## DEPARTMENT OF THE INTERIOR UNITED STATES GEOLOGICAL SURVEY

GEORGE OTIS SMITH, DIRECTOR

## **BULLETIN 523**

# NITRATE DEPOSITS

BY

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## WASHINGTON GOVERNMENT PRINTING OFFICE

1912



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## By HOYT S. GALE.

#### INTRODUCTION.

### CHILEAN NITRATE DEPOSITS.

Dana says, "The nitrates, being largely soluble in water, play but an unimportant rôle in mineralogy." However, some immense deposits, said to be the largest in the world, occur in northern Chile, in the deserts of Atacama and Tarapaca. No attempt will be made here to describe or review these, as the literature contains many accounts of them, some of which are listed below:

- Forbes, D., On the geology of Bolivia and southern Peru: Quart. Jour. Geol. Soc. London, vol. 17, 1861, pp. 7-62.
- L'Olivier, V., Le nitrate de soude dans l'Amérique du sud: Annales chim. phys., 5th ser., vol. 7, 1876, p. 289.
- Flagg, J. W., Nitrate of soda, its locality, mode of occurrence, and methods of extraction: Am. Chemist, vol. 4, 1874, pp. 403–408.
- Pissis, A., Nitrate and guano deposits in the Desert of Atacama, London, 1878, published by authority of the Chilean Government.
- Muntz, M. A., Recherches sur la formation des gisements de nitrate de soude: Compt. Rend. Acad. Sci., vol. 101, 1885, p. 1265.
- Ochsenius, C., Einige Angaben über die Natronsaltpeter-Lager landeinwärts von Taltal in der chilenischen Provinz Atacama: Zeitschr. Deutsch. geol. Gesell., 1888, pp. 153-165.
- Abercromby, Ralph, Nitrate of soda and the nitrate country: Nature, vol. 40, 1889, p. 186.
- Buchanan, J., The extraction of nitrate of sodium and iodine in northern Chile: Jour. Soc. Chem. Ind., vol. 12, 1893, p. 128.

Newton, William, The origin of nitrate in Chile: Geol. Magazine, vol. 3, 1896, p. 339. Darapsky, L., Das Departement Taltal (Chile), Berlin, 1900.

- Semper and Michels, Die Salpeterindustrie Chiles: Zeitschr. f. Berg-, Hütten-, u. Salinenwesen preuss. St., 1904, pp. 359-482.
- Simmersbach, B., and Mayr, F., Die chilenische salpeterindustrie: Zeitschr. prakt. Geologie, 1904, pp. 273-277.
- Penrose, R. A. F., jr., The nitrate deposits of Chile: Jour. Geology, vol. 18, 1910, pp. 1-32.
- Clarke, F. W., The data of geochemistry, 2d ed.: Bull. U. S. Geol. Survey No. 491, pp. 242-246, 1911.
- Newsom, J. F., Chilean nitrate deposits: Bull. Min. and Met. Soc. America No. 46, March 30, 1912, vol. 5, No. 3, pp. 56-61.

#### IMPORTS OF NITRATES.

The most important of the nitrate salts commercially are sodium nitrate (cubic niter) and potassium nitrate (niter or saltpeter). These salts are largely utilized in this country, as is shown by the statistics of imports. Nearly all the nitrates imported come from Chile. The domestic production, if there is any, is insignificant.

The following statement of the imports for the year 1911 is supplied by the Bureau of Statistics, Department of Commerce and Labor:

Imports of nitrates, 1911.

	Quantity.	Value.
Potassium nitrate, crude	 7,944,757	\$265,061
Potassium nitrate, refined	7?7,486	37,739
Sodium (cubic) nitrate	544,532	16,814,268

The foregoing figures include nitrates imported "for consumption," and do not quite agree with the statement contained in the following table, which includes all nitrates imported. The difference may represent material held over in warehouses from a preceding or to a succeeding year.

Imports of nitrate of potash and nitrate of soda into the United States from foreign countries during the year ending Dec. 31, 1911.

Country.	Nitrate of crude s	f potash or altpeter.	Nitrate of soda.		
	Quantity.	Value.	Quantity.	Value.	
Germany	Pounds. 22,046	\$367	<i>Tons.</i> 101	\$4,508	
Canada Chile. British India.	7, 923, 701	264, 694	9,323 535,454	418,600 16,391,147	
	7,945,747	265,061	544, 878	16, 814, 256	

#### <sup>b</sup> MINERALOGY OF THE NITRATES.

The nitrates known to occur in nature are as follows:<sup>1</sup>

1. Soda niter (nitrate of soda, cubic niter)	NaNO3
2. Niter (nitrate of potash, saltpeter)	KNO3
3. Nitrocalcite	$Ca(NO_3)_2 + nH_2O$
4. Nitromagnesite	$Mg(NO_3)_2 + nH_2O$
5. Nitrobarite	$Ba(NO_3)_2$
6. Gerhardtite	$Cu_4(OH)_6(NO_3)_2$
7. Darapskite	NaNO <sub>3</sub> .Na <sub>2</sub> SO <sub>4</sub> +H <sub>2</sub> O
8. Nitroglauberite	$\dots$ 6NaNO <sub>3</sub> .2Na <sub>2</sub> SO <sub>4</sub> +3H <sub>2</sub> O

<sup>1</sup> Dana, E. S., System of mineralogy, 6th ed., 1892, pp. 870-873.

1. Soda niter, or nitrate of soda (cubic niter), in natural form has the same crystalline form and cleavage as calcite; that is, it is rhombohedral. Composition,  $NaNO_3 = nitrogen$  pentoxide 63.5, soda 36.5. Deflagrates on charcoal with less violence than niter, causing a yellow light. Colors the flame intensely yellow. Is also deliquescent. The pure salt forms transparent, colorless, anhydrous rhombohedra, whose angles closely approximate to right angles, whence its name "cubic niter." It is very soluble in water, and its solubility increaces much with increase of temperature, 100 parts of water dissolving about 70 parts at 0° C. to about 80 parts at 15° and 125 parts at 68° C.

2. Niter, or potassium nitrate (saltpeter), in crystalline form is orthorhombic. Composition,  $\text{KNO}_3 = \text{nitrogen pentoxide 53.5}$ , potash 46.5 = 100. Occurs naturally as thin white granular crusts or masses or in minute needle-form crystals, and as a thin coating on earth, walls, and rocks. Is a transparent crystalline salt with a cooling, rather sharp, saline taste. Deflagrates strongly when thrown on burning coals. Imparts a strong violet color to the flame when color is not masked by the presence of much sodium. Dissolves readily in water and is not altered by exposure.

3. Nitrocalcite, or nitrate of lime (calcium nitrate), occurs in nature in efflorescent silken white or gray tufts and masses and has a sharp and bitter taste. Composition (hydrous calcium nitrate),  $Ca(NO_3)_2 + nH_2O$ . On burning coals it slowly fuses with a slight detonation and dries. It is very deliquescent before but not after being desiccated by heat. It occurs in Kentucky in limestone caverns; also in Arizona, and doubtless in many other localities.

4. Nitromagnesite, or nitrate of magnesia, is described as a white salt occurring in efflorescences and having a bitter taste. Composition (hydrous magnesium nitrate),  $Mg(NO_s)_2 + nH_2O$ . It is reported to be found in limestone caverns along with nitrocalcite, but its existence as a natural product has not been definitely determined.

5. Nitrobarite, or barium nitrate, occurs in colorless crystals, in part covered with a thin brownish-black coating, resembling wad. Composition,  $Ba(NO_3)_2$ =nitrogen pentoxide 41.4, baryta 58.6=100. It is reported from Chile.

5

6. Gerhardtite is a basic cupric nitrate, with the composition  $Cu(NO_3)_2.3Cu(OH)_2 = nitrogen$  pentoxide 22.5, cupric oxide 66.2, water 11.3 = 100. Crystalline, transparent, with a highly perfect cleavage, yielding thin flexible laminæ of a deep emerald-green color and brilliant vitreous luster. Easily fused, coloring the flame green, and, with soda on charcoal, is easily reduced to metallic copper, with deflagration. Soluble in dilute acids, but insoluble in water. It was first reported from a few specimens found with acicular crystals of malachite in cavities in cuprite at the United

Verde copper mines at Jerome, Ariz. Another occurrence in the Clifton-Morenci district, in the same State, is described by Lindgren,<sup>1</sup> specimens having been determined by Hillebrand.

7. Darapskite is a double salt composed of the nitrate and sulphate of sodium. Composition, NaNO<sub>3</sub>.Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O = nitrogen pentoxide 22.0, sulphur trioxide 32.7, soda 38.0, water 7.3 = 100; or sodium nitrate 34.7, sodium sulphate 58.0, water 7.3 = 100. Tetragonal, occurring in square tabular crystals, colorless and transparent. The water is readily expelled by heat, without decrepitation. It is reported from the Pampa del Toro in Atacama, Chile, where it is said to be intimately associated with blödite and soda niter.

8. Nitroglauberite occurs as a white, homogeneous mass with fibrous crystalline structure. Composition,  $6NaNO_3.2Na_2SO_4 + 3H_2O =$  sodium nitrate 60.1, sodium sulphate 33.5, water 6.4 = 10Q. Soluble in water. Occurs in the desert of Atacama, Chile.

## USES OF SODIUM AND POTASSIUM NITRATES.

Sodium nitrate is used for many of the purposes for which the potassium salt is employed, but its hygroscopic nature makes it unavailable for the manufacture of gunpowder or fireworks. For making nitric acid, for supplying that acid in sulphuric-acid manufacture, and for use as a fertilizer, it has, however, entirely replaced potassium nitrate. It is also the principal source of the potassium salt, which is obtained from it by double decomposition with the potassium chloride of Stassfurt.

Potassium nitrate (niter or saltpeter) is used chiefly in the manufacture of gunpowder or other explosives, but is also used for fireworks, for lucifer matches, for curing meat, for manufacture of certain kinds of glass, for flux in metallurgical assays, for some dyeing, and in medicine.

Munroe<sup>2</sup> has summarized the consumption of nitrate of soda in the United States for 1905 for the manufacture of various commodities as follows:

Consumption of nitrate of soda in 1905.

	Short tons.
Explosives	. 133, 034
Fertilizers	. 42, 213
Chemicals	. 38, 048
Sulphuric, nitric, and other acids	. 29, 301
Glass.	. 11, 915
Dyestuffs	. 261
	254, 772

<sup>1</sup> Lindgren, Waldemar, Copper deposits of the Clifton-Morenci district, Arizona: Prof. Paper U. S. Geol. Survey No. 43, 1905, p. 121.

<sup>9</sup> Munroe, C. E., The nitrogen question: Proc. U. S. Naval Institute, vol. 35, No. 3, 1910, p. 715.

## DEPOSITS OF NITRATE SALTS.

## GENERAL NATURE.

Nitrate salts, although not generally found in large amounts, are widely distributed in natural deposits and occur in several forms. They are found in all fertile soils, though usually rather sparingly, but are not generally supposed to be recoverable from these for commercial use as nitrate salts except possibly under some rather unusual conditions. (See pp. 14, 26.) They are also found in more or less concentrated deposits—the so-called cave niter deposits—which are generally small but are widely distributed in this and in other countries.

#### CAVE NITER.

Cave niter deposits include potassium, sodium, calcium, and other nitrates found in protected portions of fractured or cavernous ledges or in shallow caves, notably in arid or desert regions. Some such deposits have from time to time become more or less well known through attempts to exploit them as sources of commercial nitrate salts. A number have been brought to special notice by the field work done in connection with the fertilizer investigations made by the United States Geological Survey during the latter half of the year 1911, especially investigations relating to potash salts.

The term "cave deposits" is applied to certain accumulations of niter salts but does not imply that the material necessarily originated in a cave. Potassium or sodium nitrate is frequently found in crevices or under overhanging ledges or in caves in cliffs of many kinds of rock, especially in situations where the rock affords a good protection from the solvent action of rain or snow waters, and particularly where precipitation is small and ground water too low to dissolve and carry off these very soluble salts. In such places clear white crystalline salts are found in veins several inches thick in the fractures of the rocks and also in protected portions of the loose material that have fallen to the base of the cliffs. These nitrate salts also form coatings or even stalactites on the walls or roofs of overhanging ledges. Such deposits, though occurring in widely scattered localities, exhibit much similarity and many of them have doubtless a common origin.

## SOURCE OF DATA.

1

Published accounts of deposits of nitrate salts occurring at many localities throughout the United States, and in fact throughout the world, are numerous. Some of these accounts have been collated and are republished in the following pages. The original accounts are scattered, and many of them were found rather by chance than by bibliographic search, being included as minor or accessory notes under titles covering entirely extraneous subjects. The following compilation is therefore not supposed to be complete, and it is hoped that it can be augmented and republished later, when additional data shall have been accumulated. Together the references furnish an interesting commentary on these deposits considered as a type. Their description as "cave" deposits and the frequent suggestion that they are derived from guano or animal remains comes from many independent sources. Such testimony can not, however, be accepted as conclusive or as covering all deposits, for there seems to be little doubt that some nitrates or nitrogen compounds may have originated in other ways.

To the reported occurrences of such nitrate salts, as described in the literature, are added several short descriptions and some chemical analyses personally obtained by the author from several localities. In a number of the following quotations the term niter is doubtless used loosely as referring to any of the natural nitrate salts.

Among many earlier references to the subject the following quotation is taken from a mineralogy by Phillips: <sup>1</sup>

Niter, nitrate of potash. Niter or saltpeter occurs in crusts, and in capillary crystals of which the forms are not discernible; it is whitish or of a yellowish-white; is translucent or transparent; brittle, saline, and cooling to the taste; it deflagrates when placed on a hot coal.

It occurs on or near the surface of the earth, and on old walls, etc.

It is found on many of the plains of Spain; and on the chalk near Evreux, in France, from which it is gathered seven or eight times every year; and in the deep grottoes of Mont Homburg, in Germany. In Italy it is afforded by the calcareous soil of Molfetta. Hungary, the Ukraine, and Podolia furnish Europe with abundance of niter. In Arabia it occurs in a valley between Mount Sinai and Suez. Persia affords it, and it is very common in India, especially on a large plain about '0 miles from Agra in Bengal, which is said to have been formerly well peopled. It is found at the Cape of Good Hope. The mountainous regions of Kentucky, which are calcareous and full of caverns, afford it to the inhabitants of North America. In South America the plains bordering the sea near Lima are covered with it.

#### REVIEW OF OCCURRENCES.

#### EASTERN UNITED STATES.

That nitrates occur in the caverns of Alabama, Georgia, Tennessee, Virginia, Kentucky, Indiana, and other States is generally and even popularly recognized, in part through tales that relate the use of niter derived from such sources for the manufacture of gunpowder during war times. These deposits have also been described and their manner of origin has been discussed.<sup>2</sup>

1

<sup>&</sup>lt;sup>1</sup> Phillips, William, An elementary introduction to the knowledge of mineralogy, 3d ed., 1823, p. 189.

<sup>&</sup>lt;sup>2</sup> Hess, W. H., The origin of nitrates in cavern earths: Jour. Geology, vol. 8, 1900, pp. 129–134. Nichols, H. W., Nitrates in cave earths: Jour. Geology, vol. 9, 1901, pp. 236–243. Merrill, G. P., Rocks, rock weathering, and soils, 1897, pp. 372–373; also, The nonmetallic minerals. their occurrence and uses, 2d ed., 1910, pp. 315–321.

The following footnotes are contained in the first edition of a mineralogy by Phillips,<sup>1</sup> with citations of the original sources quoted therein:

Nitrate of potash.—A native earth is said to exist on one of the southern branches of the river Potomac, in Maryland, bordering on Virginia, from which saltpeter is manufactured. The material was rusty or reddish brown and soft enough to be scraped by the finger nail. The base seemed to be a bolar or argillaceous earth. On powdering some of it and adding sulphuric acid I was saluted by the fumes of the nitrous acid. (Law, in Med. Repos., vol. 12, p. 296.)

Native saltpeter exists in Kentucky associated with particles of quartz and sandrock. Of this it is reported there are extensive strata, horizontally disposed. In the specimens I have seen the saltpeter seemed to be distributed through the whole rocky mass, to cement the siliceous particles together, and to assist their coherence, though in some parts the saltpeter filled up fissures between the parallel layers of the sandrock and occupied in like manner veins and cracks across the strata.

The saltpeter caves in Virginia and Kentucky have been mentioned already. The estimate of their product is highly consoling to our country. Their history as well as that of the saltpetrous sandrocks afford curious problems for chemists to solve. (Brown, 6 Trans. Am. Philos. Soc., 13 Med. Repos., p. 367.)

The occurrence of niter as crystalline crusts on mica slate on Nantahala River, in Cherokee County, N. C., is noted in a list of minerals from that State.<sup>2</sup>

References to the occurrence of these salts are contained in a mineralogical list published in 1888 by the United States Geological Survey,<sup>3</sup> and in a later revision of this list, which was not published. Unfortunately, the source of the information does not accompany the notes. The following localities are cited:

Alabama: Niter is found in limestone caves and was mined during the Civil War.

Arkansas: Niter or saltpeter is found in Marion and Newton counties, in caves of the limestone region.

Illinois: Niter is reported as occurring in caves in Jackson County and on Cave Creek.

Indiana: Niter occurs in caves in Harrison and Crawford counties.

Kentucky: Niter occurs in Mammoth Cave, Edmonson County, and in small quantities in hundreds of caves in limestones in the southern and central parts of the State.

Missouri: Saltpeter has been found in caves in Pulaski, Maries, Calloway, and Ozark counties. "It occurs in magnesian limestone. It is no longer gathered."

Tennessee: Niter or saltpeter is reported in "many caves in limestone formation, and especially in the Cumberland table-land; not of much account."

<sup>&</sup>lt;sup>1</sup> Phillips, William, An elementary introduction to the knowledge of mineralogy, New York, 1818, p. 137. <sup>2</sup> Genth, F. A., and Kerr, W. C., The minerals and mineral localities of North Carolina: Geology of North Carolina, vol. 2, 1885, p. 81.

<sup>&</sup>lt;sup>8</sup> Williams, Albert, List of useful minerals of the United States: Mineral Resources U. S. for 1887, U. S. Geol. Survey, 1883, pp. 688-810.

West Virginia: Saltpeter or "peter dirt" is found in caves in Greenbrier, Monroe, and Pocahontas counties, and has been mined there.

More specific reference is made to the occurrence of niter earth in Wyandotte Cave, Indiana, "similar to that used for the manufacture of saltpeter during the war of 1812."<sup>1</sup> An analysis of the material is quoted which shows an equivalent of 6.55 per cent niter, and another analysis, of bat guano from caves, is given, as follows:

## Analysis of bat guano from Wyandotte Cave in Indiana.

Loss at red heat	44. 10
Organic matter	4. 90
Ammonia	4.25
Silica	6.13
Alumina	14. 30
Ferric oxide	1. 20
Lime	7.95
Magnesia	1. 11
Sulphuric acid	5. 21
Carbonic acid	3. 77
Phosphoric acid	1. 21
Chloride of alkalies and loss	5. 87

100.00.

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The recovery of niter from the caves of Indiana is also mentioned in a later report of the State Geological Survey <sup>2</sup> in the descriptions given of Saltpetre Cave in Monroe County, Wyandotte Cave in Crawford County, and Saltpetre Cave in Crawford County.

The records concerning Wyandotte Cave go back only to 1812. During the war with England the demand for gunpowder became so great that much of the nitrous earth in the caves of Indiana and Kentucky was utilized in the manufacture of potassium nitrate, or saltpeter, one of the principal ingredients of gunpowder. What is now called the "Old Cave," was the only portion of Wyandotte then known to the whites, and to it the name of "Indiana Saltpetre Cave" was given by a Dr. Adams, who first preempted the land on which the cave was located, for the purpose of manufacturing saltpeter. He carried on the business on an extensive scale from 1812 to 1817, and remains of leaching hoppers, troughs, etc., can yet be seen near the mouth of the cave, and at "Saltpetre Cave," about a third of a mile distant. The close of the war made the "peter" business unprofitable, and Dr. Adams relinquished his claim.

#### WYOMING.

Cross<sup>3</sup> describes an occurrence of potash niter in the Leucite Hills, Wyo., on North Table Butte, the summit of which he reached through a cleft on the northern side. He says:

On the eastern side of the gap through which the top is gained a cavity or recess with overhanging roof, of irregular shape, several feet in length and depth, was found

<sup>&</sup>lt;sup>1</sup> Cox, E. T., Eighth, Ninth, and Tenth Ann. Repts., Geol. Survey Indiana, 1879, p. 163.

<sup>&</sup>lt;sup>2</sup> Blatchley, W. S., Indiana caves and their fauna; Twenty-first Ann. Rept., Geol. Survey Indiana, 1896, pp. 136, 149-151, 173.

<sup>&</sup>lt;sup>8</sup> Cross, Whitman, Igneous rocks of the Leucite Hills and Pilot Butte, Wyo.: Am. Jour. Sci., 4th ser., vol. 4, August, 1897, pp. 115-141.

#### WYOMING.

in nearly massive rock. It was fully exposed to the prevalent northwesterly breeze, and rain could penetrate to the inner wall only when driven by very strong winds. In this sheltered space was found a very unusual mineral in a rather coarse, granular aggregate, and of sufficient mass to allow collection of specimens several inches in diameter. It seemed to occur as a partial crust to the cavity and as a filling for irregular fissures which extended downward and backward into the body of the rock. A columnar mass several inches in diameter connected roof and floor of the recess at one point where they were no less than 1 foot apart. Fragments of rock were attached to the column, and its stalactitic shape is probably an accident. This white granular substance was analyzed by L. G. Eakins and found to be essentially nitrate of potash. The exact result is given below:

#### Analysis of niter, etc.

K <sub>2</sub> 0	44. 91)	00.40. 14.
$a N_2 O_5$	51.49	96.40 niter.
CaO	1.09	
SO <sub>3</sub>	1.59	3.31 gypsum.
H <sub>2</sub> Ô	. 63	
Na	.07	101 19
C1	. 09	.16 halite.
	99.87	

It is regretted that the nature of this substance was not recognized in the field, in order that close observations of its occurrence might have been made. As far as known there is nothing to indicate the derivation of this 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 mention in manuals of mineralogy. This occurrence is, however, entirely different from all others of which notice has been found in literature. While extended discussion of the genesis of this deposit of niter is at present useless, it may well be pointed out that ammonia gas is a common exhalation product of volcances in their fumarolic stage, and that ammonium chloride, sal ammoniac, is deposited in clefts, fissures, or tubular cavities of lavas at Vesuvius, Ætna, Solfatara, Hecla, and other volcances. The lavas of the Leucite Hills contained fluorine, chlorine, and sulphurous compounds, as will be shown by the rock analyses, and it is certainly a noteworthy coincidence, if nothing more, that one of the bestknown occurrences of sal ammoniac is in the leucitic lavas of Vesuvius, rich in potash.

As regards the occurrence of North Table Butte, there is no special reason to assume a volcanic conduit at this point, yet this occurrence would seem to suggest such a channel at no great distance.

Other minerals were not seen in this cavity, the niter being deposited directly on the rocks. The presence of soda niter at the Boars Tusk, described below, renders this occurrence all the more interesting. Although the nature of the niter was not definitely recognized at the time of its discovery, the peculiar astringent taste was noted then and the true character as a nitrate was speedily established. Specimens of this niter may be seen in the National Museum.

In several places where the breccia (which composes the mass of the column known as the Boars Tusk) was open and cavernous a scanty white coating was observed on protected rock faces. Unfortunately the character of this substance was not suspected, and only a single small specimen was with difficulty procured for analysis. It proves to be a soda niter containing a little potash, as shown by the following analysis made by L. G. Eakins.

#### Analysis of soda niter.

. 32.09)	
. 4.97	87.98 NaNO <sub>3</sub> .
. 61.58	10.00 KNO <sub>3</sub> .
24)	
33	.71 gypsum.
68	.54 water.
. Trace.	
<b>99.</b> 89	
	. 32. 09 . 4. 97 . 61. 58 . 24 . 33 . 68 . Trace. 99. 89

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 intimately 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. ł

#### COLORADO.

The occurrence of nitrate salts in unusual amounts in soils, forming a type distinct from that of the "cave deposits," has been discussed by Headden,<sup>1</sup> who calls attention to a condition existing in Colorado which may be analogous to that in the much-exploited "niter fields" of southern California (p. 26). He states that remarkable quantities of nitrates have already accumulated over large areas in widely separated portions of Colorado. These areas are all characterized by a brown color on the surface and appear oily or wet, sometimes glistening. The spots have been generally supposed to owe their appearance to "black alkali." On testing, however, "black alkali" or sodium carbonate was rarely found to be present in excess and examination revealed comparatively large quantities of nitrates. Such spots are invariably barren, and experiment has shown that an excess of nitrates is injurious or fatal to plant growth and might produce the effects observed. The soil of these areas, especially in the less advanced stages of nitrification, has a soft, velvety feel under the foot and in later stages becomes mealy on the surface. Some of the soil, especially that of a clayey nature, is deflocculated, becomes muddy, and retains water with great tenacity.

In summary, Headden says:

We have found large areas in the eastern and likewise in the western portions of the State, sections about 380 miles apart. Also in the southern portion near the New Mexican boundary and within 40 miles of the northern boundary, localities about 270 miles apart. It is not to be inferred that these niter areas are continuous, but they are in fact quite extensive, in places being continuous for miles. I have stated the conditions in Colorado, but neither these nor the occurrences are confined to this

<sup>&</sup>lt;sup>1</sup> Headden, W. P., The occurrence and origin of nitrates in Colorado soils, some of their effects, and what they suggest: Proc. Colo. Sci. Soc., vol. 10, 1911, pp. 99-122.

State. The amounts of nitrates found are also sufficiently large to entitle the suggestion to consideration. Analyses of surface samples have shown that 6.5 per cent of the air-dried soil consisted of nitrates. The area involved in this case was not less than 10 acres, and as the sample was taken to a depth of 2 inches we would have 210 tons on the 10 acres of this land taken to this depth. In another sample taken to a depth of 5 inches we found 2.6 per cent of nitrates. This was from a large piece of land, 40 acres in all, but, assuming that only 8 acres of it was as rich as this, we would have 172 tons in the top 5 inches of the land. There are hundreds of acres of land in this State which carry from 1 to 5 tons of nitrates in the top 2 inches of the soil. These conditions are met with at altitudes of from 3,300 to 7,500 feet.

The rate of fixation obtained by experiment, 5,616 pounds of nitrogen for each 4,000,000 pounds of soil per annum, is sufficiently large to further entitle the suggestion to consideration. The nitrification obtained by experiment is also significant; that is, corresponding to the formation of 5 tons per acre-foot of soil per annum.

After explaining the nitrifying action of bacteria in the soil and describing experiments to prove that this action does take place in such soil spots, Headden concludes:

The nitrates accumulated in these areas do not owe their origin to the ordinary white alkali of the country, nor have they been washed off of adjoining lands, nor yet have they been brought into these areas from adjoining lands by ground waters, unless these ground waters flow from other nitrated areas, such as a mesa rich in nitrate spots.

These nitrated areas are not in any way dependent upon the geological formations of the country.

The irrigating waters, whether river or reservoir waters, do not contain unusual quantities of nitrates, the range being from a trace to 0.5 part per million.

Fixation takes place rapidly in these soils, the maximum result obtained in 27 days corresponded to the fixation of 5,616 pounds of nitrogen per acre-foot per annum, or 17.5 tons of proteids.

Nitrification also takes place. The maximum increase obtained in 48 days was 138 per cent of the nitric nitrogen present at the beginning of the experiment, which corresponded to the formation of 5 tons of sodic nitrate per acre-foot, or 4,000,000 pounds of soil per annum.

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The areas involved, their wide distribution throughout this State, and their probable presence in other portions of the semiarid West, together with the rates of fixation and nitrification obtained by direct experiment, suggest the probability that the nitrates of Nevada, Chile, and Peru owe their origin to the fixation and nitrification of atmospheric nitrogen by bacteria, azoto- and nitro-bacter.

#### IDAHO.

Niter salts have been reported from several localities in Idaho, notably in Bannock County, near Soda Springs<sup>1</sup> and Pocatello; in Blaine County; in the southwestern part of the State, near the Utah-Nevada line; and in Wayne County, in the central part of the State. These are believed to be deposits of the cave type and are reported as of very small extent and probably of little economic value. The following analyses are reported by Stewart as repre-

<sup>1</sup> Stewart, Robert, The occurrence of potassium nitrate in western America: Jour. Am. Chem. Soc., vol. 33, 1911, pp. 1952–1954.

senting the deposit in a cave of red sandstone at the locality 35 miles northeast of Soda Springs:

Composition of crude nitrate.

	1.	2.
Residue insoluble in water	4. 22 11. 12 None. 2. 91 0. 11 30. 89 1. 54 Trace.	2. 73 11. 48 None. 2. 12 0. 17 31. 55 1. 58 Trace.

#### UTAH.

Miscellaneous occurrences.—Nitrate salts are reported by George T. Henry, of Marysvale, to have been found by chemical test in specimens of a pure white salt taken from rock ledges in Hobble Canyon, which is the next canyon south of Provo, Utah. Hobble Creek is described by Mr. Henry as running through the town of Springville, Utah.

Mineral Resources for 1887 contains a reference<sup>1</sup> to saltpeter or nitrate of potash occurring near Fillmore, Millard County, and to "several small beds near Parawan, etc., Iron County."

G. B. Loring, of Monroe, Utah, reports beds of nitrate salts, proved by tests or analysis made by Prof. Talmadge, from a locality  $2\frac{1}{2}$  miles above the Rob Roy mine in Wildcat Canyon, about 8 or 9 miles northeast of the town of Beaver. The salt is said to occur disseminated in limestone and lava, where exposed in cliffs.

Greenwich Canyon, Grass Valley.—An essentially pure potassium nitrate has been found in Greenwich Canyon, Piute County, on the east margin of the Sevier Plateau, 5 miles south, 70° E. from Marysvale Peak, near the north boundary of Piute County, Utah. The located claims are situated in the upper portion of the canyon, which is tributary to Otter Creek in Grass Valley, joining that stream at a point 4 miles south of the town of Koosharem and a short distance north of Greenwich. Two groups have been located, the lower near the fork of the main creek about  $1\frac{1}{2}$  or 2 miles above (northwest of) the Grass Valley road and the upper at least 5 miles from the Grass Valley road. These localities are represented on the map (fig. 1).

The deposit is of essentially the same type as those at Gerlach, Nev. (p. 23), and elsewhere, but the amount of salts to be seen is less. The salts are found in caves or brecciated cliffs and ledges that border the canyon valley. Evidences of habitation by bats or other nestbuilding animals are seen in the same cliffs.

#### UTAH.

The foothills or interstream ridges that range from the Marysvale Plateau eastward down to Grass Valley are capped by a basaltic lava flow, vesicular at the top, which is apparently of comparatively recent date, but which preceded the last or present canyon-cutting



FIGURE 1.—Map showing location of niter deposits and prospects in Greenwich Canyon, near Grass Valley, Plute Co., Utah.

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stage of the existing stream valleys. Modern stream valleys are somewhat uniformly intrenched below these basaltic flows, which were spread on a tilted plain sloping eastward at about the same grade as the streams. The rocks over which the basalt flowed are acidic 52096°-Bull, 523-12-2

volcanics, rhyolite or a related rock, including interbedded flows and tuffs, which are exposed at intervals all along Greenwich Canyon, especially on the north and northeast sides. These ledge exposures are considerably brecciated and weather in cavernous types, forming brown or reddish stained bluffs, possibly iron stained by leaching from the overlying basalt. The upper portions of the rhyolite flows are apparently waterlaid tuffs, evenly bedded, showing distinctly the contact with the overlying basalt.

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At the niter claims in upper Greenwich Canyon some ledges of the rhyolite lava, cavity filled and fractured, make prominent bluffs high on the north slope of the canyon. Near the base of the bluffs small excavations have revealed seams or vein material of a very soluble pure white crystalline salt, having a pungent taste. From this place specimen No. 1 of the subjoined analyses was obtained.

Samples collected from the Greenwich Canyon localities and analyzed by J. G. Fairchild in the laboratory of the Geological Survey, gave the following results:

Tests of supposed niter salts from Greenwich Canyon, near Grass Valley, Utah.

	1	2	3	4
Insoluble in water.	46.04			
No <sub>3</sub>	28.53	None	None	0.82
K	19.18 0.20	None	About 1.	3 to 4 2,65
803 Cao	Small. Small.			
CU2	None.	••••••		•••••

No. 1 represents the clearest portion of saline material available in the talus at the base of the cliff on the upper claims in Greenwich Canyon.

No. 2 is an alkali salt found on the surface of the ground in the forks of the main canyon near the lower claims. This salt appears to be leaching from a decomposing rhyolitic soil in the creek wash. Its taste suggests sodium carbonate or sulphate.

No.3 is from a cave in a brecciated rhyolite bluff on the lower claims at the north side of Greenwich Canyon, just below the creek forks. There was no evidence of bat nests at this place.

No. 4 was a limy white lenticular vug in the brecciated rhyolite or tuff at same locality as No. 3. This material is said to have been used locally for whitewash. The report by Mr. Fairchild shows it to be an impure bauxite, with a small amount of soluble nitrates, probably of potassium.

Only the sample from the upper claim proved to contain much niter and it is apparent that the quantity of such material available is very limited. It perhaps would not be warranted to attempt a

#### OREGON.

judgment of the ground as a whole from the small number of samples taken for test. The niter is apparently more abundant where bat nests are numerous and less abundant where the nests do not appear. It is not certain that the nests are those of bats.

### OREGON.

Stafford reports on the presence of niter in Oregon as follows:<sup>1</sup>

Saltpeter is reported in marsh deposits of southeastern Oregon, and, it has been claimed, in quantities sufficient to justify extraction. A very interesting occurrence is noted near Mount June, southern Lane County, where a ledge of earthy material carrying large quantities of niter is exposed. Claims have been staked by Elmer Doolittle and associates, of Cottage Grove.

A recent press notice<sup>2</sup> announces prospective developments of nitrate of soda deposits on the west side of Wagontire Mountain, about 60 miles southwest of Burns, almost on the line between Harney and Lake counties. Prospectors from Vale, Oreg., are said to be taking active interest in this ground.

## NEVADA.

Nitrate salts near Lovelock.—The existence of nitrate salts in ledges and caves on the south side of Humboldt Lake, southwest of Lovelock, Humboldt County, Nev., is said to have been known since 1868. The writer is indebted to Mr. J. R. Hunter, of Lovelock, who accompanied him on a trip to the property and who, by his familiarity with the ground and the work that has been done, was able to point out the more salient features of the deposits. He is also indebted to Mr. John T. Reid, of Lovelock, for the greater part of the following history of these deposits and of the work that has been done on them.

Reports state that the salts were first used by the Indians, who had long known the projecting point of rock in secs. 13 and 14, T. 25 N., R. 31 E., as Medicine Rock, and who had been accustomed to visiting the place and licking the rock, believing that thereby they derived some medicinal benefit. The first discovery of niter is said to have been made on a site between secs. 13 and 14, T. 25 N., R. 31 E., by William Silverwood, still a resident of Lovelock, who claims to have located claims there in 1868. From time to time others have located or relocated this and other ground in the vicinity. The matter was taken up more actively in 1887, when a small pit was dug to determine the depth of the material, after which interest in the matter was again allowed to lapse. About 1902 or 1903 the claims passed into control of the American Nitrate & Potash Co., of San Francisco, which for a time seemed about to undertake active development, but which has done no work on the property.

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<sup>&</sup>lt;sup>1</sup> Stafford, O. F., Mineral resources and mineral industry of Oregon for 1903: Bull. Univ. Oregon, No. 4, new ser., vol. 1, 1904, p. 105.

<sup>&</sup>lt;sup>2</sup> Portland Oregonian, Aug. 5, 1912.

In sec. 36, T. 24 N., R. 29 E., some disconnected exploratory work has been done by several individuals. The discoveries at this point are also reported to date back as far as 1868. James Say, proprietor since the early fifties of a station on the old emigrant road passing by this route, is said to have called attention to salts of a peculiar acrid taste which he found in neighboring ledges, but he was probably unaware of their nature. About 1902 or 1903 some preliminary experimental development work was done under the supervision of W. M. Courtis, of Detroit, but was later allowed to lapse.

The deposits occur on the west slope of the Humboldt Range. (See Pl. I.) The "Niter Buttes" are also noted by I. C. Russell<sup>1</sup> who describes the rocks and gravels that compose them and discusses the terraces and bars that record former more-elevated lake shores along them, and who locates them on the maps at the extreme southern end of the Humboldt Range near the mouth of the Humboldt River, where that stream joins the waters of the Carson Sink.

The Lovelock niter beds have been staked as mineral locations, as shown by the shaded areas on the map (Pl. I), the extent of location given being based on data furnished by Mr. Reid.

This deposit was described by Van Wagenen in a brief note published in 1902.<sup>2</sup>

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The locality was visited by the writer on August 8, 1911, when a somewhat hurried review of the northern group of claims was made and a number of samples were collected for analysis from the under side of projecting or overhanging ledges, which are here composed of an acidic (probably rhyolitic) lava, at places a coarse volcanic breccia. The following analyses of the material were made in the laboratory of the Geological Survey:

	1	2	3	4	5	6	7	8	9	10
Insoluble in water Soluble in water: NOg Na Cl	94.25 None.	92.81 'None.	95.37 None.	95.18 None.	34.32 0.61 23.74 Trace. 29.60	30.89 35.65 20.20 Trace.	4.00 53.12 26.26 Trace.	92.86 None.	78.06 None. 3.54 2.84	10.58 0.68 34.59 None.
SO3 CaO	Trace.	None.	Very little.	Trace.	29.00 7.98 Not over 2.	Trace. Very little.	0.53 0.53	0.19 Trace.	N o t over 2. Very little.	Very little.

Analyses of supposed niter salts collected near Lovelock, Nev. [J. G. Fairchild, analyst.]

Nos. 1 to 4, inclusive, were from reported niter ground in approximately the southwest corner of sec. 5, T. 24 N., R. 31 E. (Pl. I). The material has a rather strong saline taste, but contains no niter. The

<sup>1</sup> Russell. I. C., Geological history of Lake Lahontan, a Quaternary lake of northwest Nevada: Mon. U. S. Geol. Survey, vol. 2, 1885, pp. 109-110 and map, p. 106.

<sup>2</sup> Van Wagenen, T. H., Nitrate deposits, Humboldt Co., Nev.: Min. and Sci. Press, vol. 84, 1902, p. 63.



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BULLETIN 523 PLATE



MAP SHOWING DISTRIBUTION OF NITER CLAIMS NEAR LOVELOCK, NEV.

#### ŃEVADA.

general situation of the ground from which these four samples were collected, though reported as niter-bearing, is, however, different in character from that where the remaining samples were taken, and no apparent relation to the overhanging cliffs or cave formations was observed. Therefore the negative character of these tests bears no significant relation to the rest of the analyses.

Nos. 5 to 10, inclusive, were collected in the group of claims extending from sec. 33 to secs. 13 and 14, T. 25 N., R. 31 E.

No. 5 consisted of a sample of salts, shown by the tests to be mainly sodium chloride, which occurred as a crusted coating under a projecting ledge of red brecciated rhyolite.

No. 6 was collected at the discovery monument of the Queen placer claim, 160 acres, located April 5, 1911, in the "Lake mining district, Churchill County, Nev., about 5 miles south of the Big Five Reservoir, at the big bluff in the foothills where it juts against the valley." The salts were incrusted under a ledge projecting in cave form. In the sample collected approximately 70 percent of the water-soluble portion proved to be sodium nitrate.

No. 7 was collected in the same locality as No. 6, but from a somewhat different position. Both represent the selected portion of the white incrusted salts chipped from the ledge face or from seam fillings. The analysis shows that about 75 per cent of the water-soluble portion of this sample is composed of sodium nitrate. The rock is evidently a red brecciated lava, probably rhyolite, carrying large included bowlders, rounded and subangular blocks of shale, and other country The point is a prominent rock headland on the margin of the rock. valley, topped by one of the rock-cut terraces of a lower important stage of Lake Lahontan levels. At least four other distinct shoreline terraces show at higher levels. The rock is seamed and coated by marked incrustations of white salts in more protected parts. One much-fissured zone shows a foot or two of quite strongly charged A carload of about 20 tons is reported to have been taken material. at this place and shipped for experimental treatment. The only salts visible, however, are those occurring in weather-protected portions of the ledges, especially where decomposed or much jointed. So far as can be judged from the surficial aspect of the deposit the quantity of such material available is probably not great.

Nos. 8 and 9 gave negative tests for nitrates. No. 8 was collected from decomposed rhyolite in talus form at the foot of the main ledge, detrital from the overhanging ledge, but probably weather leached; No. 9 was taken from the thoroughly decomposed soil sliding down over the outcrop of this lava rock in place.

No. 10 was collected in a cave one-fourth to one-half mile east of the section stone marking the corner between secs. 14, 15, 22, and 23, T. 25 N., R. 31 E. The stone which stands about 3 miles north of the

Queen placer claim close to the remains of an old stone house that stood on the immigrant trail of the pioneer days, is distinctly marked with the customary notches and is probably an original corner. Tests showed the sample to consist mainly of sodium chloride with a little niter, but the type of occurrence is essentially similar to that at the Queen placer. Excavations in the cave have revealed human bones supposed to be Indian remains purposely buried. Some sacks of the ore taken from the cave contained material consisting of incrusted salts coating the face of the ledge at the back of the cave and represented the purest white salt in evidence.

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Samples similar to those described were collected by L. J. Pepperberg from cliffs in the NE.  $\frac{1}{4}$  sec. 14, T. 25 N., R. 31 E., and were analyzed by F. F. Fitzgearld, with the following results, which have not before been published:

	Supposed niter salts.	Adjacent rock.	Leached rock top of cliff.	
SiO <sub>2</sub>	1.56 } 0.57 0.78 3.88			
Na H•O.	$33.31 \\ 0.52$	2.59		
CI	50.10 9.90	2.50	0.42	
NO <sub>3</sub>	Trace.	None.	None.	
	100.62		<b></b>	

Analyses of supposed niter-bearing material from near Lovelock, Nev.

The water-soluble portion of these samples proved to be essentially sodium chloride.

It is to be noted that the only considerable showing of niter salts contained in the present series of samples is represented by the two specimens of the best material from the crevices in the rock on the Queen placer claim. Furthermore, the water-soluble portion of this is shown to be essentially sodium and not potassium nitrate, with some sodium chloride. It is possible that the composition of the salts at this place has been influenced by the saline constituents of Lake Lahontan waters, which have undoubtedly covered the ground.

In explanation of the origin of the niter it is suggested, although admittedly far from conclusively proved, that the prominent headland that these ledges must have formed in Lake Lahontan at or succeeding the period in which the rock bench was cut by wave action along the lake shore was probably inhabited by ducks, sea gulls, or other birds, possibly in large numbers, even as similar rocks are thus inhabited in Great Salt Lake to-day. Decomposition of organic matter in contact with alkaline material might account for the pro-

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duction and dissemination of nitrate salts, which may nave penetrated widely the fissures and crevices of the much-fractured rhyolite. The subject is further discussed on page 30 in a more general review of the origin of nitrate deposits.

Potassium nitrate north of Gerlach.—An occurrence of almost pure potassium nitrate in natural form has been found in the northern part of the Granite Range, Washoe County, Nev. (See index map, Pl. I.) The claims were visited in October, 1911, by George Otis Smith, Alfred H. Brooks, and the author. The locality is in T. 37 N., R. 22 E., and is reached by road and trail from Gerlach, a station on the Western Pacific Railway. The route from Gerlach lies north along the western margin of the Blackrock Desert for about 12 miles, thence northwest across a large alkali flat at the east base of the Granite



FIGURE 2.—Map showing location of upper and lower groups of niter claims near Gerlach, Washoe County, Nev.

Range, and thence, following tributary drainage, to Leadville, a mining camp near the northern end of that range. From Leadville the route followed was by trail across the divide and down the western flank of the range to the prospected ground, which is about 3 miles distant and 1,400 feet lower than the place where the trail crosses the crest of the range. Figure 2 shows the location of the claims.

The niter salts occur under ledges and in cavelike cliff formations in a canyon on the upper waters of Grass Valley Creek, an upper tributary to Little Highrock Canyon. (See Pl. II.) A small amount of exploratory prospecting has failed to reveal much more of the character of the deposit than shows at the surface. It is, however, essentially similar to that at Lovelock and elsewhere. The niter is found as a white crystalline salt in crevices and concentrated in veins in the slide rock at the base of the cliffs, partly or wholly in positions protected from leaching by rain, snow, or surface waters. A collection of samples representing the salts, or supposedly saline-bearing material, was made at points indicated by crosses on the map (fig. 2). Analyses follow:

	1	2 a	3	4	5	6	7	8	9
Inorganic and insoluble Water-soluble portion:	98.88	34.10	10.04	91.83	14.58	98.36	76.75	88.09	98.59
NO <sub>3</sub>	Trace.	Trace.	52.40 Small	3.07	50.42	0.72	9.96 Some.	5.44 Trace.	0.32
К Na	0.3±	5.45 0.67	33.61 1.07	0.80 0.50	31.42 1.28	0.42 0.04	4.97 0.58	1.40 0.96	0, 26 0, 04
Cl CaO		b 3.18	Trace. Small.	0.30 Some.	Trace. Small.	Trace.	0.30 Some.	0.45 Some.	
P <sub>3</sub> O <sub>5</sub>		0.64		Trace.		• • • • • • • • •	¢0.5		

## Analyses of niter samples from deposits north of Gerlach, Nev. [J. G. Fairchild, analyst.]

a No. 2 is a guano with abont 49 per cent loss on ignition. b Nonvolatile chlorine. c Approximate.

Nos. 1 and 2 come from the upper nitrate claims; No. 1 is from a sugary siliceous-like seam in rhyolite lava exposed in a cliff on the north side of upper Grass Valley Creek (W.  $\frac{1}{2}$  sec. 13, T. 37 N., R. 22 E., Nev.); and No. 2 is supposed bat guano from upper corner under cave near seam from which No. 1 was taken.

Nos. 3 to 9 are from the lower claims. No. 3 is a white crystalline salt from a seam about 3 inches thick, occurring in soil and slide rock at base of an overhanging cliff of rhyolite lava in the lower canyon of Grass Valley Creek (near middle of north side sec. 15, T. 37 N., R. 22 E.). No. 4 is a blackened coating staining the cliff face near the locality of No. 3, supposed to be a leaching from bat guano. No. 5 is a white crystalline salt dug from a fissure in the face of the cliff about 50 feet west of the locality of No. 3. No. 6 is a specimen of shattered rhyolite rock collected from a prospect pit near a blast hole in the same locality as Nos. 3 and 4. No. 7 is a brownish or blackened earthy deposit from a fissure in the face of the cliff, containing many rock fragments, near the locality of Nos. 3 and 4. No. 8 is an iron-stained rhyolite rock, containing salt in seams and cracks, taken from a brecciated cliff in the forks of Grass Valley Creek about 200 feet east of the locality of No. 3. No. 9 is from a prospect pit on the south side of Grass Valley Creek, just above the forks of the creek and about 600 feet east and a little south of the quarter section corner on the north side of sec. 15, T. 37 N., R. 22 E. It consists mainly of rock fragments with no evident coating of salts.

In considering these analyses from a commercial standpoint it should be borne in mind that the samples containing the richer salts are all selected samples, representing only what appeared to be the very best material that was available in the prospects, and that there

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A. UPPER CLAIMS.





NITER CLAIMS NORTH OF GERLACH, IN THE NORTHERN GRANITE RANGE, WASHOE COUNTY, NEV.

is as yet no really sufficient evidence that the quantity now in evidence can be much increased by further development.

These analyses show that the water-soluble portions of the purer salt samples (3 and 5) are essentially pure potassium nitrate in natural form, the insoluble impurities being chiefly earth or rock fragments accidentally included in scraping up the samples. Such a salt in merchantable quantities would be worth about \$65 a ton in eastern markets. As the potassium oxide of a pure potash niter constitutes 38.7 per cent of the salt and the nitrate radicle the remaining 61.3 per cent, it appears that the water-soluble portions of samples 3, 5, 6, 7, 8, and 9 consist chiefly of potassium nitrate with a relatively small proportion of sodium nitrate.

The sample of guano shows a potassium content, but has little nitrogen in nitrate form. It contains soluble nitrogen in the form of ammonia, and probably also in the albumenoid form, but the latter was not chemically determined.

The country rock in the vicinity of the Gerlach niter prospects consists almost entirely of acidic volcanic lavas showing vesicular, ropey, and flow structures exposed in many places in cliffs and ledges. Glassy obsidian is found throughout the area as fragments in soil that covers the hill slopes, as well as in layers intercalated with other forms of the flow rock. The country rock is probably rhyolite.

It has been generally assumed by those interested in the development of these deposits that the nitrate salts are formed by leaching from the country rock and that they accumulate or are preserved in places protected from the weather. On the basis of this assumption it has been supposed that some portions of the bedrock may be sufficiently rich in niter to be mined or quarried and treated directly for recovery of the salts. However, the fact that the salts are nearly always observed in ledges and cliffs which have been and now show evidence of being inhabited by bats or other nest-building animals leads to the very strong suggestion that the origin of the niter is to be found in comparatively recent organic agencies. If the niter salts have originated through decomposition of bat or other guano at the surface of the ledges alone, the deposit can scarcely be of sufficient extent to be of much commercial value. (As to origin see also p. 30.)

Niter salts near Railroad Valley.—Niter salts have been prospected, it is said, in some of the canyons bordering the west side of Railroad Valley, which is situated nearly in the center of the State. (See index map, Pl. I.)

## CALIFORNIA.

Williams<sup>1</sup> reports that fine samples of soda niter were taken from a deposit near Calico, San Bernardino County, Cal., and were said to have been sent to San Francisco for examination.

<sup>1</sup> Williams, Albert, Nitrate of soda: Mineral Resources U. S. for 1882, U. S. Geol. Survey, 1883, p. 599.

Gilbert Bailey<sup>1</sup> notes potash niter found in the desert northeast of Salton, Riverside County, Cal., and also mentions soda niter as crystals lining a cave in the Calico district.

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Other deposits which appear to belong to a class differing somewhat from the common or cave type have been recorded as containing nitrate salts of possible economic value. Gilbert Bailey<sup>2</sup> gives a rather full account of some extensive deposits of low-grade niter beds situated principally in Inyo County, Cal., along the lower valley of Amargosa River above its junction with the southern end of Death Valley. These nitrate beds have long been known, but continued prospecting seems to have failed to reveal material of sufficient richness or quantity to justify serious attempt at development.

A considerable number of analyses of these niter-bearing earths are quoted, some of which show high percentages of nitrate salts. It is understood, however, that average samples of these earths usually run low in their nitrate content, generally less than 1 or 2 per cent, the higher values being obtained from occurrences of comparatively local extent. These soils are presumed to have received their nitrate salts as the result of bacterial action on organic matter contained in the soils. In the dry desert climates the salts are supposed to have been brought in solution by capillarity to the surface, where by evaporation they are commonly deposited in rich nitrate-bearing saline crusts, their preservation there being chiefly dependent on the unusual dryness of the climate. The average content of the soil for any considerable depth would probably run very low. The localities of such deposits are listed by Bailey <sup>3</sup> as follows: "In Inyo County in the Confidence, Tecopah, and Upper Canyon beds; and in San Bernardino County in the Valley, Round Mountain, Saratoga, Lower Canvon, Salt Springs, and Owl Spring beds."

Other deposits of apparently similar occurrence are reported along lower Colorado River <sup>4</sup> about 30 miles south of Needles, Cal., and at places between that locality and Yuma.

Hilgard <sup>5</sup> describes some places in California where nitrates occur in the soil in exceptional abundance. Such, for instance, is an alkali tract lying in the bottom of Merced River in a local basin of impervious limestone surrounded by a low ridge which is only exceptionally overflowed by the river; so that even the salts that have bloomed out on the surface are not usually washed away. An analysis of this soil follows.

<sup>&</sup>lt;sup>1</sup> Bull. Cal. State Mining Bureau No. 24, 1902, p. 169 and map.

<sup>&</sup>lt;sup>2</sup> The saline deposits of California: Bull. California State Min. Bur., No. 24, 1902, pp. 154-180.

<sup>&</sup>lt;sup>3</sup> Op. cit., pp. 170-180.

<sup>Turner, H. W., The sodium nitrate deposits of the Colorado: Min. and Sci. Press, vol. 94, 1907, pp. 634-635.
Graeff, F. W., Nitrate deposits of southern California: Eng. and Min. Jour., vol. 90, 1910, p. 173.
<sup>5</sup> Hilgard, E. W., Alkali lands, irrigation, and drainage in their mutual relations: Rept. University Cali-</sup>

<sup>&</sup>lt;sup>5</sup> Hilgard, E. W., Alkali lands, irrigation, and drainage in their mutual relations: Rept. University California, College Agr., appendix, for 1890, 1892, pp. 25-26.

#### ARIZONA.

Composition of alkali salt from Merced bottom, Merced County, Cal.

Soluble salts in 100 parts of soil crust	1.00
Sodium sulphate (Glauber's salt)	3. 88
Sodium nitrate	10.72
Sodium carbonate (sal soda)	63.00
Sodium chloride (common salt)	1.21
Sodium phosphate	4.10

The following composition is quoted from Hilgard as representing the soluble salts in an alkali crust at the San Joaquin Valley Agricultural Experiment Station, near Tulare City, Cal.:

Composition of alkali salt in San Joaquin Valley, near Tulare City, Cal.

Potassium sulphate	3.25
Sodium nitrate	16.40
Sodium sulphate	20. 91
Sodium chloride	12.21
Sodium carbonate	27.02
Sodium phosphate	1.87
Organic matter	17.07
Ammonium carbonate	1.27
-	100.00

Bailey records <sup>1</sup> the occurrence of niter at several other localities, as follows:

Pilot. The Pilot niter district, located on the old beach line east of Searles-Lake, at the south end of the Slate Range. It takes its name from Pilot Peak, a famous landmark of the desert that is about 20 miles south of this district.

Danby. The existence of niter has been reported \* \* \* in the playa deposits near the salt beds at Danby Lake, and locations were filed upon the land in 1901.

Volcano. Locations covering 4,800 acres have been made along the old beach lines [of Lake Le Conte, the former high level of the Salton Sea] east of the Mud Volcanoes, in T. 10 S., R. 14 E. in this [San Diego] County. The few specimens brought in gave from 3 to 5 per cent of niter.

#### ARIZONA.

Lindgren notes the occurrence of gerhardtite, a nitrate of copper, in the Clifton-Morenci district, Arizona,<sup>2</sup> where this mineral is found in the cliffs of granite porphyry in the deeply eroded Chase Creek Canyon at Metcalf. He describes the mineral as formed by the trickling of atmospheric waters over and through rocks containing a small percentage of copper.

Dana also notes that gerhardtite has been found in the copper mines at Jerome, Ariz.

Potassium, sodium, and calcium nitrate are reported by Guild<sup>3</sup> from several localities in Arizona, as follows:

This well-known compound (niter,  $KNO_3$ ) is frequently formed on old walls, in caves, and on the sides of mine shafts, usually, however, in such small quantities as

<sup>1</sup> Bailey, G. E., The saline deposits of California: Bull. California State Min. Bur. No. 24, 1902, pp. 178, 180.

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<sup>&</sup>lt;sup>2</sup> Lindgren, Waldemar, Copper deposits of the Clifton-Morenci district, Arizona: Prof. Paper U. S. Geol. Survey No. 43, 1905, p. 121.

<sup>&</sup>lt;sup>8</sup> Guild, F. N., The mineralogy of Arizona, Chemical Pub. Co., Easton, Pa., 1910, p. 81.

• to escape observation. It is even said to develop in old mortars to the extent of 5 per cent (Dana, System of Mineralogy). The writer has observed it associated with sodium carbonate as a thin white covering on the surfaces of the overhanging limestone shelves in the ancient cliff dwellings of Walnut Canyon, about 12 miles from Flagstaff. The walls of the canyon here are made up of layers of soft and hard limestone, or more appropriately calcareous sandstone, which has disintegrated, yielding a series of shelves that have been very conveniently utilized as dwellings by the ancient inhabitants of Arizona.

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Nitrocalcite "is a hydrous nitrate of calcium sometimes met with in limestone caves, where doubtless an interaction has taken place between the calcium carbonate and bat guano or other organic compounds. A bacteriological action may also be concerned in its formation more or less direct from the atmosphere. It has been reported as occurring in the Mammoth Cave in Kentucky. A sample of this mineral mixed with a large quantity of earth was received at the University of Arizona during the summer of 1907 and identified as calcium nitrate by Dr. A. E. Vinson of the Agricultural Experimental Station. Correspondence with the sender of the sample brought the following interesting information:

"The calcium nitrate occurs in vents in the lower Carboniferous limestone, fissures that cut across the bedding planes and are therefore perpendicular. There are several of these vents grouped close together exposed to full view in the railroad cut facing the Gila River about 2 miles above Winkelman. The face at this spot is sheer wall about 100 feet high and the vents filled with the nitrate are visible from top to bottom. None of them are more than 6 to 8 inches wide, and the nitrocalcite seems to be mixed with red iron."

Cameron<sup>1</sup> quotes reports of nitrate deposits at Briggs, Yavapai County, Ariz.

## NEW MEXICO.

Nitrate salts are quoted by Cameron<sup>1</sup> as reported at Pena Blanca, near Mesquite, Dona Ana County, and at Queen, Eddy County, N. Mex.

Williams<sup>2</sup> states that nitrate of soda had been reported as occurring in the extreme southeastern portion of New Mexico in considerable quantity. "It is deposited here by a few springs, the greater number being in [the State of] Chihuahua, Mexico, just across the boundary line. No disposition is made of the product, beyond the shipment of a limited quantity to Chihuahua by Mexicans."

#### TEXAS.

W. B. Phillips has reported nitrate of soda in Candelaria, Presidio County, Tex., the type of deposit possibly being similar to that of the deposits in adjacent parts of Mexico, especially in the State of Chihuahua.

Potassium niter in Texas<sup>3</sup> is also noted as occurring in "tufts, masses, or incrustations in cave deposits from El Paso County, north

<sup>&</sup>lt;sup>1</sup> Cameron, F. K., A preliminary report on the fertilizer resources of the United States: S. Doc. No. 190, 62d Cong., 2d sess., 1912.

<sup>&</sup>lt;sup>2</sup> Williams, Albert, Mineral Resources U. S. for 1882, U. S. Geol. Survey, 1883, p. 599.

<sup>&</sup>lt;sup>8</sup> Simonds, F. W., The minerals and mineral localities of Texas: Bull. University Texas No. 5, 1902. p. 60.

of Van Horn, specimens of which were collected by E. M. Skeats. It is said to occur also in San Saba County."

Williams <sup>1</sup> quotes niter as occurring in caves in "Burnet, San Saba, and other counties to the west of them."

## BRITISH COLUMBIA.

Niter is reported in Canada<sup>2</sup> as having been found in cavities in calcareous tufa on Nazco River and at Big Bar, Fraser River, British Columbia.

## NITRATE SPECIMENS IN THE NATIONAL MUSEUM.

Specimens of niter from the Leucite Hills, Wyo., of calcium nitrate from Mammoth Cave, Ky., and of the white granular salt from Gerlach, Nev., are in the collections of the National Museum. Other than these the collections contain no examples of niter salts from the United States, although the German and Chilean localities are well represented.

## ORIGIN OF NITRATE SALTS.

#### PRIMARY SOURCE.

A general summary of the natural occurrence and of the chemical and geological relations of nitrogen compounds has been published by F. W. Clarke,<sup>3</sup> and from it the following review is chiefly obtained:

Nitrogen composes about three-fourths of the atmosphere, in which it is uncombined and essentially inert. In combined form in the earth's surface or in the ocean or other waters it forms an inappreciably small part. It is abundant in organic matter.

All the nitrogen in organic matter came originally from the air. Through the agency of microbes or bacteria certain plants withdraw nitrogen directly from the air. By decay or combustion of organic matter some of this nitrogen is again set free, and some remains in combined forms.

Salts of nitrogen occur in most soils, where they are necessary for the support of plant growth. They accumulate especially in cave earth, if there is an abundance of decomposing organic matter and if the soil is protected from the leaching action of surface waters. In some arid regions, as in Chile, nitrates exist in enormous quantities.

Oxides of nitrogen are produced by electrical discharges yielding with the moisture of the air nitric and nitrous acids. Nitrogen in the form of ammonia is also present in the air. Some volcanic waters contain nitrogen in the form of ammonium compounds.

<sup>&</sup>lt;sup>1</sup> Williams, Albert, List of useful minerals in the United States: Mineral Resources U. S. for 1887, U. S. Geol. Survey, 1888, p. 794.

<sup>&</sup>lt;sup>2</sup> Hoffman, G. C., Annotated list of the minerals occurring in Canada: Geol. and Nat. Hist. Survey Canada, 1890.

<sup>&</sup>lt;sup>3</sup> The data of geochemistry, 2d ed.: Bull. U. S. Geol. Survey No. 491, 1911, pp. 18, 40, 49, 109, 258-259.

#### OCCURRENCE IN SOILS.

Nitrogen exists in the soil in at least three forms—in organic material (albuminoid nitrogen), as ammonia or ammonium salts (ammoniacal nitrogen), and as nitric acid or nitrate salts (nitric nitrogen). The average amount of nitrogen present in agricultural soils is given by authorities as from 0.1 per cent to 0.3 per cent, though occasionally, as in certain soils rich in organic matter, reaching 4 or 5 per cent.<sup>2</sup> Hilgard, as elsewhere quoted (pp. 26–27), describes places at which nitrates occur in soil in California in exceptional abundance, and Headden has described similar conditions in Colorado (pp. 14–15).

## HYPOTHESES OF ORIGIN.

Probably the greater part of the nitrates contained in soils are the product of bacterial action. Doubtless some at least of the local concentrations of nitrate salts accumulated from this source. Organic substances decompose in the presence of certain nitrifying organisms which are almost everywhere available in soils and elsewhere, producing ammonia and then nitrous or nitric acid. In contact with the free air in a natural soil nitrates are finally produced. The nitrification takes place only in the presence of some base with which the acid formed will combine.

Attention may here be called to an apparent relation of salt produced to the character of the country rock in which the salt occurs. At Gerlach, Nev., and Grass Valley, Utah, the potassium nitrate salts are found in a brecciated country rock which is an acidic lava, rich in potash-bearing minerals. At Lovelock, Nev., the sodium base may have been supplied from residues left by the Lahontan lake waters. In the cave deposits of the Eastern States, which are mostly reported as occurring in limestone caverns, the common salt is calcium nitrate. Thus the nitrate salt is to a certain extent at least a product of decomposition or combination with the country rock in which it is found.

It is still an unsettled question as to how largely the volcanic hypothesis will explain the origin of nitrates either disseminated or in the more concentrated deposits. Ammonium salts and nitrides are undoubtedly present in volcanic sublimates. The association of borates with nitrogen compounds in salines or in solution is suggested as indicative of a volcanic origin for the nitrogen, since the volcanic origin of many of the borate occurrences seems fairly well established.

No generally accepted or satisfactory explanation for the origin of the South American nitrates appears yet to have been found.

Undoubtedly some or perhaps most of the accumulations of nitrate salts have been transported in water solution and owe their imme-

<sup>2</sup> Merrill, G. P., Rocks, rock weathering, and soils, 1897, p. 372.

diate position or condition to the manner of crystallization from the evaporating waters that contained them. Thus some deposits may have been formed by the evaporation of sea, lake, or spring waters, in which their ultimate origin is remote, or may have been accumulated through solution from bacterial or other sources near by.

## THE PROCESS OF NITRIFICATION.

The following is an extract from a treatise on industrial chemistry,<sup>1</sup> describing the history of the theories concerning nitrification and a summary of the conditions under which the nitrifying bacteria are active:

Nitrates are continually being produced in fertile soil; if they are removed by washing, they are speedily replaced by a fresh formation. The production is greatest in the case of well-manured soils.

The occurrence of potassium nitrate as an efflorescence on soils, rocks, and old walls, especially in hot climates, has long been known. East Indian saltpeter is obtained by lixiviating the soil surrounding the house drains in old villages (C. J. 1868, 318). The enormous deposits of sodium nitrate in the rainless table-land of Peru are of the highest technical importance.

The process of nitrification has in former years been artificially conducted on a large scale, nearly all the niter employed on the continent of Europe being produced in this manner. This manufacture is now superseded, saltpeter being produced more cheaply at the present time by the reaction of sodium nitrate with potassium chloride. The niter-yielding "beds" or "walls" formerly constructed consisted of porous earth, enriched with animal manure and wood ashes, watered at first with urine and afterward with water. After two years the niter beds were sufficiently rich in niter to be worth extraction; 1,000 pounds of soil might then yield 5 pounds of crude niter. General information regarding this manufacture will be found in Dumas's "Traité de chimie." The French mode of operation is described in detail in Boussingault's "Agronomie, chimie agricole et physiologie," 2, 1861, 23.

Numerous theories have been held as to the manner in which nitrates are produced in soil. It has been assumed that nitrogen gas is oxidized in a moist porous soil by ordinary oxygen or by ozone, or that ammonia is oxidized in a similar manner, or by the ferric oxide generally present in soil. Nitrogenous organic matter is supposed to contribute to the production of niter by acting as a source of ammonia or nitrogen gas. An account of most of the theories of this description will be found in a lecture on nitrification by Clöez (Lecons de chimie et de physique professées en 1861, à la Société chimique de Paris). The theories in question were in fact entirely unsatisfactory, as, although nitrogen, ammonia, and many nitrogenous organic bodies could be oxidized by powerful means so as to yield nitric acid, chemists were unable to produce this acid under the conditions of a natural soil unless soil itself was present.

The first suggestion that nitrification might possibly be due to the action of a living organism came from Pasteur in 1862. A. Müller, in 1873, suggested that the process was due to a ferment. Schloesing and Müntz, in 1877, satisfactorily proved that nitrification was the work of a living agent. They showed in this and subsequent communications that the nitrifying agent could be transplanted from one medium to another,

<sup>&</sup>lt;sup>1</sup> Thorpe, T. S., Dictionary of applied chemistry, vol. 2, 1891, pp. 698-700 (contribution by R. Warington). Abbreviations of the titles of journals and books referred to: A. a., Annales agronomiques; A. Ch., Annales de chimie et de physique; C. J., Journal of the Chemical Society of London; C. N., Chemicai News; C. R., Comptes rendus hebdomadaires des séances de l'Académie des sciences, Paris; Pr., Proceedings of the Royal Society.

that its action was strictly limited by the conditions necessary for the life and activity of bacteria, and that its function was destroyed by temperatures  $(55^{\circ})$  and reagents (as chloroform), which are fatal to such organisms. The principal papers of Schloesing and Müntz are C. R. 84, 301; 85, 1018; 86, 892: 89, 891, 1074. The main conclusions were confirmed by Warington (C.J. 33, 44), and afterward by many other investigators.

The nitrifying organism is one proper to the soil; it occurs also in sewage and in river water; it is usually present in air or rain. The organism does not occur in soil beyond a certain depth below the surface. In the heavy soil of Rothamsted, Herts, out of 39 samples of soil of about 0.2 gram each, taken at various depths down to 3 feet, only one failed to produce nitrification when introduced into a weak urine solution. At 5 feet one-half the samples failed to produce nitrification. Below 6 feet the soil had apparently no nitrifying power (C. J. 51, 1887, 118).

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Schloesing and Müntz attempted to isolate the organism producing nitrification. After making many successive cultures in weak sterilized sewage, they found finally remaining a small round or oval coccus, which they believe to be the organism in question. No satisfactory proof was, however, given that they had obtained a pure culture. Attempts to isolate the organism by cultivation on gelatin have failed.

Lately, P. F. Frankland (Pr. 47, 296), by employing the dilution method of isolation, has apparently succeeded in obtaining the organism in a pure state. When cultivated in an ammoniacal solution containing only mineral salts its form is that of a very short bacillus; grown in broth it becomes distinctly a bacillus. It is characteristic of the organism that when grown in ammoniacal mineral solutions it refuses to propagate on gelatin. From broth cultures a tardy growth on gelatin may be obtained. The organism is of very slow growth, and produces little, if any, turbidity in ammoniacal mineral solutions.

Still more recently the organism has been isolated by Winogradsky (A. de l'Institut-Pasteur, 1890, 213, 257). By successive cultivations in mineral solutions he has at last only two organisms present. In these he observed the formation of gelatinous clots at the bottom of the vessel; these clots possessed the power of nitrifying in a high degree. He collected these clots, washed them, and spread them on gelatin. After 10 days he seeded fresh ammoniacal solutions from those parts of the gelatin surface on which no growth had appeared. He thus obtained the organism pure. When young it is nearly round, but is most often ellipsoid; diameter, 0.9-1.0u; length, 1.1-1.8u. The longer ones show the strangulation preceding division; the form is occasionally spindleshaped, with blunt ends. Chains of three of four individuals are rare. There are no spores. The organism is generally immobile, and collected at the bottom of the solution in a mass of zoogleea; but for a short period in the course of nitrification a general mobility sets in, and the liquid becomes turbid; a day after the organism is again in repose. Provisionally, the author designates it a nitromonas.

Little is yet known of the action of the organism when alone, nearly all the experiments on nitrification hitherto made having been confessedly performed with a mixture of organisms.

The substances which are nitrifiable by soil, or in solutions seeded with soil, are very numerous; they include ammonia, ethylamine, urea, asparagine, thiocyanates, albuminoids, gelatin, etc. In every case apparently in which an organic substance is nitrified the formation of ammonia precedes the formation of nitrous or nitric acid, ammonia, or rather ammonium carbonate, is thus perhaps the only nitrifiable substance. Whether the nitrifying organism is itself capable of attacking organic matter and producing ammonia, or whether the action of other organisms is necessary to effect the preliminary formation of ammonia, is yet undetermined.

The products of nitrification may be nitrites or nitrates. When nitrification takes place in a natural porous soil, only nitrates are produced. Nitrites appear in soil only as products of roduction when air is excluded by an excess of water. When nitrification is started in a solution by the addition of soil, the oxidation may be purely

nitric in character, or nitrites may be abundantly formed in the earlier stages of the process, especially if the solution is strong, alkaline, and at a relatively high temperature; but in the end the nitrites are all converted into nitrates. If, however, successive cultures are made in sterilized ammoniacal solutions, starting with a solution nitrified by soil, a point is soon reached at which nitrites only are produced, and these nitrites never change into nitrates. An alkaline condition of the solution is highly favorable to this change in the character of the process. Some difference is thus established in the agent, and it is quite possible by seeding solutions from different sources to obtain a purely nitrous and a purely nitric process of oxidation in similar solutions and under identical external conditions. That the nitrites are not here a product of reduction is shown by their special formation in solutions of ammonium carbonate destitute of organic matter (v. also Munro's experiments, C. N. 56, 1887, 62). The nitrifying organism separated both by P. F. Frankland and by Winogradsky is found to be only capable of yielding nitrous acid. From these facts we must conclude, either that the oxidation of ammonia to nitrites, and of nitrites to nitrates, is a distinct process performed by different organisms, or that the original organism producing nitric acid in the soil becomes weakened by continued cultivation in certain soluions and loses its faculty of converting nitrites into nitrates. The true explanation is not yet known.

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The oxidizing power of the organisms in soil is by no means limited to the oxidation of ammonia or of organic matter. Müntz (A. Ch., May, 1887) has shown that iodides may be converted into hypoiodites and iodates, and that bromides undergo a similar change. The oxidation of iodides is not apparently a secondary reaction of nitrification, for it may take place in the absence of nitrifiable matter. It is interesting to observe in this connection that iodates occur in the deposits of sodium nitrate in Peru.

The conditions under which nitrification takes place have been pretty well ascertained. For the nitrifying organism to act with vigor the substances necessary for its nutrition must be present. We should suppose, according to the accepted ideas respecting the nutrition of such organisms, that a supply of organic carbonaceous matter would be necessary; we have already stated, however, that the nitrifying organism has been found to flourish and actively discharge its functions in purely inorganic solutions. Winogradsky has recently established this fact by rigorous experiments, and has shown, by determinations of carbon in the solutions, that the nitrifying organism is capable of producing organic matter from carbonic acid and ammonia without the aid of light. He suggests that, as in the animal body ammonium carbonate is converted into urea, so in this organism an amide may be the first compound produced.

For the nutrition of a living organism the presence of certain ash constituents is essential. It has been shown that nitrification can not take place in the absence of phosphates (C. J. 45, 641). The necessity for other ash constituents has not yet been made the subject of experiment.

The presence of free oxygen is essential to nitrification. Schloesing (C. R. 77, 203, 353) has determined the rate of nitrification in soil containing different proportions of water and maintained in atmospheres containing various proportions of oxygen. With soil holding 16 per cent of water a considerable amount of nitrification took place when  $1\frac{1}{2}$  per cent of oxygen was present in the atmosphere, but the rate of nitrification increases for four fold when 21 per cent of oxygen was present. An increase in the proportion of water to 24 per cent raised the rate of nitrification in atmospheres containing a small percentage of oxygen, the quantity of dissolved oxygen being thus increased.

For nitrification to take place there must be some base with which the nitrous and nitric acid produced may combine. When a solution of ammonium carbonate or urea is nitrified, the action proceeds till one-half of the nitrogen is oxidized and then

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stops, ammonium nitrite or nitrate being the final product. The whole of the ammonia is nitrified only when an excess of base is present. The substance which acts best for this purpose is calcium carbonate; this is also the base usually present in soils. If the solution to be nitrified contains a soluble alkali, nitrification is hindered if the alkalinity exceeds a very small amount, and does not commence at all when the alkalinity is still further increased. The highest degree of alkalinity which has been found compatible with nitrification corresponded to 368 parts of nitrogen as ammonium carbonate per million of solution. With sodium monocarbonate the limit was nearly the same; with disodium carbonate a much smaller degree of alkalinity sufficed to prevent nitrification. The same distinction was found to exist between the basic and acid carbonates of ammonium.

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It follows from what has been just stated that only weak urine solutions can be nitrified. In Warington's experiments a 12 per cent solution was the maximum strength nitrifiable. This fact must be borne in mind when liquid manure or gas liquor is applied to land. If, however, an excess of gypsum is added to urine before the introduction of soil, solutions of far greater strength may be nitrified, the gypsum reacting with the ammonium carbonate as soon as it is formed, ammonium sulphate and calcium carbonate being produced (C. J. 45, 653; 47, 758). The favorable influence of gypsum on nitrification has been noticed by several investigators.

The activity of nitrification is largely dependent on temperature. The process has been shown to occur at temperatures as low as  $3^{\circ}$ . As the temperature rises the rapidity of the action increases, the optimum temperature being, according to Schloesing and Müntz,  $37^{\circ}$ . Above this point there is, according to the same authorities, a rapid decline, very little nitrification taking place at  $50^{\circ}$ , and beyond  $55^{\circ}$  there is no action. The influence of temperature is a point requiring further study.

In the case of solutions, darkness is far more favorable to nitrification than light. When a solution is exposed to a strong light, nitrification ceases altogether.

In a moist, aerated soil, at ordinary temperatures, the nitrification of an ammonium salt commences almost immediately after its application. When, on the other hand, a few milligrams of soil are introduced into a relatively large bulk of a suitable ammoniacal solution, a period of several weeks may elapse before nitric or nitrous acid appears, after which time nitrification will proceed with rapidly increasing speed. This long, so-called "incubation period" is probably due to the slow growth of the organism, and the difficulty it finds in adapting itself to altered conditions. If, when nitrification is completed, the solution is decanted, and the bottle filled up again with an ammoniacal solution similar to the first, nitrification will now commence in a comparatively short time, and by repeating this operation nitrification may be brought to begin in a few hours. When two solutions of different degrees of concentration are seeded with soil at the same time, nitrification will always commence first in the weaker solution.

The process of nitrification is suspended by a high temperature  $(55^{\circ})$ , and by the presence of chloroform, carbon disulphide, phenol, mercuric chloride, and other bodies which are injurious to the life of bacteria. The drying of a soil, even at a low temperature, is fatal to the nitrifying organisms which it contains.

If both organic matter and denitrifying organisms are present, all nitrates present may be destroyed; the nitrifying organism is, however, uninjured, and will resume its activity as the organic matter disappears.

Natural soils and river waters usually contain both nitrifying and denitrifying organisms, and the character of the process which occurs is determined by the conditions of the moment. The same soil which rapidly nitrifies when in a moist, aerated condition, becomes a vigorous denitrifying medium when waterlogged. The nitrifying river water becomes denitrifying when polluted with sewage. The products of denitrification are various, according to the nature of the organisms present; nitrites, nitric oxide, nitrous oxide, or nitrogen gas may be produced. In the case of the three lastVALUE.

named products there is, of course, a loss of nitrogen in the form of gas. For the literature of the subject v. C. J. 53, 1888, 742. Müntz has shown that chlorates, bromates, and iodates are reduced equally as nitrates.

The following references may be of use:

The conditions of nitrification, Schloesing (C. R. 77, 203, 353), Warington (C. J. 35, 429; 45, 637), Munro, (C. J. 49, 632); The nitric acid in soils, Lawes, Gilbert, and Warington (J. R. A. S. 1883, 331), Lawes and Gilbert (C. J. 47, 380), Dehérain (A. a. 1888, 287); The nitrification of manures, Dehérain (A. a. 1887, 241), Schloesing (C. R. 109, 423, 883); The nitric acid in drainage and well waters, Lawes, Gilbert, and Warington (J. R. A. S. 1881, 241, 311; 1882, 1; C. J. 51, 500).

## SUMMARY.

As explained in the foregoing pages, nitrogen exists chiefly as the uncombined gas that forms the greater part of the atmosphere. In relatively much smaller proportion, however, it occurs combined in three forms, namely, in organic matter, as ammonia and ammonium salts, and nitric acid, and nitric acid salts or nitrates. The agencies which are known to accomplish the conversion of the inert gaseous nitrogen into the combined forms are the assimilating action of growing organisms (plants and animals); the action of microbes or bacteria; and fixation by the discharge of electricity through the air. The occurrence of ammonium salts in volcanic waters is noted without an attempt to explain the origin of the salts.

The present paper is intended to deal chiefly with the nitrogen salts known to occur in nature in the nitric acid or nitrate form.

The extreme solubility of nitrate salts renders it unlikely that concentrated deposits will remain anywhere except in places not subject ` to or protected from the solvent action of rain, surface, or moving ground waters. Thus nitrate salts are found chiefly in caverns, caves, or under overhanging ledges, or, as in the Chilean and other South American occurrences, in a region of most exceptional aridity.

The frequently reported deposits of nitrate salts in caves or overhanging ledges in this country as well as elsewhere probably constitute 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.

### VALUE OF THE DEPOSITS.

By far the greater part of the nitrate salts formed are probably carried off in solution by water and distributed or lost sooner or later, and only in the few most favored localities are the crystalline salts themselves retained. Hence it seems fair to assume that most of the reported occurrences of these salts are of little or no economic value. This opinion appears to be to a certain extent confirmed by

the history of nearly every attempt to develop such deposits. Many fine specimens or samples showing high percentages of nitrate salts are obtained, but the deposits do not continue into the mass of the rock, and only rarely can sufficient material for a single shipment be collected.

Nevertheless an assertion that none of the nitrates of this or similar types of deposits will prove commercially workable is probably not warranted. Such deposits have proved to be of value under exceptional conditions, as when they were utilized for the manufacture of gunpowder, during war times, in the Eastern States; and it is entirely possible that changing conditions may render some of the western deposits valuable. It must be recognized, however, that so far as may be judged from present evidence, few, if any, of the known deposits at present warrant much outlay for development as a source of commercial nitrate salts.