

CALICHE. A STUDY OF THE SO-CALLED DESERT LIMESTONE OF ARIZONA.
WERE BIOLOGICAL FACTORS CONCERNED IN ITS DEPOSITION?

1920-21-22

By

Stuart W. Griffin

A THESIS

Presented to the Faculty of the University of Arizona
as a Part of the Requirements for the Degree of
Master of Science.

1920

CALICHE. A STUDY OF THE SO CALLED DESERT LIMESTONE OF ARIZONA.

WERE BIOLOGICAL FACTORS CONCERNED IN ITS DEPOSITION?

CALICHE-ORIGIN OF THE TERM.

The word caliche, doubtless originally of Latin derivation, although more recently traceable to the Spanish, is loosely employed by the residents of the southwestern United States and Mexico in referring to layers of rather dense crystalline formation which frequently crop out on the surface in these regions. The late Professor William F. Blake,¹ Geologist and one time Director of the Arizona

¹

Caliche of southern Arizona *Trans. Am. Inst. Min. Eng.* 31, 1901, pp 220-226.

School of Mines, whose classic will frequently be quoted by the writer, suggests that this term has been taken from the Latin "Calx", which would be entirely appropriate to the calcareous beds in question.

OCCURENCE - STRUCTURE - COMPOSITION OF CALICHE.

The caliche under consideration is a limy formation and of hardness varying from that of solid rock to loosely cemented sand and gravel which may be crumbled between the

✓

fingers. These calcareous layers are not to be confused with the soluble saline crusts of Chile salt-peter (impure sodium nitrate) occurring in South America, and known also among the native there as caliche.

In the southwest large areas of mesa² land are

2 Twenty-seventh Annual Report, Arizona Agricultural Experiment Station, 1916, p. 298.

underlaid at various depths by deposits of lime-cemented soil, sand and gravel commonly called caliche, but recently named "desert limestone" by geologists. More frequently it is hidden from view by a few inches to several feet of soil, although it is not uncommon after the torrential rains of July and August to see the bare light buff or whitish formation revealed on the surface. Often it occurs as a continuous sheet from two to several feet in thickness. Because of its dense character caliche takes water poorly and harder layers are extremely resistant to root penetration. The nearness of these deposits to the surface doubtless accounts in large part for the scarcity of trees over considerable areas. Consequently the vegetation which gains a foothold and persists must of necessity be shallow-rooted and adapt itself to scarcity of water. The creosote bush and certain kinds of cacti may be cited as natural vegetation which have demonstrated their ability to survive, even under these most unfavorable and trying growing conditions.

Although these regions, because of the caliche, are less valuable for agricultural purposes, chemical analyses³

3 Twenty-sixth Annual Report, Arizona Agricultural Experiment Station, p. 567.

show caliche to be reasonably well supplied, at least with the mineral plant foods. Where covered with a fair amount of soil, these desert limestone regions may become increasingly important in the production of special crops, such as guayule and desert olives. Blake⁴ further states

4 Loc. cit.

"~~that~~ the top of the caliche is more dense than the lower portion. The surface of this top crust or layer is comparatively smooth though undulating, while the lower portions under the crust are irregular, cavernous, earthy and very porous, blending gradually with the materials of sandy and gravelly beds from which they are divided by no sharply defined plane of stratification or separation. The caliche invests, surrounds, and includes sand grains, gravel, and more or less earthy material, and seems to have had the power especially in its upper crust of extruding the coarse material of the soil to a great extent. The deposit does not form a regular horizontal bed conformable with the rude stratifications of the gravels and sands, but conforms roughly with the general surface, rising and falling with the undulations of the mesa. These are in places repetitions of the compact layers separated by a few inches of amorphous and more earthy deposits. In cross fracture this upper crust

Of the caliche exhibits distinct fine lines of successive layers in thin sheets along which the rock splits with some ease. Close observation detects in some places small perforations like pin holes at the top, which enlarge gradually below and penetrate the entire compact crust, becoming lost in the irregular amorphous granular mass. These holes are often occupied by rootlets of plants." It must be stated here that the writer had great difficulty in finding samples showing the pin holes mentioned above.

The above exhaustive description corresponds in the main with the observations of the writer and those of Dr. A. E. Vinson for many years Chemist of the Arizona Agricultural Experiment Station under whose guidance and direction this research was undertaken. However, there are certain minutiae of structure which apparently either escaped Professor Blake's observation or were not in his opinion of sufficient importance or bearing on the problem to warrant mention.

The mesas or high planes of Tucson and vicinity are typical of the occurrence of caliche. The surrounding mountain ranges include the so called valley of several hundred square miles, penetrated by two channels of drainage, the Santa Cruz and the Rillito. Both of these streams, during considerable portions of the year, run "upside down"; that is dry on the surface, but exhibiting an underground flow, especially strong near the channels and including, with less and less intensity, the outlying areas. The Tucson

valley was filled during past ages with wash from the mountains which seems to show a preponderance of granitic and basaltic rock. The mountains were once higher and more precipitous than at present and the valley relatively lower and deeper. Thus the material now constituting the floor of the valley was at one time largely an intergral part of these ranges.

Characteristic well logs for the higher mesa lands of this section show a stratum of hard caliche underlying the soil from a depth of a few inches to five or six feet; sometimes more, sometimes less. Beneath this there may occur several feet of a mixture of fine earth, sand, and gravel - sometimes relatively loose, sometimes cemented- and of such nature that it can be broken up with a pick only with the greatest difficulty. Somewhat paradoxically, this material is more difficult to excavate than the very dense hard cap so frequently found at the top of the caliche layers. The explanation probably lies in the relative thinness and brittleness of the hard shell or cap compared to the less dense, but tougher formation below. At greater depths caliche may again be encountered, but generally of a softer variety. Below this may be found layers of cemented sand and gravel, but rarely if ever the dense calcareous layer characteristic of the surface. If the well is continued to sufficient depth, good water is almost invariably found. The depth

as a rule decreases with the decrease in elevation as we approach the river bottoms.

Chemical analyses of caliche have shown it to be in large part carbonate of lime, including varying amounts of potassium, sodium, magnesium, iron, aluminium, phosphates, silicates, sulphates, and other compounds. Analyses are given on page

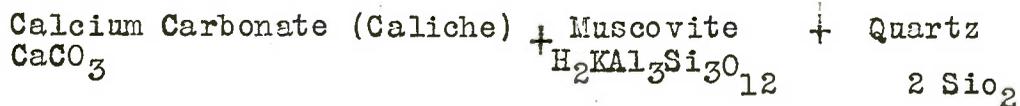
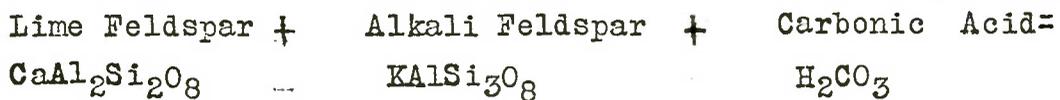
ULTIMATE ORIGIN OF CALCAREOUS MATERIAL PREDOMINATING IN CALICHE.

There has been considerable speculation concerning the probable method of deposition of these calcareous layers as they are now found, and numerous arguments presented pro and con in support of and in objection to the various theories advanced. In so far as the writer has been able to determine, none of the propositions put forward up to this time has had the undivided support of the geologists, mineralogists and chemists who have taken the time and trouble to make first-hand investigations and to look up the rather scarce literature now available on the subject. Although these different theories do obtain as to what has happened subsequently, it appears there is a general concurrence of opinion as to the ultimate origin of the calcareous matter, some of which later was laid

down as caliche. As stated by Guild⁵ "This calcareous

5 Mineralogy of Arizona pp. 49-51.

matter owes its ultimate origin to the decomposition thru the influence of dilute solutions of carbonic acid, of complex calcium silicates of the soil and rock. The following reaction is given as illustrative:



The above reaction is interesting in that it explains the formation of the chemical compound calcium carbonate. We are now free to speculate as to what may have happened to this calcium carbonate subsequent to its chemical formation. Physical, chemical or even biological phenomena may now intervene and, in conjecture at least, calcium carbonate may undergo numerous experiences before it is finally deposited as the most important constituent of what is revealed to us today as caliche.

PURPOSE OF THIS RESEARCH

It is not the purpose of the writer to attempt a geological research or dissertation. The various geological theories will be stated, and in connection with these it is proposed to introduce several purely chemical relationships established by analyses by which we had hoped to render plausible a theory that calcareous algae may have functioned in connection with the elaboration of the lime cementing material of which the thin dense caps, characteristic of a certain form of caliche, are very largely composed.

SOME THEORIES REGARDING DEPOSITION OF CALICHE

Blake's Theory

Professor Blake⁶ assigns the source of caliche to conditions

⁶ Loc. cit.

of mild aridity in Arizona which cause the ground water to be drawn by capillarity upward towards the surface and there evaporated. Blake supports this opinion by analyses of the well waters in the vicinity where he made his study. These waters he found to be charged with the mineral constituents of caliche, which upon evaporation would result in the deposition of a surface crust, mainly lime carbonate. Therefore, Professor Blake regarded "the presence of caliche over extended areas in arid regions as good evidence of the

existence of subterranean water." He further states that "the occasional rains in mid-summer and mid-winter do not penetrate to great depths, but are sufficient to leach out the soil to a depth of a few inches or feet, turning the calcareous solution back and downwards and producing the denser upper crust where it meets the upward flow. It may be called a subterranean deposit of travertine; but it is not the result of a flow from springs, or from any source at the surface, nor is it formed by the lateral movement of water. Unlike ordinary travertine it is the result not of descending, but of ascending currents." Such he conceives to be the origin of caliche.

Again certain investigators have stated that these deposits are easily and fully explained by the evaporation of some ancient lake, covering, in ages past, the region where the crust is now found. Most scientists now agree that this theory is untenable when all the phenomena are considered; at least some other factors being operative in addition to that of simple evaporation of meteoric or other water in situ.

Guild's Ideas

Professor F. H. Guild⁷ holds that the caliche layers near

7 Loc. cit.

the surface are due to the evaporation of meteoric waters in situ; while the deeper seated layers are accounted for by "the evaporation of waters brought up by capillary attraction to some definite position which depends upon local conditions, such as fineness of material, pressure, etc. In either case the deposition takes place beneath the surface and never precisely upon it." This sub-surface evaporation being caused, according to Guild by the quick drying condition obtaining here after a rain. The sun rapidly drying out the surface, forming in effect a mulch and preventing further action of capillarity. At this point evaporation begins and capillary attraction ends. Repetition of this action finally builds up a deposit of considerable thickness which upon careful examination will show faint stratifications as might be expected from such a method of formation. Repetition of caliche beds in the Tucson valley he believes to be due to the probability that under-ground waters once occupied higher levels than now. Evaporations at points slightly above these levels would account for the alternate layers.

Forbes' Theory

Dr. R. H. Forbes, formerly director of the Arizona Agricultural Experiment Station recognizes only the descending percolation of the mineralized water. He believes that all of these deposits deep and shallow were likewise formed by evaporation of rain water which having become carbonated had then dissolved mineral constituents from the soil, percolated downward several feet then evaporated leaving the limy deposit.

In a statement to Professor Tolman⁸ Dr. Forbes

8 The Geology of the Vicinity of Tumamoc Hills p. 73

argues in substance as follows:- Caliche may be considered roughly as a mixture of clay (colloidal) and of carbonate of lime. Carbonated rain water puts the former in the condition of suspension and the latter into solution. In these forms clay and calcium carbonate were carried three or four feet into the desert soils by occasional rains. The arid atmosphere then dries out the soil and at the average level of such drying a more or less compact caliche stratum is formed. In situations where the soil surface is filled in later, frequently new caliche strata are formed just below each new soil level, the most recent formation being found nearest the surface, the older ones below. Forbes finds support for this contention in well borings near Tucson.

Tolman's Theory

Dr. C. F. Tolman⁹ one time Professor of Geology in the

9 Loc. cit.

University of Arizona agrees with Forbes in part, making certain reservations and modifications. Tolman recognizes not only the downward percolation of the water, but also calls attention to a subsequent drawing up to the surface by evaporation. He believes that this evaporation operates "whenever the drying out of a soil after rainfall overtakes the downward percolation of the water and taps the reservoir of moisture that is retained even under arid conditions, just under the porous soil surface. To develop crust there must be some ready supply of calcareous matter and therefore no active underground drainage to remove the same. In the vicinity of Tucson the widely distributed Paleozoic limestones were the source of much of the calcareous cement of the soil. As the gravel deposits are accumulated the caliche layers are built into them and slowly recrystallized by the percolation of the deeper water." Tolman goes on to state that caliche develops very rapidly giving as illustrative material an instance in which the natural deposit was broken up, old lime and brick mixed in and the whole leveled and packed. Vegetation was kept down and the surface was frequently flooded, the idea being to

keep it packed. After an interval of two years examination revealed the development of two inches of typical caliche crust within half an inch of the surface. In other instances where the ground was not flooded the caliche was recognized with difficulty.

Lee's Statements

W. T. Lee¹⁰ in an exhaustive study and report on

10 Underground Waters of the Salt River Valley, Arizona, U. S. Geol. Survey, 1905, pp. 107-111.

subterranean conditions near Phoenix discusses caliche at length. Lee believes that under certain conditions the conceptions of both Blake and Forbes may be in accordance with fact. However, he also cites various cases in which the ideas of one or either of these earlier investigators would be untenable unless materially modified. As another probability relative to the method of its deposition he argues that when caliche is relatively free from foreign material it may be cemented to such compactness that it becomes impervious to water. As a result, in the Salt River Valley, water is frequently found under pressure, due to confining strata of this

dense cementing material. Bicarbonates are found in nearly all waters of this region. This means an excess of carbon-dioxide resulting in a temporary solution of extra carbonates. A relief of pressure alone has been proven enough to allow the escape of the carbon-dioxide causing the soluble bicarbonates to change to comparatively insoluble carbonates which are then deposited. It is, therefore, entirely possible that under certain special conditions deposition of caliche may take place at practically any depth beneath the surface (neither Blake nor Forbes recognize this) where the pressure upon water is sufficiently relieved for the escape of carbon dioxide gas. Lee goes on to note various experimental observations in support of this postulate.

It occurs to the writer that such a relief in pressure and lessened solubility of solute would result in the phenomena of crystallization from solution and, therefore, microscopic analyses of such a specimen should reveal a distinctly high proportion of readily recognized crystals of calcium carbonate. As a matter of interest it may be mentioned that such material has previously found its way into the Experiment Station Laboratory and has been examined microscopically. Specimens sent from the San Simon Valley, Cochise County, proved to be almost

pure crystals of prismatic calcium carbonate, having somewhat the form of diatoms. This sample was also sent to Washington and this opinion confirmed by the Smithsonian Institution. However, the physical nature of this material would probably preclude its being recognized as a form of caliche, the substance being comparatively light and loose in nature. These particular crystals may or may not have been thrown out of solution by relief of pressure in the method outlined by Lee. Nevertheless, the fact remains that simple crystallization from solution does account for deposition of calcium carbonate in certain cases in Southern Arizona. The writer calls attention to this point in support of the proposition that no single theory or hypothesis will eventually be found adequate in explanation of the various phases of the problem. The deposits of calcium carbonate, more or less impure, occurring in this region may rationally be explained in a multiplicity of ways. The clue to the particular mode of formation in a given locality may be sought in a careful study of the properties, both physical and chemical, of the material at hand. Given an almost inexhaustible supply of calcareous matter on which to work under such a variety of climatic conditions as are supposed to have obtained in the southwest in the eras past, would it not be somewhat remarkable if a single theory could be formulated which would unerringly fit conditions in each and every case.

We believe that simple crystalization did doubtless occur in some instances: that Blake's interpretation may in some cases be tenable, in which he assumes a more or less definite underground flow bringing the materials thru underground passages in solution from a distance to the place where they are left by surface evaporation; that Forbes may be correct in that, granting a given set of conditions, calcareous materials are taken into solution at or near the surface by carbonated rain water and subsequently deposited by evaporation only a little distance below. Accepting Forbes postulate as all inclusive we should want to know about the deposition of caliche in subterranean cavities where evaporation would be^a negligible factor.

We might wish to inquire from Blake an explanation of the presence of caliche far up on the hill sides beyond the reach of any permanent supply of underground water. In such cases wells have been sunk thru the upper courses of the caliche and then two or three hundred feet before water is reached. It is almost inconceivable that underground erosion would have lowered the water from a few feet (necessary for capillarity) to several hundreds of feet below the surface. Caliche at the surface of a

high dry plain can hardly be due to a permanent underground water supply.

It would appear that there are causes not yet recognized which have functioned in certain instances and under certain peculiar conditions in the deposition of impure calcium carbonate.

Caliche According To Cleland

In Cleland's well known text¹¹ we find him

11 Geology Physical and Historical 1916, p. 62.

referring to the desert limestone of the southwest U.S. and of Venezuela S.A. He apparently accepts the opinion of Blake in that in "arid regions the underground water may by capillarity bring to the surface large quantities of lime which upon evaporation are deposited as desert limestone."

Vinson's Theory

In 1916 Vinson proposed the idea that the dense

12 Loc. cit.

caps frequently topping off caliche layers were of organic origin. It was in reference to possible application to this theory that the analytical work done by the writer was accomplished. Dr. Vinson has kindly given the writer

the following statement relative to his conception of the origin of the dense calcareous cap:- " In the Twenty-seventh Annual Report of the Arizona Station I advanced a new theory for the formation of caliche, in which I attributed it to biological processes similar to those acting in forming other tufas known to be of organic origin. In this theory I do not attempt to account for the source of calcium carbonate. While it usually occurs as a cementing material in masses of sand and gravel or as a cap immediately above such deposits, places are known where the calcium carbonate was evidently formed by chemical precipitation as prismatic crystals. In other localities soft caliche without cap occurs. These range from soil with lime content to nearly pure calcium carbonate.

Theories of caliche formation in general refer to the cemented sand and gravels with dense highly calcareous caps. Such theories attribute the deposition to evaporation, either of water brought up by capillarity from the ground water or the return of rather shallow penetrating meteoric water. In either case evaporation is presumed to take place below the surface, giving rise to the hard cap at the point where capillary water repeatedly changes to vapor. These theories are not consistent with certain facts easily observed. First: The caps are laminated, being made up of layers of differently shaded material showing frequent changes in the character of silt and clay that were deposited with the carbonate of lime. They often

contain pebbles of considerable size, having laminations of approximately the same thickness entirely encrusting them. These pebbles are cemented in the cap while thousands of similar neighboring pebbles lying in contact with the cap are in no way cemented. This can be explained only by assuming that the cap was formed at the surface, and growth stopped when it became buried under the overlying soil or under fresh deposits of massive caliche. Second:- The caps are quite free from coarse materials with the exception of the scattering pebbles just mentioned, and range from thin crusts to nearly an inch in thickness. They may be traced without a break for considerable distances in open cuts. It is difficult to imagine the formation of such caps beneath the surface since this would necessitate the displacement of the former gravelly soil by a considerable thickness of calcium carbonate with its accompanying silt and clay clearly coming from different sources. Third: The successive caps do not run parallel, but within a few feet may vary a foot or more to only a few inches apart. Places may even be found where one cap directly touches the other. The lower caps show as perfect preservation of their well finished surfaces as the upper caps. It is almost inconceivable that such large amounts of calcium carbonate in solution could have been passed thru a lower cap without having seriously disintegrated the same. Neither could meteoric water

have traveled downward thru one cap, dissolve calcium carbonate and returned to build up an upper cap without having left evidence of its action on the lower cap.

Fourth: Generally, although not always, each cap is overlaid with a thin layer of uncemented soil. This soil layer is non-adherent to the cap and if overlying caliche and caps could be removed, the cap in question could be swept clean. The bottom of the dense caliche overlying one of these soil layers is an exact cast of a rough soil surface. After varying thickness of the massive caliche a new cap is formed. This condition may be repeated several times near the surface of the caliche as we now find it. Caps are almost wanting in the lower massive part of the formation, but frequently thin crusts, apparently abortive attempts at cap formation, may be traced some distance.

While the facts cited militate strongly against sub-surface formation, at least of the cap, they are entirely consistent with biological origin. The mass of caliche may have been formed by the cementation of gravels by evaporation of precipitation, but during periods of relative calm with little or no detritus being added to the valley fill, algal growth may have covered the rough surface and built up the dense caps. The laminations could have originated from silt carried by calcareous waters or have been due to atmospheric dust. Accidental pebbles finding their way into

the algal beds would have been cemented in the manner described. Considerable addition of fresh soil material would have interrupted the algal growth and stopped the formation of the cap. Lenticular deposits of fresh material appear to have been deposited and cemented, perhaps by algae, till another favorable period permitted the growth of a new cap. This would account for the close approach of one cap to another without in any way affecting the lower cap. Algal secretion of the cap also accounts for its uniform formation over curved and impervious surfaces such as those of the imbedded pebbles or rocks."

The older theories of caliche formation by sub-surface segregation seem inadequate to explain the presence in one case of uncapped, more or less tightly calcareous cemented subsoils and in another of rock-like capped caliche while highly calcareous gravelly loams without underlying caliche formations still exist in the same general region. It would seem that such causes as solution percolation, capillarity and evaporation acting under almost if not entirely identical climatic condition would have produced similar results."

In his earlier report of 1916 Vinson mentions other observations rendering the biological theory plausible. "Leaking hydrants supplied with the hard Tucson city water rapidly become covered with lime secreting algae and deposits of appreciable thickness are soon formed. These

deposits can not be due to evaporation. On the contrary flowing hydrants on the University grounds supplied with the less hard slightly black alkaline water form only light lime deposits. On hot summer days with intense insolation caliche roads under lawn sprinklers become green with algae (probably lime secreting) in two or three hours. If these deposits were continuous and extraneous matters were introduced undoubtedly caliche like deposits would be formed."

ALGAE, PROVEN AGENCIES IN DEPOSITION OF CALCIUM CARBONATE

As it is now a generally accepted fact that biological agencies are very commonly instrumental in the laying down of calcium carbonate deposits, the writer would not consider it appropriate in this paper to enter a lengthy dissertation in development and support of this phenomena. Johnston and Williamson¹³ inform us that "Organic agencies

¹³ Journal of Geology, 1916 pp. 279-737

are doubtless the predominant occasion of the deposition of calcium carbonate ~~and~~ and are in part a biological question." In this paper the abstraction of free carbon dioxide from fresh water by growing plants is referred to as an established principle and attention is called to the researches of Murray who says that " the calcareous algae common in the warmer oceans no doubt secrete their skeletons in the same

way. " In 1918 Marshall A. Howe¹⁴ published an article,

14 Publication 213 Carnegie Institution of Washington
pp. 291-296.

entitled "Calcareous Algae from Murray Island, Australia",
in which he discusses in detail these interesting and re-
markable plants. J. Claude Jones devoting several pages
to "The Tufa Deposits of the Salton Sink"¹⁵ shows that

15 "The Salton Sea "Carnegie Institution of Washington
pp.79-83

algae are at present engaged in building up calcareous
tufas and in the past have in all probability been re-
sponsible for the ancient tufa formations. In his bib-
liography Jones among other references sites the work of
W. H. Weed¹⁶ in which it is shown that the "algae associated

16 "Formation of Travertine and Siliceous Sinter, By The
Vegetation of Hot Springs." U.S. Geological Survey, Ninth
Annual Report , p. 619.

with the tufas are known to produce calcareous deposits
elsewhere." The above mentioned phenomenon in application
to the deposition of the limy incrustations on the branches
of submerged brush, stones and other objects in the present
Salton Sea is accepted also by Dr. D. T. Mac Dougal in his
monograph "A Decade of the Salton Sea".¹⁷ That calcareous

17 Reprint from the Geographical Review, Vol. 3. No. 6,
June 1917.

algae are not limited to saline water has also been demonstrated beyond question¹⁸. Relative to this point Dr.

¹⁸ Effect of Algae on Bicarbonates in Shallow Reservoirs.
Journal American Water Works Association II 1915, p. 703.

Vinson's statement concerning limy deposits associated with algae on leaky Tucson hydrants is recalled.

CHEMICAL ANALYSES AS CRITERIA

It is an established principle that chemical analyses when carefully studied and interpreted with reasonable modification may be used as criteria¹⁹, not only proving identity

¹⁹ Bastin. Journal of Geology 1909 pp. 445-472, also Journal Geology 1913, pp. 193-201. "Chemical Composition as a Criterion in Identifying Metamorphosed Sediments."

of rock formations, but in revealing information as to their mode of deposition. However, the chemist in so doing must of course give adequate recognition to the established principles of physical, geological and biological science obtaining in general and not irrelevant to the problem at hand. The pages of geological and mineralobical literature are full of analyses made by the chemist, and chemical data is constantly employed in settling the various controversies engaged in by the followers of one theory or another .

The writer does not share the opinion of certain investigators that chemical analyses may be irrelevant to the particular phase of the research in which he is now engaged, nor does he grant the necessity of developing proof of this point before proceeding further. It appears that in caliche we have a problem in which geologists are notably at variance one with the other and concerning which mineralogists have not so far introduced supplementary evidence sufficiently definite to settle the question. It would seem to the writer that there are cases where deposition of caliche takes place from causes not as yet recognized, or at least not pointed out in particular, previous to Vinson's studies.

COMPOSITION OF TUFA DEPOSITS OF THE SALTON SINK

Reasoning from the observations of a decade on the water of the Salton Sea, Vinson was lead to suspect the biological origin of at least certain of our caliche layers. Since 1907 he has been engaged in annual analyses of these waters in cooperation with the Desert Botanical Laboratory of the Carnegie Institution and has noted among other interesting facts ²⁰ that calcium carbonate, potassium and

20 Unpublished Paper by A. F. Vinson and S. W. Griffin
"(The Fate of Potassium and Phosphorus Lost from the Water of The Salton Sea)"

phosphorus had failed to concentrate in the same ratio as

the total dissolved salts. The ratio of potassium and sodium slowly decreased from about 1:48 to 1:90. In the early analyses of these waters it was possible to obtain from one or two liters sufficient of the yellow ammonium phosphomolybdate to make a weighing. A few years later no evidence of phosphorus could be obtained from three liters of water.

It has been shown by Jones that the tufas (encrustations on submerged brush) of the Salton Sink have been deposited by algae and that calcium carbonate disappearing from the Salton Sea could be accounted for in these tufas. In connection with this study I determined the potassium, sodium and phosphorus of the old travertine of the ancient lake known as Blake Sea and also the recent calcareous encrustations on the submerged mesquite brush of the present Salton Sea. These analyses were done mostly in triplicate and the results averaged as follows:-

SALTON SEA TUFAS

% _____	P ₂ O ₅	K	Na	Ratio K to Na
Old Ledge	.126 .123 .125	.19 .20 .21	.16 .17 .15) 1: . 79
Average__	<u>.125</u>	<u>.20</u>	<u>.15</u> .16	
	<u>.092</u>	<u>.15</u>	<u>1.31</u>	
New Deposits	.086 <u>.083</u>	.21 <u>.21</u>	1.22 <u>1.26</u>	1:6.6
Average __	.087	.19	1.26	

The high sodium content of the recent tufa deposit and the resulting low potassium-sodium ratio is doubtless due to the branches being removed from the sea water without rinsing. The older ledge, having been repeatedly subjected to the rinsing action of rain water, has lost much of the sodium that it originally contained. Such discrimination in dissolving effect or selective leaching, as it may be styled, has been proven to occur by Watson.²¹

21 Abstraction of Potassium During Sedimentation, p. 6.

Dr. of Philosophy Thesis University of Virginia.

Under certain peculiar conditions factors other than those of simple solubility are operative. Even in the case of the new deposits the potassium-sodium ratio is something like 1:6 compared with a similar ratio of 1:48 to 1:90 in the case of the water from which these elements were being removed. Thus coincident with disappearance of potassium and phosphorus from the Salton water there are found appearing these tufa deposits comparatively high in the elements being lost from the water. These deposits are admittedly the cause of calcium carbonate disappearing from a solution by no means saturated with that compound or the corresponding bicarbonate. The presence of algae explain this phenomena. Calcareous

Methods of analyses. Ten grams of the dry pulverized sample was leached for ten hours with constant boiling point hydrochloric acid as required for soils in the methods of the Association of Official Agricultural Chemists. The resulting solution (after removal of dissolved silica) was made up to 250 c. c., and 50 c.c. used in each case for potassium, sodium and phosphorus determinations, as per methods A. O.A.C.

matter was extracted from the water, used and deposited by these plants. Now the writer wishes to point out that other important elements are in the same category with the lime, as far as their relation to the algae and to the tufa deposits is concerned. The analyses of these tufas linked up and compared with the past work of Vinson on the waters shows almost unmistakably that both phosphorus and potassium should also be recognized as having been extracted from the water, used and then laid down with the lime by the algae. The writer is unable to find literature either for or against this proposition. It appears that in case analytical work has been done paralleling that under discussion such work has not been published. # However, it would occur to any one that, unless the corner stone of our agriculture science is unsound, both potassium and phosphorus as well as calcium should enter into the metabolic processes of the lime-secreting plants.

⁷/₇
 An analyses made in 1912 by C. H. Catlin and appearing in "The Salton Sea" published by the Carnegie Institution showed the following general composition of the incrustation on the woody stems and stones taken from the present sea. Determinations of potassium, sodium and phosphorus were evidently not undertaken.
 Water (at 110° C = 2.02; SiO₂ = 3.56; FeO & Al₂O₃ = 1.68; CaSO₄ = 3.47; CaCO₃ = 70.20; MgCO₃ = 4.66 Undetermined = 14.40

CHEMICAL EVIDENCE SUPPORTING VINSON'S THEORY

The chemical evidence of organic life having participated at any time or manner in connection with the laying down of caliche has not been completely worked out. We had hoped to develop an argument based upon certain relationships obtaining in connection with the phosphorus, potassium and sodium and in particular with the phosphorus. With this in mind, and in connection with field studies, specimens of caliche were obtained at various places in and near the city of Tucson. In every case care was taken to dig well into the exposed bank so that the sample obtained would be representative of the non-weathered material. Three samples (each sufficient for numerous analyses) were taken from each location. The reason for sampling in triplicate may be explained by the following rough sketch illustrating somewhat the type of conditions prevailing at the points sampled.

Thus samples were taken first, of the thin dense cap; second, of the thick massive caliche, third, of the intervening soil layers. The table given below is illustrative of the results obtained.

Partial Analysis of Caliche

% _____	:P ₂ O ₅	: K	: Na	: Ratio K. to Na
Dense Cap	.124 .123 .125	.16 .16	.32 .28	1: 1.8
Average	.124	.16	.30	
Massive	.045 .044 .045	.25 .25	.30 .29	1: 1.2
Average	.045	.24	.30	
Soil	.078 .080	.48 .50	.23 .23	} 1:.47
Average	.079	.49	.23	

Certain interesting comparisons are now possible between the tufa deposits of known algal origin and the dense caliche cap of suspected algal origin. For instance, we have a positive check in phosphorus content between the old tufa ledge and the dense caliche cap, the old ledge showing .1245 and the cap .125%. This difference of one point in the third place is of course negligible and well within the limits of experimental error. The figures .124 and .087 also are not incomparable.

We are also impressed with the fairly high percentage of readily soluble potassium in the dense cap as well as in the tufa formation; .16 comparing not unfavorably with .20, although it must be admitted that .24 (potassium on the massive caliche) gives even a more striking contrast to the tufa potassium. This point is mentioned as it might be used as a negative evidence, in as much as it is not proposed to apply the algal hypothesis to the deposition of the massive caliche.

The comparatively high potassium-sodium ratio in case of the dense cap (1:1.8) looks favorable to our proposition in comparison with the slightly higher ratio for the old tufa. Seeming discrepancy in the data on the brush incrustations are doubtless due in part to the fact already mentioned (not rinsing), and also because of mechanical

difficulties encountered in the removal of the incrustations from the brush. Invariably small scrapings of wood would contaminate the samples of limy material removed. This, although not entirely vitiating the results did somewhat militate against their accuracy

Again it would seem probable that the phosphorus relationships were more particularly suited to such comparisons than the potassium or the potassium-sodium ratio. Phosphates being moved but slowly by water might be considered quite truly indicative of ancient relationships in chemical composition.

Granting for the moment that the dense cap has been formed by lime secreting organisms, either in water or on surfaces that are frequently wetted with limy water, we would expect the dense cap to show higher phosphorus than the massive caliche on which it was superimposed; the massive being considered as the constantly wetted surface already there, and having been deposited thru some other agency. Our table gives us a phosphorus percentage of .124 for the cap compared with only .045 for the massive. We have here an interesting relationship, and one which is clearly in favor of the algal hypothesis. During intervals of comparative quiet, when little debris was being introduced and there was little interruption to the work of these organisms,

the smooth cap may have been laid down, this cap containing about three times as much phosphorus as the massive caliche on which it was built.

In comparison of the potassium of the dense cap and of the massive caliche at first the figures seem entirely negative as far as the biological theory is concerned. It was expected that analyses would show higher potassium in the dense cap than elsewhere. However, if algae had functioned in the laying down of the potash in the dense cap, it would doubtless be in a comparatively soluble form and not as a component of the various difficultly soluble complex silicates, characteristic of inorganic origin. Thus it appears that the solvent effect of such water as may have come into contact with the caliche would have been much more marked on the potassium content of the dense cap than on the potassium of the massive layer. It was noted in analyses that the insoluble residue (sand, silt etc.) was much greater after the acid leach on the massive varieties than on the cap. Arid sands and silts are notably high in potash as they have not been subjected to the rigorous weathering conditions of humid sections. Such sands and silts are not barren silicon dioxide, but may be more nearly represented by one of the feldspar formulae, such as $KAlSi_3O_8$. Potash in such a form is resistant to solution, being made available only after long exposure to action of carbonated waters. Thus, it may well be that the comparatively high sand and silt of the massive caliche has

appreciably increased the amount of potassium revealed by our acid leach. Rather, we should prefer to know the percent of potassium in the readily available form in case of the massive caliche, feeling that this would give us a more applicable basis of comparison with the cap. It may be stated here that the insoluble residue after the acid leach was practicably negligible in the case of the dense cap when compared with the caliche below. The above discussion explaining the seeming negative aspect of the potash ratio between the dense cap and the massive caliche may be applied also to a comparison of the dense cap and the soil layer. Here the difference is even more marked, but the preponderance of sand and silt in the soil is of course also very great. Therefore, we should expect high potassium due to the complex alkali silicates.

A comparison of the phosphorus in the cap and in the interlying soil layer is favorable to our theory, (.124: .078), and as mentioned above it seems that the phosphorus comparisons are more truly indicative of method of deposition than are the potash ratios.

Such past chemical analyses of caliche as are available ²² show it not only to be well supplied with phosphorus and

22 26th Annual Report Arizona Agricultural Experiment Station, p. 567.

potassium, but comparison of phosphorus in the cap and in the inter-lying and over-lying soils are much in favor of the cap. A similar relationship between the massive caliche and the

soil can not be shown. This is certainly evidence of a positive nature and in favor of our theory. As stated above, waters move phosphates slowly; the massive caliche (lime cemented material probably of inorganic deposition) should not show high phosphorus in comparison with the cap, nor probably in comparison with the inter-lying soil layers. Chemical analyses have proven such to be the case.

MICROSCOPY-PROPOSED STUDY

It is realized that a thorough research in the microscopy of caliche might properly accompany further study. So far, a limited number of microscopic examinations have failed definitely to corroborate the proposition that algae were active in building up the dense caps. However, Vinson reports the finding of diatoms in one sample. This is interesting evidence, and would at least point the way to further advance and accomplishment in this absorbing study.

ACKNOWLEDGMENT

For suggesting the problem, and for guidance and advice given in method of research and in the preparation of this manuscript, the writer wishes to thank Dr. A. E. Vinson, Professor of Agricultural Chemistry.