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CALICHE IN ARIZONA

J. F. Breazeale and H. V. Smith

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CALICHE IN ARIZONA

By

J. F. Breazeale and H. V. Smith

INTRODUCTION

Inquiries relative to the origin and nature of the lime hardpan, or caliche, which is found widely distributed in southern Arizona, are often received at the Experiment Station. The mesa lands between the Santa Cruz and the Rillito rivers, near Tucson, and the same type of lands near Phoenix, offer excellent examples of the occurrence of this formation. These caliche beds not only excite the interest of the tourist, but they are also a matter of much importance agriculturally. They are often so impervious as to prevent the penetration of water into the soil, and are so dense that it is often necessary to break them by blasting before trees can be planted.

The object of this bulletin is to explain the chemical and physical nature of such deposits, and, if possible, to describe the different conditions under which they were formed.

"CALICHE"

The meaning of the term "Caliche" is not very definite. The word is of Latin origin; Calx, meaning lime, was used originally in Spain to designate crusts of lime which flake from plastered walls, or pebbles burned into clay brick. It is sometimes applied as a name for cracks which form in pottery.

The term was carried to Chili, Peru, and Argentina by the Spaniards, and there applied to the deposits of sodium nitrate, or saltpeter, either on account of the presence of lime in these beds, or of their resemblance to beds of lime hardpan or true caliche. The early Spanish settlers in the Southwest applied this term to calcareous hardpan, and, in Arizona, the term "caliche" is now used almost exclusively to designate such formations. Caliche and hardpan will be used as synonomous terms in the following discussion.

CALICHE AND HARDPAN

Caliche may be defined as a true hardpan. However, the term "hardpan" is very indefinite also. To the ordinary individual this term applies equally as well to a puddled condition of the clay subsoil, or plowsole, as it does to the worse types of bog iron formations, that are common in the lowlands of the Northwest. It must be remembered that the formation of caliche and other hardpans is brought about by the solution, the transportation, and precipitation of some cementing material. In the bog formation above referred to, this cementing material is iron, in certain other sections it is silica, and occasionally it may be organic matter. Iron, silica, and organic hardpans occur in humid regions, but caliche, or calcareous hardpans, seldom occur outside of arid or semi-arid regions. The caliche in Arizona is always calcareous.

OCCURRENCE OF CALICHE

Caliche usually occurs either as strata of thin sheets of fairly pure calcium carbonate, or as a conglomerate, that is as sand, gravel, etc., embedded in calcium carbonate, or as a mixture of uncemented material. Caliche is a natural cement, and its structure depends upon the conditions under which it was formed. The purity of the caliche, or its percentage of carbonate of lime, varies widely, depending upon the amount of foreign material which it contains. It seldom occurs as a regular, horizontal stratum, but in irregular layers, varying from a fraction of an inch to many feet in thickness. Caliche may appear upon the surface, but is more often covered by a layer of soil. It is often continuous over many acres, and conforms roughly to the contour of the land. In thousands of places it is exposed by railroad cuts, washes, wells, cellars, etc., where accurate cross-sections may be studied.

Caliche may occur upon the hills also, as a coating of fairly pure calcium carbonate over volcanic rocks, it may occur as a vein in crevasses, or it may occur in sheets over a valley fill. It occurs only where there has been a supply of calcium carbonate in a solution of carbon dioxide, and where the drainage is not sufficient or rapid enough to remove the water. In all cases there must be an adequate supply of calcium carbonae, or limestone. This usually comes from the Paleozoic limestones that are widely distributed in southern Arizona, from igneous rocks, or from the soil. The gravelly mesa soils where caliche often occurs, usually contain 5 percent or more of calcium carbonate.

We have in southern Arizona many of the conditions that are essential to the formation of caliche, namely, a very dry atmosphere, rapid evaporation, light rainfall, an abundant supply of calcium carbonate, in many sections a high water-table, and underground water which nearly always contains calcium bicarbonate.

FORMATION OF CALICHE

As mentioned before, all forms of caliche involve the solution, transportation, and precipitation of calcium carbonate. The formation of caliche is, therefore, largely a chemical phenomenon. The calcium carbonate may be dissolved and precipitated in the same stratum, as when a bed of caliche is broken up and recemented, or it may be transported in solution over long distances, and precipitated.

In pure distilled water, calcium carbonate is soluble only about 8 parts per million, but in cold water that has been saturated with carbon dioxide, its solubility is increased a hundred-fold, or over 800 parts per million. This increase in solubility is due to the presence of carbon dioxide, which, when combined with water, forms carbonic acid. The carbonic acid, in turn, dissolves the calcium carbonate and forms calcium bicarbonate. Solutions of calcium bicarbonate are fairly stable and, as long as the carbon dioxide remains in solution, the calcium carbonate may be transported great distances as the bicarbonate.

The precipitation of calcium carbonate from such solutions is brought about in two ways, either by the evaporation of the water in which it is dissolved, or by the loss of carbon dioxide by which it is held in solution. Carbon dioxide may be driven off from such solutions by boiling, by merely agitating the solution vigorously, by a relief in pressure, or by the action of plants.

The formation of caliche may be either a slow or a fairly rapid process; the density depends largely upon the rate of precipitation and the amount of foreign material in the mass. The dense, impermeable types which lie deep in the alluvial material filling valleys and basins are probably very old, while the softer types which lie near the surface in the flood plains, may be of recent origin. Many cases are reported in Tucson, where pieces of brick and gravel have become cemented together in a few years, or where a well defined stratum of caliche has formed a few inches below the surface, in a lawn that has been watered regularly. No evidence in the form of fossils has been found in caliche that would indicate a great age, geologically. It has all been formed in the present era.

The position, structure, and chemical composition of the different forms of caliche indicate clearly that no one hypothesis can explain the origin of the different types. The authors have found that nearly everyone attributes the occurrence of caliche on the hills to the same cause or causes that produced it in the valleys, and this assumption has led to much misunderstanding. In the following discussion several types of caliche will be considered, and a reasonable explanation for the formation of each type will be given. However, caliche occurs in all grades and mixtures. A very old and impermeable stratum may be broken up, and recemented in a few years. The reader is cautioned, therefore, against drawing conclusions that may be too exact.

Recently the authors produced a column of caliche, as a conglomerate, by means of the apparatus shown in figure 1.

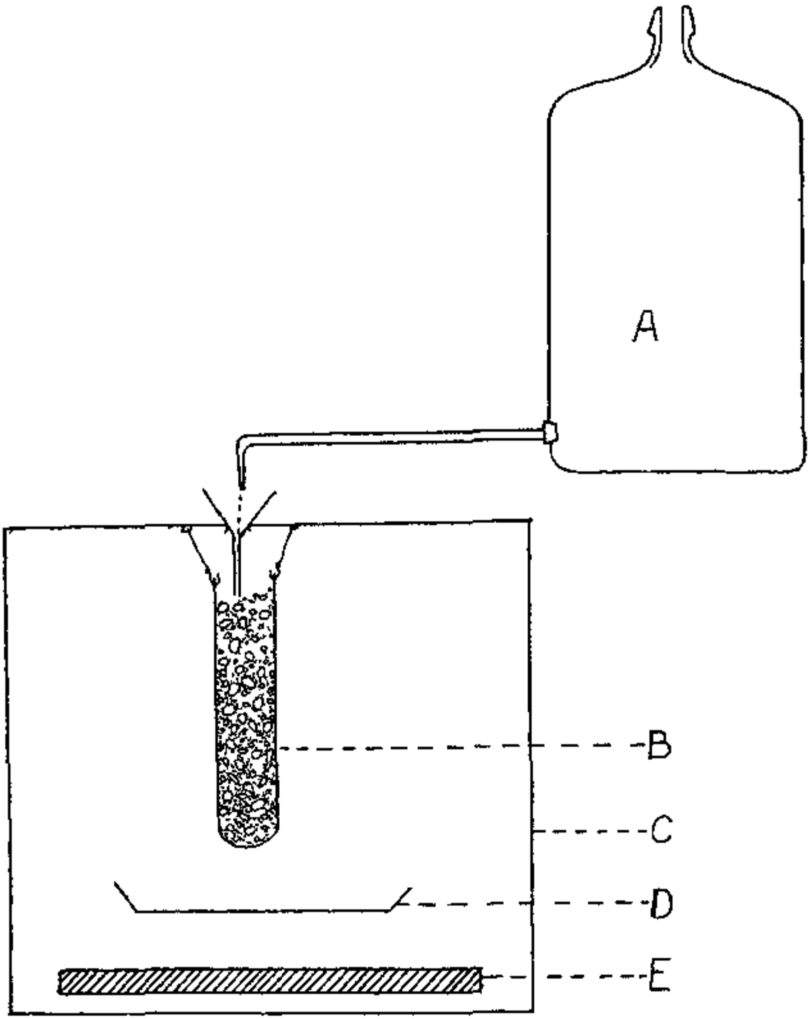

Fig. 1.—Illustration showing apparatus used in making a core af caliche.

A supply of a solution of calcium bicarbonate was made every day, by bubbling carbon dioxide into cold water which contained a quantity of finely-divided calcium carbonate. This solution was then placed in the reservoir, A, and allowed to drip slowly into a funnel which carried the solution down into a small cloth bag which had been filled with a mixture of sand and small gravel, B. The bag was hung in an electric oven, C, which was heated by a hot plate, E. The door of the oven was kept open, so that the temperature on the inside registered about 90° C. The flow of the solution was regulated so that as much as possible was evaporated within the mixture of sand and gravel. The overflow was collected in a pan, D.

After running a few days, the column began to harden at the top, and after several weeks, a core of moderately hard caliche, that resembled the natural product, was obtained. This experiment is described in order to emphasize the rapidity with which caliche may be formed.

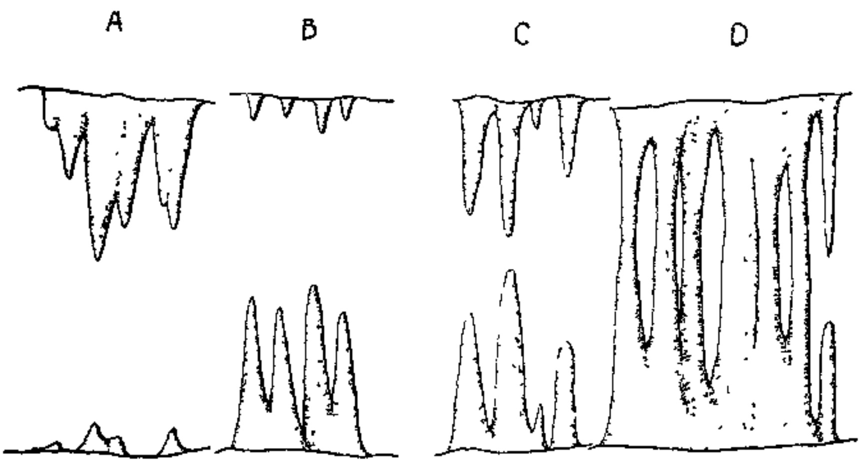

Fig. 2—Illustration showing the formation of stalactites and stalagmites in caverns.

STALACTITES AND STALAGMITES

A familiar example of the solution and precipitation of calcium carbonate by percolating water is seen in the formation of stalactites and stalagmites in the caverns that are common in southern Arizona and in all limestone regions. Water, when charged with carbon dioxide in percolating through the soil, dissolves a certain amount of calcium carbonate. When this water drips through the ceiling of a cavern, either the water is evaporated, or the carbon dioxide is driven off, and a precipitation of calcium carbonate takes place. If the cavern is relatively dry and well ventilated, the water is often evaporated at the ceiling, and a stalactite will be formed: Fig. 2 (A). On the other hand, if the cavern is humid, the water may drop to the floor, lose part of its carbon dioxide by concussion and heat, and precipitate the calcium carbonate as a stalagmite, Fig. 2 (B). A stalagmite weighing many tons, may form from a stalactite no larger than a pencil. If conditions are such that a fairly moderate and uniform evaporation takes place, the stalactite and stalagmite may be of approximately the same size, Fig. 2 (C). If precipitation continues long enough, a solid column may be formed, Fig. 2 (D).

Stalactites and stalagmites are usually very pure forms of calcium carbonate, for the reason that the lime has been precipitated from filtered water, in the absence of foreign matter. Nearly all caverns were formed originally as many are now being built up, that is, by the dissolving action of water which is partly charged with carbon dioxide.

TYPES OF CALICHE

In many sections of the State a type of soft caliche is found which ranges in thickness from a narrow band up to several feet, and is usually covered by a layer of alluvial soil 2 or 3 feet in depth. Under field conditions, this caliche is permeable to water, and is soft and pliable. It usually consists of about 40 percent calcium carbonate, and 60 percent of sand, clay, silt, and other material. Where no cementing action has taken place the lime carbonate exists in a finely-divided condition.

If removed from the soil and worked up with a limited amount of water, the mass becomes plastic like putty. When the mass hardens upon exposure it becomes very dense, and may be used as a surfacing material for roads, or for building material.

The prehistoric ruins of Casa Grande, near Florence, are composed largely of caliche, which was dug from a nearby pit, moistened, and moulded into forms. These ruins have been standing exposed to the elements for many centuries, and many of the walls are still in a fair state of preservation.

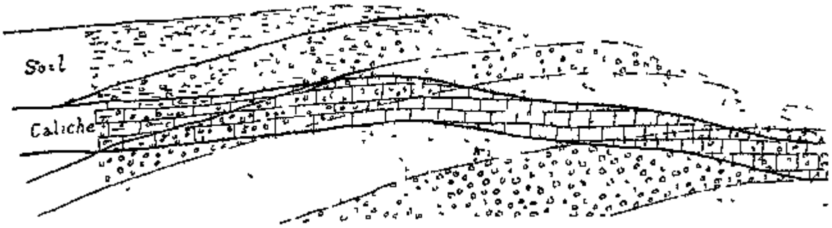

Fig. 3.—Illustration showing the crossbedding of caliche with other strata

Evidently caliche of this type was not laid down, as such, by desert streams during the age in which the valley fill deposit was being formed; that is, the carbonate of lime would not have been brought down in suspension, as was the clay or silt, and deposited in a stratum over the surface. This fact is brought out clearly by the position of the caliche in the crossbedded material, Fig. 3. The caliche stratum does not necessarily conform to the strata of silt or clay, but often cuts through such strata. The position of the caliche is more determined by the distance from the surface of the soil, than it is by the presence of strata of silt or clay. In many localities, one is impressed with the uniformity of the depth of the hardpan from the surface.

While semi-arid, southern Arizona is not a desert, the mean annual precipitation varies from 10 to 15 inches, although great deviations from the mean occur. Tucson for example has a mean annual precipitation of 11.51 inches, yet in 1905, 24.17 inches of rain fell, while in 1924 only 5.16 inches were recorded, so for a time each year the soil is wet to a depth of 2 feet or more. Assuming that a certain soil has a water table below 20 feet, or too low for capillary pull to be a factor, during a part of the year there will be a well defined moisture plane, or a horizon, where the moist soil of the surface shades off into dry soil.

Assuming that a soil has no hardpan, but that it contains 5 percent of calcium carbonate, if no erosion or deposition is taking place, the rain water which is charged with carbon dioxide will penetrate the soil, dissolve some calcium carbonate, and carry the dissolved salt downward until a state of moisture equilibrium is reached. The water will be evaporated largely in place, and the calcium will be precipitated as calcium carbonate, or caliche, instead of being drawn back to the surface by capillarity, as formerly supposed.

The downward movement of water into a soil is caused by gravity and other forces. When these forces are at equilibrium no movement of water is possible. At a depth of 2 feet, in a soil at equilibrium, the upward movement of water by capillarity is negligible, so the rain water which has penetrated to that depth, either must be distilled by the heat of the soil, or it must be absorbed by organisms, or by plants for purposes of transpiration. In either case, some calcium carbonate will be precipitated at a depth of 2 feet from the surface of the soil.

The next rain may carry more calcium carbonate down to the same level, where it will be precipitated. If the movement of water is continually downward, the movement of the calcium carbonate will be downward also, and thus a stratum will be built up at the lower edge of the moisture plane. Under natural conditions, as long as the stratum remains soft and permeable, it usually remains in the horizon that marks the extreme penetration of water.

The penetration of water controls the position of the hardpan, but the hardpan may have little or no effect upon the penetration of water.

The hardpans that are common through the Great Plains, or the area stretching from Texas to North Dakota, have been formed, largely, in this way.

In the soil, limestone may be reduced to a very fine state by atmospheric agencies, in which condition, it is easily held in suspension, and may be transported by water, and thrown down as a stratum without ever going into solution. After such a stratum is formed, it may be cemented together by calcium carbonate into a compact and impermeable mass by the solution and precipitation processes described already.

MOVEMENT OF THE HARDPAN

As mentioned before, hardpans, as long as they are soft and permeable, occur at approximately the same depth in the soil, that is, at the lower edge of the moisture plane. In the Great Plains, sometimes a hundred feet of soil has been eroded from the surface, yet the hardpan remains in the same relative position to the surface of the soil.

If the hardpan has been formed by the evaporation of downward-moving water, and equilibrium has been established in the soil, a soft stratum of caliche, probably 8 inches in thickness, would be formed 2 feet below the surface. If erosion should remove one foot of soil, equilibrium would be upset, and the tendency of the moisture plane would be to move downward. The rain water, charged with carbon dioxide, percolating through the soil might reach the upper edge of the hardpan unsaturated, and would dissolve some of the calcium carbonate. If the hardpan is permeable, the saturated solution would move down through the stratum, and appear at the lower edge where it would be evaporated.

The dissolved calcium carbonate would be precipitated at the lower edge, so the caliche stratum would be formed from below, and remain at approximately the same distance from the surface. It would continue to move downward as fast as erosion removed the surface soil.*

However, if more debris is deposited upon the surface, the hardpan would not move upward, but would remain stationary, and a second stratum of caliche might be formed above the first by the evaporation of water, which carries carbonate of lime. Such a condition may be seen in a great many places.

In many places in the Great Plains, and other regions of light rainfall, clay hardpans are found that are cemented with a very small amount of lime, often less than 5 percent of calcium carbonate. When soils with such hardpans are placed under irrigation, the moisture plane is lowered, and the hardpan is often gradually disintegrated. Many such hardpans soften up during periods of winter rains, and reappear during periods of summer drought.

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*The idea of a movable hardpan was suggested by Mr. E. C. Chilcott, of the United States Department of Agriculture.

EFFECT OF PLANT ROOTS UPON THE FORMATION OF CALICHE

The part that is played by transpiring plants upon the formation of hardpan is very pronounced, and is shown almost always wherever the caliche is exposed to view. Often the position of a root may be traced by a well defined zone, or incrustation, of fairly pure calcium carbonate. The authors have found such crusts that run over 70 percent of calcium carbonate, while the soil, a few inches from the root would analyze less than 20 percent.

When plants are growing upon the surface, the loss of water from the lower depth of a soil, is usually due largely to transpiration. In the process of transpiration the plant takes up water and leaves the dissolved salt, which is precipitated. The small lumps of soft caliche, which are so common upon the mesas that are covered with creosote bush, are often formed in this way. When examined closely these lumps will be found to contain dead roots, or small holes where roots grew formerly. Usually plant roots follow moisture, and do not penetrate a soil below the lower edge of the moisture plane. The position of a caliche stratum which has been formed by plants, may correspond to the position of a caliche which has been produced by the evaporation of water by heat. The formation of a stratum of caliche by plants is always hastened by the evaporation of water from the surface of the soil.

FORMATION OF CALICHE IN SOILS WITH A WATER TABLE NEAR THE SURFACE

In the foregoing discussion only caliche that has been formed by the precipitation of calcium carbonate from downward-moving waters, has been considered. The hardpan, in all such cases, marks the extreme penetration of water. In all such formations the movement of water by capillarity is of little importance.

However, in many parts of Arizona, especially in the flood plains, there is at present or there has existed in the past, free underground water, or a water table, within a few feet of the surface. Under such conditions, the capillary movement of water is of great importance. While water does not move by capillarity to any appreciable degree in a soil at its field-carrying capacity, in a soil that is in contact with free water, that is, in a soil with a high water table, the upward movement by capillarity may be pronounced. Nearly all underground water in Arizona contains calcium bicarbonate. This may be carried upward by capillary water to the extent of the capillary pull, which will amount to about 3 feet in a sandy soil, or to 5 feet or more in a clay. Here the calcium carbonate is precipitated by the agencies which have been described already, and a stratum of caliche will be formed 3 to 5 feet above the water table. Such a condition will exist when the movement of water is continually upward, and caliche may be formed, although the surface soil may never be wet.

In all regions where caliche occurs, however, there is some rainfall, and the carbonated rain water with its dissolved calcium bicarbonate will move downward until it reaches a state of equilibrium. The precipitation of the calcium carbonate may then occur at, or above, the horizon which marks the precipitation from the water that has been drawn up from below. In such cases caliche may be formed, either in a single stratum from both ascending and descending waters, or in two or more strata.

It will be seen that no one theory of the formation of caliche can be applied to all cases, and that more than one factor is always operative. A certain stratum of caliche might have been formed by a certain set of factors, yet another stratum within a few inches of the first, might have been formed by a different set of factors.

Under conditions where caliche is forming from underground waters, by evaporation, if the stratum is not impervious, the sudden lowering of the water table may cause the formation of another stratum below the first. However, if the first stratum becomes cemented and impervious to water, no second stratum is likely to form. In other words, precipitation will take place only where there is evaporation or a release of pressure.

CALICHE CEMENT UPON ROCK SURFACES

In many places in Arizona, a crust of fairly pure calcium carbonate, often of recent origin, may be seen as a coating on many kinds of rocks. This condition is very noticeable upon the volcanic hills south of Tucson, and has been described by Tolman (5). The cement, or caliche, is deposited usually upon the rock surface, in layers of less than a centimeter in thickness. It occurs in the draws, or ravines, which run down the hills, rather than on the exposed ridges, and spreads out as the base of the hill is reached. Often many small pieces of rock are cemented together in the form of a conglomerate.

Upon the volcanic hills there is no water table, and often little or no soil. The caliche could not have been formed from underground sources, nor could it have been leached from the soil and reprecipitated as described already. The basalts of these hills are very porous, and many of the cavities were filled with calcium carbonate and calcium sulphate. In the process of the formation of caliche, these salts were leached from the rocks on the higher ridges by rain water charged with carbon dioxide, and the calcium bicarbonate was carried in solution down slope into the ravines and small washes. Here, running in thin sheets over warm rocks, some evaporation took place, much carbon dioxide was lost, and calcium carbonate was thereupon precipitated in thin layers over all of the material which happened to be covered with water.* The calcium sulphate was carried off by the runoff into the Santa Cruz River.

Occasionally, on the slope, a rock of irregular shape may be found covered partially by other rocks, and between these rocks cavities of considerable size may occur. The rain water, from which calcium carbonate was precipitating, has trickled into these cavities, and often hundreds of small stalactites and stalagmites have been formed upon the inner walls of these miniature caves.

CALICHE IN CREVASSES

Caliche often occurs in veins in rock masses, where fracturing has produced crevasses or fissures. These veins of caliche may be horizontal or upright, or they may be tilted at any angle. The precipitation of calcium carbonate under such conditions was much the same as that described in other cases of caliche formation. Water, carrying calcium bicarbonte, penetrated these cavities where evaporation took place, or where carbon dioxide was lost and calcium carbonate was precipitated. The purity of the caliche formed under such conditions varies with the amount of foreign material enclosed. When precipitated between igneous rocks, for example, it is usually very pure.

THE HARD CEMENTED CALICHE OF THE MESA LANDS

Probably the most interesting type of caliche in Arizona, is that represented by the caliche which occurs in successions of hard, cemented, impermeable strata, that are very much in evidence upon the mesas in southern Arizona. In that section of Tucson, which is built upon the mesa, practically every fence post is set in caliche. In digging a cellar or cesspool, or in laying a pipe line, it is usually necessary to drill or blast through a bed of this material, ranging in thickness from one foot to 10 feet or more. Such caliche covers an area of probably 300,000 acres in Pima county alone, equally as much in the Salt River Valley, and also large areas in other parts of the state.

Farming or gardening upon a soil which is covered or underlaid

*This is the opinion of Dr. R. H. Forbes.

by such a formation is very difficult. Neither plant roots nor water will penetrate certain of the strata. If a fruit or shade tree is to be planted, it is customary to first break the caliche by blasting or drilling, and then to dig a large hole, 3 feet square or more, which is filled with good soil. The tree is then planted in this good soil.

As this type of caliche is of so much economic importance, a detailed description of its usual structure, its physical and chemical composition, and the most reasonable hypotheses of its origin will be given.

W. P. Blake, (1) former Director of Arizona School of Mines, at the Richmond meeting of the Institute of Mining Engineers in 1901, stated, "There has been much speculation in regard to the origin of caliche. It has been generally assumed to be a deposition from some ancient lake, or body of water, once covering the area in which it is found. But such a theory is untenable when all the phenomena are considered. The formation is clearly the result of the upward capillary flow of calcareous waters, induced by constant and rapid evaporation at the surface in a comparatively rainless region."

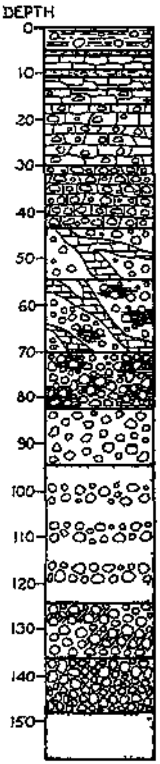
Tolman, (5) in discussing the geology of the volcanic hills southwest of Tucson quotes the opinion of Director Forbes of the Arizona Agricultural Experiment Station to the effect that the two constituents of caliche, colloidal clay and carbonte of lime, one carried in suspensions and the other in a solution of carbonated rain water, penetrate the desert soils to a depth marked by the penetration of water from an occasional rain. At the general average level at which the wetted soil dries out through the drying action of arid atmosphere, a more or less compact stratum of caliche is formed. When the surface is filled from time to time, new caliche strata are formed. Tolman also recognizes the effect of the upward movement of underground water.

Guild, (3) attributes the occurrence of layers of caliche near the surface of the soil, to the evaporation of meteoric waters *in situ*, while deep layers are formed by the evaporation of water, which has been brought up by capillarity from underground sources.

Lee, (4) in discussing the underground water of the Salt River Valley expresses the opinion that many of the caliche layers in this valley were formed by the upward movement of ground water which contained calcium bicarbonate, and the subsequent evaporation of this water below the surface of the soil.

The opinions of these investigators represent the prevailing opinions as to the origin of caliche. Nearly every one attributes the formation to one of two factors, either the evaporation of descending surface water, or to the evaporation of ascending ground water. Blake mentions, but discounts the possibility of caliche being formed in old lakes.

There is no doubt but that many of the factors that operate in the formation of caliche were active during the era in which this particular type of caliche was formed. Small nodules of soft caliche, which have been formed by roots of plants during recent years, are often found imbedded in dense, cemented strata of evident great age. However, it is the opinion of the authors that the caliche, which occurs upon the mesa land around Tucson, was deposited from small lakes, or playas, or from shallow pools of stagnant water. The precipitation of calcium carbonate was probably hastened by the presence of algae and other water plants in these pools.



Explanation. The percentages of $CaCO_3$ at the various depths as indicated in inches on the accompanying profile are as follows:

0	— 6	=16.4
6	— 6¾	=94.0
6¾	— 9¾	—61.0
9¾	— 10¾	=76.0
10¾	— 13¼	=50.6
13¼	— 16½	=37.2
16½	— 30	=40.2
30	— 44	=10.4
44	— 55	=17.8
55	— 70	= 6.0
70	— 82	= 7 5
82	— 94	= 1.5
94	—124	= 0 0
124	—136	= 1.5
136	—148	= 0.0
148	—158	= 0 0

Fig. 4.—Illustration showing a typical caliche profile

A typical soil profile of the Pinal series, the soil type on which the University is built is shown in figure 4. It is from a cut 158 inches deep in the El Encanto Estates east of the City. The surface 6 inches of soil is a loamy sand containing 23 percent of material not passing through a 2-mm. sieve. This coarser material has the appearance of lime concretions but a close examination shows them to be only lime-coated pebbles. Immediately below this loose surface material, as shown in figure 4, is a dense layer of very pure lime three-fourths of an inch in thickness capping a 3-inch layer of softer caliche which has a lower lime content. Another half-inch of very compact material is found under this chalky layer and as in the upper compact layer its lime content is higher than the less dense strata above or below the one extending 2½ inches below. At a depth of 13 inches a little gravel appears to be mixed with the lime and the whole is cemented into a hard, solid mass.

The percentage of sand and gravel increases slightly to a depth of 30 inches where a vein of gravel is encountered. These lime-and-gravel mixed deposits contain in the neighborhood of 40 percent lime which is the maximum amount possible in this type of soil if only the pore spaces are to be filled.

The gravelly strata which underlie the caliche-cemented layers become less rich in lime with increased depth until at the 82-inch depth only 1½ percent of lime is found. Below this only traces of lime occur to the bottom of the hole, 158 inches below the surface. The log of a well drilled to furnish water for the estates shows a repetition of these caliche strata down to a depth of at least 71 feet, and possibly more, although caliche as such is not indicated in the log below this level.

Such is the character of the soil in which this dense stratified caliche is found.

As illustrated in figure 5, the strata occur usually as a succession of compact sheets, arranged one above the other in irregular manner, and separated from one another by thin layers of soil or granular, earthy deposit. The sheets of caliche vary from less than a millimeter to several centimeters in thickness, and often a dozen or more sheets may occur in a horizon of less than a centimeter. These thin sheets are usually impermeable to water, however, the whole mass, may be so broken by fissures and irregularities in deposition that water may percolate the soil.

The fact that these sheets of caliche are impermeable to water is good evidence that they were not formed within the soil, either by descending surface water, or by ascending ground water. Assuming that the evaporation of ascending ground water formed one very thin, impermeable sheet of caliche, this sheet would effectively check evaporation, and further precipitation of calcium carbonate would be checked. In order to have deposition continue, it would be necessary to assume either continued evaporation from the surface or a reduction of pressure. Often a stratum of caliche 20 feet thick occurring as a succession of impermeable sheets is found. It seems impossible to believe that such a formation could have been built up from below, as outlined by Blake. If it had been built up from below, the caliche probably would have been more or less uniform, rather than existing in thin sheets separated by earthy material. If an impermeable stratum had been formed from water that had risen from a definite level, the subsequent lowering of the table would not necessarily tend to form another stratum.

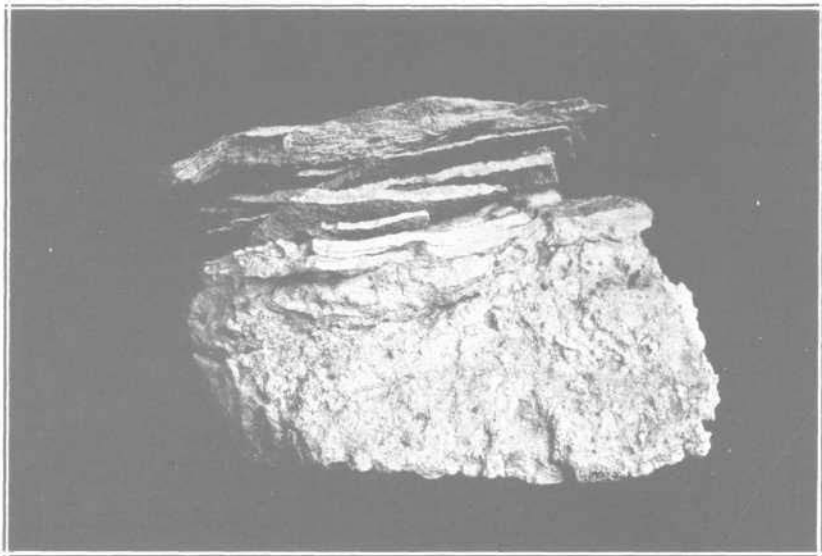


Fig. 5.—Illustration showing a piece of caliche capped with sheets of dense calcium carbonate. The spaces between the sheets were filled with loam and sand.

The assumption that the caliche was formed from underground water, carries with it the idea of a high water table. Practically the only place where caliche can be formed is at or near the surface, for here is where evaporation takes place, or where pressure of carbon dioxide is relieved. A high water table is found frequently in the flood plains, but it has been many centuries since water has risen upon many of the mesas to a level where capillary pull towards the surface would be effective. Free water would have to occur within 8 or 10 feet of the surface before any appreciable deposition of caliche could be expected.

CHARACTER OF THE UNDERGROUND WATER NEAR TUCSON

If the caliche had been formed by the evaporation of underground water, the carbonates of both calcium and magnesium would have been precipitated out, and in such cases, the caliche would contain calcium and magnesium in the same proportion as these elements existed in the original ground water. Tucson lies between the drainage basins of the Santa Cruz and Rillito rivers, but the volume of both surface and underground water is much greater in the Santa Cruz than it is in the Rillito basin. The chemical composition of the two underflows is very different. The Santa Cruz shallow underflow as it approaches Tucson has a relatively high salt content, and is "hard," while the Rillito underflow is usually low in total salts, and is "soft."

In Table I are shown analyses of the Santa Cruz basin water from five shallow wells between San Xavier Mission and Tucson. These wells were above, and all within 10 miles of the city, where the water table is about 40 feet below the surface. The results are expressed in parts per million.

TABLE I.—ANALYSES OF SANTA CRUZ UNDERFLOW.

Well	1	2	3	4	5
Total salts	376	368	680	784	1560
Calcium (Ca)	60	30	112	120	150
Magnesium (Mg)	21	6	29	17	39
Bicarbonate (HCO_3)	240	144	240	336	312
Chlorine (Cl)	42	28	56	70	168
Sulphate (SO_4)	102	157	278	285	697

The average ratio of calcium to magnesium in these waters is 1.0 of magnesium to 4.2 of calcium.

In Table II are shown the analyses of water from five shallow wells in the Rillito Valley, above Tucson.

TABLE II.—ANALYSES OF RILLITO UNDERFLOW.

Well	1	2	3	4	5
Total salts	228	160	352	384	268
Calcium (Ca)	75	18	57	45	69
Magnesium (Mg)	9	Trace	Trace	Trace	5
Bicarbonate (HCO_3)	120	102	168	192	240
Chlorine (Cl)	28	10	20	38	Trace
Sulphate (SO_4)	43	39	120	97	40

It will be seen that the underflow in the Rillito basin is very low in magnesium, the average ratio being about 1.0 of magnesium to 15 or 20 of calcium.

Analyses of many samples of the dense upper crusts of caliche strata collected from different places between these two drainage basins, show that the caliche runs usually about 90 percent or more of calcium carbonate, and 1 or 2 percent of magnesium carbonate. Caliche of such composition scarcely could have been precipitated from Santa Cruz underflow as it exists today, if we must assume complete evaporation of the underground water. The caliche probably could have been precipitated from Rillito underflow, however, if this underflow had existed in sufficient amounts. The possibility of a change in the underflow since the formation of the caliche must be considered.

It will be noted also, that the waters from both the Santa Cruz and Rillito basins often contain relatively large amounts of sulphates. A complete evaporation of these waters would precipitate appreciable amounts of gypsum. The sheets of dense caliche however, do not ordinarily contain more than about 1 percent of gypsum. This indicates either a partial rather than a complete precipitation, or a condition under which gypsum might have been precipitated, and subsequently leached. The dense sheets of caliche show no indications of leaching.

In the same way, many objections are evident to the hypothesis that the dense, impermeable caliche was formed by the evaporation of descending surface water, as outlined by Forbes and others.

Many samples of the thin, dense sheets of caliche have been collected recently at depths of one foot or more below the present surface of the soil. These samples run as high as 90 to 94 percent of calcium and magnesium carbonates. The other 8 or 10 percent consist of clay, iron oxide, etc. The purity of these samples indicates that they were precipitated upon the surface, from relatively clear solutions, and in the absence of appreciable amounts of materials such as sand, gravel, etc. If the precipitation occurred within the body of the soil caused by the evaporation of downward moving water, the caliche would have filled the pore spaces and surrounded these earthy materials. It would have been a conglomerate, and impure to the extent of the foreign matter. If caliche consisted of large crystals of calcite, it is possible to assume that all foreign material had been pushed aside during the process of crystallization. But the caliche does not exhibit the crystalline structure of calcite, it occurs more like a cement, and suggests a rapid development, in comparison with ordinary slow, geological processes.

It appears safe to assume that, if precipitated within the soil mass, the purity of the caliche would not have exceeded that represented by the pore space of the soil. If precipitated upon the surface from still water, only those impurities which were held in suspension would be included. These impurities are largely of a colloidal nature.

SEPARATION OF CALCIUM AND MAGNESIUM

As mentioned before, the dense sheets of caliche usually have a low percentage of magnesium carbonate, while the soil above and below these strata may run relatively high in magnesium. In pure water, calcium carbonate is soluble about 10 parts per million, while magnesium carbonate is practically insoluble. As both salts are relatively insoluble, a separation of them as carbonates is difficult. They occur combined in nature, as dolomite which is exceedingly insoluble.

In the presence of carbon dioxide, however, calcium carbonate is soluble to the extent of 1,000 parts per million as calcium bicarbonate, while the solubility of magnesium bicarbonate, under the same condition, may run as high as 12,000 parts per million. This wide difference in the solubility of the bicarbonates probably is in nature the principal means of the separation of the two salts. In a precipitation caused by the total evaporation of the water, all the calcium and all the magnesium would be precipitated, and remain insoluble as caliche. This would represent conditions in a soil, where complete evaporation was taking place and where no leaching was going on. If a partial precipitation took place from a solution, as might happen in shallow pools upon the surface which were subject to occasional overflow, the calcium carbonate might be precipitated in greater proportion than the magnesium, and the magnesium bicarbonate might be carried off to the sea. The small amount of magnesium carbonate in the dense, sheets of caliche indicate partial, rather than complete precipitation.

Another property of calcium which distinguishes it from magnesium, is the tendency of calcium carbonate to precipitate around solid particles of other material, and to form a cement, or concrete. Magnesium does not possess this property to any great degree, in fact, the presence of magnesium in cement is very objectionable, as it interferes seriously with the "setting" of the concrete. If, therefore, a mixture of a solution of calcium bicarbonate and magnesium bicarbonate is evaporated partially in the presense of sand and gravel, the calcium carbonate will tend to crystallize more readily than the magnesium. In the natural formation of caliche, calcium carbonate would remain in the soil, while the magnesium would be carried off toward the sea.

As mentioned before, nearly all ground and flood waters in Arizona contain calcium sulphate, as well as calcium bicarbonate. When no evaporation takes place, but when there is a relief of pressure, carbon dioxide escapes, and calcium carbonate is precipitated. The loss in carbon dioxide has little or no effect upon the solubility of calcium sulphate, which remains in solution. In this way a separation of calcium carbonate and calcium sulphate is made.

PEBBLES UPON THE SURFACE OF CALICHE

When caliche occurs as a conglomerate, the pebbles which it contains are usually water worn. Some of the pebbles, by their state of erosion, indicate that they have been transported long distances, while others are more angular, and probably have not been moved very far from the original rock. In thousands of cases a condition like that shown in figure 6 is seen.

The caliche occurs in a succession of dense sheets at all depths in the soil, as has been described already, while over the upper sheet, which is usually fairly pure calcium carbonate, many pebbles are scattered. The stratification of the caliche runs unbroken beneath these pebbles as is shown in the figure, but the pebbles are attached to the top of the caliche by a thin layer of calcium carbonate. The pebbles are covered with very thin, laminated layers of calcium carbonate.

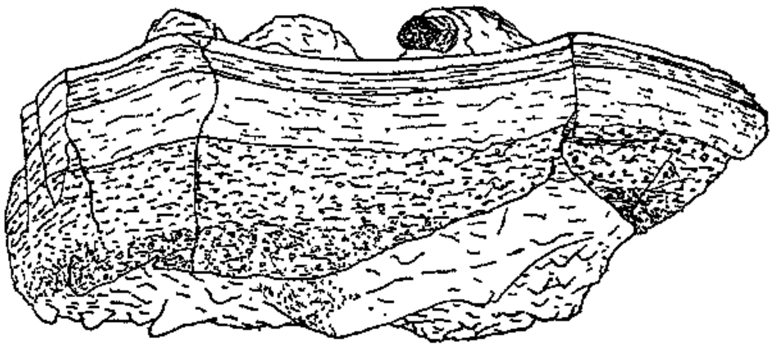


Fig. 6.—Illustration showing a piece of caliche stratum with pebbles cemented upon the surface. Natural size.

Such a phenomenon may be explained in more than one way, it is true, but when combined with other evidence, it indicates that the caliche stratum was formed upon the surface, and that afterward the pebbles were washed in and became attached to the top sheet. If the pebbles had been in place during the formation of the caliche, that is if the caliche had been formed below the surface of the soil by the evaporation of either descending or ascending water, the pebbles would probably have been included in the stratification. The laminated layers around the pebbles consist of very pure calcium carbonate.

CALICHE PROBABLY FORMED IN LAKES OR POOLS

The valley fill in many of the drainage basins in Arizona is very thick. The depth to bed rock in the Santa Cruz basin near Tucson, for example, has not been determined accurately, but it is at least 2,000 feet. The fill is equally as deep in the San Simon and in other valleys. This depth of debris in the Santa Cruz Valley represents largely the products of erosion from the Catalina, Rincon, and Santa Rita mountains. This valley fill is all stratified, and the pebbles and rock fragments are nearly all water worn. Unquestionably the fill was laid down by the streams which came down from the mountains on either side of the valley or by the rivers which came from the south and southeast, causing the fill material to migrate laterally. Deposition ceased many centuries ago, and erosion is now taking place, so the floor of the valley today is probably much lower than it was when its highest point represented the flood plain of the Santa Cruz River.

During the long period which was required to build up the 2,000 feet or more, there was at times an abundance of water in the valley, and the entire surface was subjected to overflow. The soil in this valley is usually dispersed, that is, it puddles easily, and does not take water readily. If an area is leached with pure water, the water will, at first, percolate the soil but, if the leaching is continued, the soil soon becomes impermeable, and water will stand upon the surface until it evaporates. During past ages, conditions were probably ideal for the formation of small, shallow pools, or playas, where water stood for a long period of time. These playas may have been only a few yards in diameter, or they may have covered several acres. They were subjected to occasional overflow, and their contours were being changed continually by deposition of sediment from such overflows. During this time, evaporation must have been very great, and it must have required large amounts of water in order to maintain a marshy condition over any great area. The stagnant water must have furnished an excellent place for the growth of algae, marsh grasses and such vegetation.

If the flood water which filled these playas contained calcium bicarbonate in solution, and if such water was evaporated, a deposit of calcium carbonate, or caliche, would have been made.

A few miles southwest of Tempe, in the Salt River Valley, S. E. corner Section 20, Township 1 N., Range 4 E., a typical playa of fairly recent origin may be seen. This playa covers over 40 acres and was covered originally with coarse vegetation. A part of it has been reclaimed and is now planted to cotton. The soil in this playa is very heavy, and the entire area is underlain by a thick stratum of very dense caliche.

The first requisite for the formation of a playa is that a barrier must be formed which prevents a part, if not all, of the flood water from running off. The second requisite is an impermeable subsoil which prevents drainage. Under such conditions, as shown in the Tempe area, flood water will collect and stagnate, until it deposits its load of calcium carbonate, and is removed by evaporation.

Such a condition as that represented in this playa, might have been common during the ages when the valleys of Arizona were being filled.

It is not necessary to assume that the Santa Cruz Valley, for example, was ever a great inland lake, or that the playas were very large. The structure of the caliche indicates that it was formed usually in very small pools.

We should expect the valley fill to contain strata of caliche in all horizons, provided the flood water at all times contained calcium bicarbonate. A deep well was dug recently about 3 miles east of Tucson, and the log of this well showed a stratum of caliche, about 3 feet thick, beneath about 6 inches of soil. Deeper drilling showed a succession of sand and gravel strata, until a level of 71 feet was reached. Here another stratum of caliche, several feet thick, was encountered. Water was found at 117 feet, but the well was drilled to a depth of 351 feet. Cemented sand, probably soft caliche, was reported at depths of 130, 235, 250, 275, 308, 328, and 351 feet, respectively.

Another well, 2,000 feet deep, was drilled recently in the San Simon Valley, and the entire core was found to be calcareous. Distinct strata of cemented sand and clay were found at many depths.

The chemical composition of flood waters depends upon the nature of the soil or rocks in the water shed. If, during one era, great deposits of gypsum were exposed by erosion and were subject to leaching, the flood waters would be high in calcium sulphate. If erosion exhausted these beds of gypsum, and deposits of limestone were exposed, the flood water could change in composition and become highly charged with calcium bicarbonate. We know that such changes have taken place during the period when these valleys were being filled. We should not, therefore, expect strata of caliche to be formed in the valleys except during the eras when the flood waters contained sufficient amounts of calcium bicarbonate.

CALICHE OF ORGANIC ORIGIN

Dr. A. E. Vinson (6), expresses the opinion that lime-secreting organisms were responsible for the formation of the caliche around Tucson. He points out that, over many deposits of caliche there is a pure stratum, or cap, and that the strongest evidence of organic origin is found in these caps. It is well known that the soil under leaky hydrants in Tucson develops a growth of green algae, and that these algae soon produce a calcareous crust which resembles caliche. Vinson is of the opinion that caliche was formed upon the surface and not in the subsoil, and that it was laid down either in water, or upon soil that was wetted frequently with limy water. During the intervals that were comparatively quiet, in the periods of deposition, little debris was introduced, and the caliche cap was built up quite pure. During periods of floods, however, sand, gravel, and other debris were deposited upon the caliche, which checked the growth of the organisms, and, mixing with the caliche which was afterwards formed caused the seams of loam and loose cemented caliche, which lie between the denser strata.

It has been observed by W. T. McGeorge, of this laboratory, that many ground waters will become alkaline enough to react with phenolphthalein, when a growth of green algae appears in the solutions. This phenomenon is true with algae which are not lime secreting. Apparently, algae, when grown in a solution of calcium bicarbonate, will absorb the carbon dioxide and the calcium carbonate will be precipitated.

If the dense strata of caliche were deposited in stagnant water, the deposition may have been stimulated greatly by the presence of algae.

CONCLUSIONS

1. Caliche, wherever found in Arizona, was formed by the solution, transportation, and precipitation of calcium carbonate.
2. Water, when charged with carbon dioxide, dissolves calcium carbonate and forms calcium bicarbonate. The calcium bicarbonate is carried in solution and is precipitated as calcium carbonate, or caliche, when the water is evaporated, or when there is a relief in pressure, which drives off carbon dioxide.
3. Caliche strata may be formed beneath the surface of a soil, either by the evaporation of descending surface water, or by the evaporation of ascending ground water.
4. Caliche may be formed in a soil by means of plant roots. Plants growing upon the surface absorb soil water for transpiration purposes, and the calcium carbonate that is dissolved in the soil solution is precipitated as caliche.
5. As long as they are permeable to water, caliche strata will move downward in a soil as fast as erosion removes the upper soil surface.
6. Caliche probably is formed upon the surface of a soil by the evaporation of surface or flood water. The formation under such conditions is hastened by the presence of algae and other water plants.

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