amount of nitrification was incidental, as all are agreed that this process may go on anywhere provided the nitrogenous material necessary for the appropriate bacteria to feed on be present. This process of nitrification was very active during the last ten days of the experiment.

I know nothing about the quantity of energy necessary for the fixation of one part of nitrogen, though, this has been estimated, nor the source from which, in this case, it is obtained by the organisms that effect it. I do not know whether

one or many classes of organisms are concerned in effecting this fixation, but I know that the flora existing on the surface of these rocks is abundant and complex. What may have developed in these samples of pulverized stones, I do not know, but if a small fragment of these sandstones be dropped upon sterile mannite agar in an Erlenmeyer flask one promptly obtains an abundance of bacterial colonies, and later a very rich mixed growth. I have tried this experiment many times and have yet to record a failure. A series of samples were tested and the results showed a fixation of 3.08, 3.12, 3.22, and 3.5 mgs. nitrogen in thirty days. The analytical results in these cases are too low, rather than too high, yet there was a consistent increase in the amount of nitrogen, a fixation of upwards of 3.0 mgs.

A second series of experiments were made with quite different material and with more care even than in the preceding series, the results being as follows:

Fixation obtained with Samples of Rocks on Mannite Agar
fifty gs. in thirty days.

	Nitrogen fixed in milligrams
Sandstone above shale	None
Face of shale bank	0.2
Sandstone	5.6
White mass above shale	19.6
Sandstone	32.9
Sandstone 25 ft. above shale	25.2

Another series of experiments was made to confirm these results. The samples were taken with the usual precautions; chisel, hammer, forceps and test tubes were sterilized. Small fragments of the respective samples were dropped on mannite agar (25 c. c.) in 250 c. c. Erlenmeyer flasks and incubated for thirty days. Five small pieces with an old weathered surface, when such pieces could be picked out, were taken. The total weight of the rock sample added was estimated at 3 gs. in weight. In cases in which the total nitrogen thus added was significant, it has been deducted, but this was the case in one instance only. In these results I attach but little importance to tenths of a milligram. The big fact that I am seeking is that of fixation and that in amounts that demonstrate this so positively that we can acknowledge a deviation from the facts by a tenth or two of a milligram with a remainder big enough to be worthy of consideration. The series given is not our original one, the record of which I unfortunately have mislaid or lost. The series here given is one of rock samples gathered in our immediate section, whereas the original series represented other sections and three states. The results were all decidedly positive. We have now tested about sixty samples in all and have had but one negative result. This was in the case of a sandstone from Grand Junction, Colo., given in the preceding table. All other results, whether the samples

were from Colorado, Oregon or Montana, were positive. A single sample from Nevada, sent by a commercially interested party, gave positive results. This sample was sent in an ordinary ore sack and of course no claim for the bacteriological integrity of the sample can be made. Still, it was the rock just as it was packed up and received by me, and I personally accept the results with as much confidence as I do those in any other case.

Number	Rock	Fixation obtained in Thirty Days	
		Locality	Milligrams Nitrogen fixed
1	Limestone	H. & M. Glade	2.80
2	Sandstone	Near Alford & Maxfield's Quarry	1.37
3	Sandstone	Near Alford & Maxfield's Quarry	2.73
4	Limestone	Cliff near quarry	3.05
5	Limestone	Cliff near quarry	3.64
6	Limestone	Cliff near quarry	2.57
7	Gneiss	Poudre Canyon	2.52
8	Gneiss	Poudre Canyon	3.08
9	Light sandstone waved markings	Soldier's Canyon	4.59
10	Dark red sandstone	Soldier's Canyon	3.73
11	White sandstone	Soldier's Canyon	2.25
12	Red sandstone	Soldier's Canyon, west of quarry	3.43
13	Red sandstone, rotten	Soldier's Canyon, west of quarry	5.65
14	Friable red shale	Dixon Canyon	4.75
15	Red sandstone	Dixon Canyon	1.35
16	Rhyolite	Succer Creek, Oregon	7.31
17	Red sandstone	Buffalo Horn Creek, Mont.	9.93

The growth on the agar plates was of course a mixed one. Sample No. 17 alone gave a growth that was to all appearance practically a pure bacterial growth and, rather contrary to my expectations, the fixation is the highest in the series. When I examined this growth I could find nothing but spores, which is not surprising in so old a culture. The plate was seeded with five small fragments of the sandstone. The checks were sterile.

FIXATION AS A CAUSE FOR PRESENCE OF NITROGEN CONSONANT WITH OTHER FACTS

The facts presented show that the presence of nitric nitrogen is universal on the face of weathered rocks where the conditions are favorable. This modification where the conditions are favorable has in view the fact that nitrates may be washed off the rocks as fast as they may be formed. This is possibly the case in many instances in a humid climate. Again, if the rocks are impregnated with acid salts such as aluminic sulfate it is probable that neither fixation nor nitrification would take place. I know of two localities where the face of sandstone ledges is strongly impregnated with alunogen. I have samples of rhyolite which are heavily impregnated with a sulfate of alumina. This latter sample contains only a trace of nitric acid and it is probable that even this trace did not have its origin in the sample but owes its presence here to washings from some rock close by. It really needs no statement to indicate that the total nitrogen is always in excess of the nitric nitrogen, though this would not necessarily follow if the occurrence

of the nitrate were an instance of concentration, when the two might coincide. The amount of nitrogen present in the rock mass diminishes very rapidly as we penetrate it. The nitric nitrogen practically disappears within a few inches of the surface in the rocks of moderate density.

The study of waters issuing from deep sources, mines and deep wells, shows that there are no soluble nitrates in the rocks through which these waters have percolated. The waters referred to came from depths up to more than 700 feet and gave no nitric nitrogen. This result is consonant with the character of deep seated waters in general, hence we are fully justified in concluding that the rock strata contain no nitrates. This is also indicated by the results of the analyses of our sandstones and is clearly shown as the results of the qualitative tests in the case of the limestones. These nitrates do not come out of the rocks themselves in the form of solutions. The nitrogen present in other forms than nitrates is also not attributable to such an origin, for it too is absent from the interior portions or present in very small quantities. In the case of the bricks, it could scarcely have been present at all immediately after burning, though the bricks that we have tested show a small amount.

Repeated reference has been made to the theory of excreta of insects, birds, and other forms of visible life as the source of the nitrogen in the nitrates. I do not understand this theory to consider in any measure the effects of microscopic life in furnishing the residua containing the nitrogen necessary to produce these nitrates. The theory is one wholly depending upon dead matter to furnish this nitrogen. The only bacterial factor considered is the existence and activity of nitrifying organisms. The existence of a nitrogen-fixing flora, involving the building up of nitrogenous compounds, is entirely omitted. The ubiquity and adequacy of a nitrifying flora is assumed with common agreement, but the equally probable existence of a nitrogen-fixing flora is not mentioned.

General reference is sometimes made to the agency of micro-organisms in the weathering of rocks. I can recall at the present time only two different references to the subject. If my memory serves me faithfully, one of these is given as a specific instance of nitrification. The theory considers the nitrifying organisms as sufficient to produce all of the nitrates with which we are concerned if the proper nitrogen supply be provided, but it requires the readily visible vegetable or animal world to furnish this material.

SUGGESTED EXPLANATIONS FOR NITRATES IN ERUPTIVES INAPPLICABLE

In the case of the nitrates occurring in eruptives, the phenomena of active volcanoes are sometimes appealed to

or these are mentioned in this connection as a possible suggestion of the manner in which these nitrates may have been formed. The presence of ammoniacal compounds, also the existence of nitrids in rocks, have been suggested as the possible sources. These may all be factors in some cases, but they are not general or universal factors, and are inadequate to account for more than a few specific occurrences of these nitrates. The assumption of the existence of ammonic salts, produced by volcanic action distributed at this time over the surface of rocks, even the eruptives, necessitates us to believe in the permanency of these salts or a slow and continuous production of them. No proof of this has at any time been put forward, and if these assumptions actually apply to recent volcanic rocks, they cannot apply to sandstones, limestones, gneisses, and other rocks, not even to eruptives that have been exposed for geological periods.

SIGNIFICANCE OF RATIO OF NITRIC TO TOTAL NITROGEN IN BRICKS AND SANDSTONES

The nitrates, under ordinary conditions, are themselves not of a very permanent character. They are soluble, greedily appropriated by plants, and are readily changed by reducing agents. It is probable that the life of the nitrates even in our semi-arid climate under ordinary conditions, is comparatively short. The ratio of the nitric to the total nitrogen in any given case is probably not at all constant. We observe that the results of our analysis show the ratio to be much higher in the case of sandstones than in the case of bricks. On the other hand, the total nitrogen in comparable samples of sandstones and brick is much higher in the latter. This can mean only one thing, namely, that the total life in the weathering brick is much greater than in the sandstones. It does not follow that nitrification has been less vigorous, but simply that the present residue of nitrates is less. In the sandstones we observe a ratio of the nitric to the total nitrogen of 66.0 per cent; the maximum ratio in the samples of brick is 47.0 per cent, and in the other two cases it is about 33.0 per cent, or one-half of that in the sandstones. The details of these cases may be very difficult to work out, but the big lines in the difference is evident, i. e., where the vegetative conditions are more favorable, the total nitrogen is higher and consequently the ratio is lower. Reference to our analytical data will show that the percentage of nitric nitrogen present in comparable samples of sandstone and brick is as high or higher in the brick than in the sandstone. The absolute amount of nitric nitrogen is about three times greater in the brick, with a low ratio, than in the sandstone with a high ratio for the nitric to the total nitrogen.

It is conceded that nitrification is a universal process,

and no question is raised about his power being resident on rock surfaces. These same surfaces also possess the power of fixing nitrogen. We have offered proof of this by showing that incubated, ground rock fixed a maximum of 297.0 p. p. m. in forty days. We deemed the fact of such importance that we have proved it by a second method, by seeding thirty-four mannite agar plates with seventeen samples of rocks from several different localities and different varieties of rocks, and incubating them with their checks for thirty days. There was not one seeded plate that failed to show a decided degree of fixation. We have tested about sixty different samples in this way and of these only one is recorded as having failed to fix nitrogen.

Our problem was to establish it as a fact that fixation takes place on the rock surfaces, but incidentally we established that in the case of our samples the assumption made in regard to nitrification is true in as high a degree as one could expect. We got an increase in the amount of nitric nitrogen present equal to 18.0 per cent in ten days, the increase being from 93.0 to 110.0 p. p. m. in this time.

FIXATION ON ROCKS A SURFACE PHENOMENON

An important feature is that these are surface phenomena. The most direct evidence of this fact that we have presented is possibly the case of the sandstones in the porch of the chemical Building, in which case we have in a flake of the stone with the outside rasped off 21.0 p. p. m., while a sample rasped from the surface carried 3360.0 p. p. m. total nitrogen. The nitric nitrogen in the flake was 12.25 p. p. m. and 2632.0 p. p. m. in the raspings. The differences between these numbers are more striking than that between those representing the loose material at the entrance, and the solid shale fifty feet in the tunnel, though the latter is really greater. The loose material at the surface carried 69.0 p. p. m. of nitric nitrogen and the solid shale only 0.017 p. p. m. A pair of samples of sandstone from the same stratum gave for the surface 233.8 p. p. m. nitric nitrogen, and for the sample that we obtained representing most nearly the interior, 1.0 p. p. m. We hold these facts to strengthen the interpretation put upon the absence of nitric nitrogen in waters except surface ones, and to establish the absence of nitrates in the interior portions of the rocks, or stated otherwise, that they are wholly confined to the surface. The depth to which we have found the nitrates to penetrate has been only slight, but it is deeper in porous sandstone than in compact limestone.

In the cases of the sandstones in the porch of the chemical building and in the foundation of the Mechanical Engineering Laboratory, we have, in the chips from the former 336.0 and in those from the latter 870.0 p. p. m., and

in the raspings from the former 3360.0 p. p. m. of total nitrogen. This nitrogen has been accumulated during the past twenty-three years.

NOT INCUMBENT ON US TO ACCOUNT FOR THE ENERGY REQUIRED

It is in no measure incumbent upon me to account for the manner in which these facts come about. Whence come the energy and the sustenance necessary for the flora of the rocks to accomplish these things are wholly subordinate to the simple facts that the total nitrogen increases, and that nitrification takes place in measures adequate to account for the quantities of nitrogen that we find as total nitrogen and as nitrates. The difficulties inherent in this problem may be many or few. I am primarily only indirectly concerned in them. Still, I am interested in these questions and a portion of the solution lies within my legitimate province. If it be asked whether a sandstone, compact enough and of such character as to serve well for a building stone constitutes a good substratum for the support of a sufficiently abundant and vigorous flora to fix and nitrify the nitrogen that we actually find; in other words, do they constitute a good soil for the growth of the flora concerned? My answer is, yes, an admirable one so far as the potential supply of inorganic food is concerned.

ROCKS GOOD SUBSTRATA FOR GROWTH OF ORGANISMS

In the sandstones there are two distinct portions, the sand-grains and the cementing material. The former are not all of the same character. In many of our sandstones we have grains of felspar as well as grains of quartz. The quartz grains yield no necessary food, but this is not the case with the felspar and mica, which are present in many sandstones, and are readily recognizable in our No. 2676, a shaly sandstone with scarcely enough sand grains in it to justify the designation of sandstone. These felspar-particles may furnish phosphorous, potassium, calcium, magnesium and chlorin. It is much more probable that the cementing material, in most, if not all cases, is the richer and readier source of these elements necessary for the proper development of the rock flora. With this idea in view, the soluble portion of the sandstones in which we found notable quantities of nitrates and some of those which we incubated were treated with dilute hydrochloric acid, one to one, and the solution analyzed.

The summation in the following analysis is, in several cases, higher than we could wish them, but the error probably falls largely on the determination of sand and, in any event,

does not affect the fitness of the analyses for the purpose for which they are presented.

Analyses of some Sandstones

	No. 2580 Percent	No. 2669 Percent	No. 2671 Percent	No. 2673 Percent	No. 2674 Percent	No. 2676 Percent
Moisture at 115 deg. C.	0.12	0.204	0.173	0.392	0.194	1.472
Ignition	1.105	1.101	0.902	0.858	0.344	1.950
Carbonic oxid	0.075	13.020	8.920	4.660	0.060	3.520
Chlorin	0.064	0.004	0.002	0.001	0.003	0.006
Sand	96.718	68.914	78.690	87.122	98.290	83.832
Soluble silica	0.416	0.678	0.392	0.554	0.428	2.352
Sulfuric acid	0.022	0.045	0.012	0.011	0.006	0.016
Phosphoric acid	0.033	0.030	0.029	0.034	0.021	0.074
Ferric oxid	1.130	0.286	0.254	1.036	0.510	2.418
Aluminic oxid	0.100	0.036	0.078	0.162	0.092	1.304
Manganic oxid (br)	0.010	0.012	0.014	0.008	0.006	0.083
Calcic oxid	0.234	10.080	10.382	5.961	0.958	2.960
Magnesian oxid	0.044	5.759	0.949	0.096	0.046	2.041
Sodic oxid	0.057	0.027	0.026	0.026	0.015	0.037
Potassic oxid	0.032	0.070	0.045	0.047	0.048	0.224
Summary	100.432	100.566	100.778	100.923	100.121	101.164

The summation in these analyses is rather high throughout, but they present the facts sought in having them made with satisfactory exactness.

The dilute hydrochloric acid solution contains all the mineral requirements of even a rather exacting micro-flora, -potash, lime, magnesia, sulfur, chlorin, phosphorus and carbonate enough in four of the six cases to insure against even neutral conditions, and organic matter is not wholly wanting. The actual findings in our determinations of total and nitric nitrogen, or the results of incubation, leave no doubt about their fitness as substrata for the development of such flora. Number 2580 carried as it was broken from the ledge 970 p. p. m. of total and 590 p. p. m. of nitric nitrogen; No. 2669 carried 310.3 p. p. m. total and 233.8 p. p. m. nitric nitrogen; No. 2673 carried 262 p. p. m. total and 1.5 p. p. m. nitric nitrogen; No. 2671 carried 12.7 p. p. m. total and 1.3 p. p. m. nitric nitrogen. Nos. 2674 and 2676 were samples used in incubation-tests and showed a fixation of 130 and 199 p. p. m. respectively. These results are better interpretations of the analytical data than any that we might offer.

The sandstones here presented are not the only ones that we have analyzed in order to determine the potash content. A mass determination made on one of our sandstones showed 1.0 per cent and another 0.924 per cent potash. The total potash was not determined in the analyses given, only the hydrochloric acid soluble, and this we have considered as a potential supply. The facts found pertaining to the rocks, as found in the ledges and results of incubation, make it clear that there is no probable deficiency in any of the inorganic requirements of the flora.

The testimony of these results is even broader than these conclusions; namely, that there is a reasonable supply of food constituents, organic as well as inorganic, for a fixation of 130 and 199 p. p. m. of nitrogen in forty days indicates

a pretty vigorous growth in these samples, and is the practical answer that I have to offer to show that the energy supply from whatever source it may be derived is adequate for all requirements in the case.

Only a partial analysis was made of the brick. The sample chosen represented the walls of the Electrical Engineering Building. These were ordinary sand brick of local manufacture. The phosphoric acid and potash was determined in this and we found for phosphoric acid (P_2O_5) 0.14 percent and for the potash (K_2O), 0.492 percent.

THE FLORA PRESENT ON SANDSTONES IS ADEQUATE TO PRODUCE EFFECTS FOUND

The results that I have obtained by incubating the pulverized sandstones and shale alone would seem quite adequate proof that however mixed the flora may be, it is capable of accomplishing the production of the necessary nitrogen for the formation of all the nitrates found. The direct incubation of the sandstones does not stand alone, for when we inoculate the mannite-agar plates we obtain uniformly an entirely satisfactory fixation. That the flora is a badly mixed one matters not a whit; the fixation is accomplished. It is wholly a matter of indifference whether the fungi, algae or bacteria, alone or associatively, bring about the results. There may be bitter antagonisms existing in this little word, but the end result is a gain in nitrogen, and in the incubation tests also a gain in the amount of nitric nitrogen. The two big, essential processes are predominant, however varied other processes, either favorable or unfavorable may be.

My understanding of the matter is that the fungi, at least some of them, can fix nitrogen; that it has been proven that green plants, under proper conditions, can also fix nitrogen, and it is now common knowledge that certain bacteria can, in pure cultures, fix nitrogen. What they actually do or can do in mixed cultures is only very inadequately known.

As far as I have recited my experiments, I have dealt with a mixed flora just as it is found on the surface of the rocks as they lie, in ledges, and similar samples could be obtained anywhere in our foothills and mountains. I have used sandstones; they are the most common, the most convenient to get, and often the best material. I have also used shales, limestones, rhyolite and gneiss. The flora in these cases is undoubtedly varying. I know as a fact that they are different. I have seen an almost pure bacterial growth on mannite agar with a fixation of upwards of 9.0 mgs. of nitrogen in thirty days, and a whole herbarium of fungi, yeasts, bacteria, etc., in other cases with a greater fixation

of nitrogen. While my judgment in these matters may not be of much worth, I have a notion that the mixed flora on rocks and in the soil may be not only a natural but in some combinations a good thing.

There can be no question but that even the bacterial flora of these samples differs greatly, and I can appreciate the difficulties in attempting to study the subject. I have tried it and am convinced. I very earnestly desired to have this subject thoroughly worked out. The best that I could do was to attempt it myself. Omitting blunders, perplexities and failures, I had some success and obtained what I held to be seven distinct organisms, but I became involved in the difficulties of morphology and this ended, up to the present time at least, my endeavors in this direction.

I cultivated these organisms on mannite agar slants and plates for seven months and they grew luxuriantly. I determined the nitrogen in the average slant and found it to be, in round numbers 0.3 mg, which, leaving aside the question of the availability of this nitrogen to the bacteria, was a meagre ration, and yet these seven organisms thrive on it. I took this as proof that they were able to supply themselves with nitrogen. These were finally transferred to a mannite solution and sand and allowed to stand thirty days. Some of them failed to fix for some reason, others of them did not fail.

I have stated that there were seven distinct organisms. I think really that there were only four, the other three being only developmental forms of one of the four.

The whole of this story is not told in these sentences. While this line of work is not at all to my taste, the questions presented by the facts are very inviting.

SOME FACTS RESTATED

We have presented the fact that nitrates do not occur as an original, integral part of any stratified, metamorphic or volcanic rock. They do occur universally on the surface of rocks just as truly as they occur in the surface soil. It is practically agreed that there is but one process by which the nitrates are formed. This requires an initial supply of nitrogenous matter which certain bacteria transform into various products, one of the end products being a nitrate of some sort, depending upon the character of the substratum on which the changes take place. If this substratum contains potash minerals which yield this base readily, potassic nitrate will be the principal nitrate; if it be a limestone, the nitrate first produced will naturally be the calcic salt. The subsequent changes that may occur depend upon the conditions that exist in the solutions of the respective localities.

The real question is not the formation of nitrates, for

we are agreed on the transformations through which the nitrogen of organic compounds passes in its transformation into nitrates. The only question presenting any difficulty is in regard to the source of the nitrogen necessarily existent in combination, either as organic compounds or ammoniac salts. These latter are themselves, for the most part, decomposition products of more complex organic matter; for this reason we omit their mention, though they may be, in some cases, the starting point for the formation of some nitrates. The question is as stated, Where do these nitrogenous organic compounds come from? We know that there is a nitrogen fixing flora with just as much certainty as we know that there is a nitrifying flora. The latter exist everywhere and is competent to explain the formation of all the nitrates found anywhere. The time required is not considered. We have shown that a nitrogen fixing flora exists in our soils and on these rocks, and is competent in both cases to build up the nitrogenous organic matter required. We have also shown that the rocks and brick contain the inorganic elements required in the growth of this flora in abundant quantities and that the fixation actually takes place. In the case of sandstones we have given an instance in which the nitrogen increased from 21 p. p. m., as the stone was placed in the wall, to 3360 p. p. m. in twenty-three years, and that the nitric nitrogen increased from a trace, as we find in fresh stones, or from 12.5 p. p. m. as we find in the interior portions of this rock at the present time, to 2632 p. p. m. The weathering of our building stones and brick presents the same process that is going on in the surface portions of rocks. It differs in degree only and not more in character than the process itself differs in the case of varieties of rocks of the same general character. We may consider, for instance, the members of a series of sandstones. They differ in the relative quantities of grains of quartz and in the character and quantity of cementing material. A white, fine grained sandstone with a silicious cement, or in an extreme case a quartzite is an entirely different subject from a coarser grained one, consisting of sand particles of different kinds, as quartz and felspar instead of quartz only, with an open ferruginous, calcareous cement. The latter presents a much better substratum for the development of organisms and will, of course, break down much easier than the former.

These are practically the conditions that we have in the soil, except that the soil particles are not cemented together and there is a greater, at least more evident, supply of organic matter. These facts are simple, they are universal and are adequate to account for all of the nitrates found in any locality, probably including the greatest deposits. That translocation and changes in character not only may, but

actually do take place, is clearly evident. I collected a sample of rhyolite which proved to be saturated with nitrates of calcium and magnesium to such an extent that when placed in a moist atmosphere it became wet and even moistened the paper sack in which it was wrapped, and yet at the base of the cliff, off of which I broke the sample, the earth was loose, dry and contained crystalline masses of mixed sodic and potassic nitrates. This is unquestionably the explanation for the presence of nitrates in recesses and cavities in cliffs. The nitrates are formed on the face of the rocks, storm or possibly other waters dissolve them and carry them down to the cavity into which they run, or if insufficient quantity to drip, the solutions may be blown in and evaporated. The process of accumulation is the same as that of the collection of alkalies in these little cavities, and as a matter of fact they are associated in such occurrences.

SUMMARY

Nitrates occur universally on the face of rocks, often in abundance.

Nitrates do not occur in the mass of rocks and are absent from the waters of deep wells and mines, but are often present in surface waters in large quantities.

The occurrence on the surface of rocks is analogous to their occurrence in the surface soil.

They occur on all kinds of rocks, but the most favorable kind found is a rather coarse grained sandstone. The cementing material in this case is ferruginous and limy.

These nitrates owe their formation to biological agents, in the sense that the nitrogen contained in them has been gathered from the atmosphere by these agents in their growth.

This process is universal and intense enough to account for perhaps the largest deposits of nitrates.

The same process is going on, under favorable conditions, on the stones and brick in the foundations and walls of our buildings, where we have found the maximum quantities of both forms of nitrogen.

Fixation, to a very satisfactory extent, has been obtained in every trial but one. Sixty trials have been made. The maximum obtained was 297 p. p. m.

Nitrification has been assumed as fully established, but in many instances the amount of nitrification has been determined and found to be as great as in soils.

The quantities of nitrates on or in the surface portions of rocks are adequate to account for their concentration in cavities, crevices and under ledges in rocks; also in the soil

at the base of cliffs in protected places and in some caves. This does not in any way preclude other contributory causes, as all nitrogenous organic matter falls a prey to the changes of decomposition.

The base with which the nitric acid is combined will depend upon the character of the rock on which it has been formed, but subsequently reactions may cause an exchange of the base. The final product is sodic or potassic nitrate, usually the former.