Geochemistry and Paleolimnology of the Trona Deposits and Associated Authigenic Minerals of the Green River Formation of Wyoming

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By W. H. BRADLEY *and* H. P. EUGSTER

THE GREEN RIVER AND ASSOCIATED TERTIARY FORMATIONS

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Physical chemistry that determined formation of thick and extensive trona and trona-halite beds and accompanying authigenic minerals in the paleolimnologic and climatic setting is discussed

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GEOCHEMISTRY AND PALEOLIMNOLOGY OF THE TRONA DEPOSITS AND ASSOCIATED AUTHIGENIC MINERALS OF THE GREEN RIVER FORMATION OF WYOMING

By W. H. BRADLEY and H. P. EUGSTER

ABSTRACT

The Green River Formation of Wyoming contains a rich record of events in the history of Gosiute Lake, which existed for roughly 4 million years during the early and middle parts of the Eocene Epoch. At its maximum extent, the area of the lake was nearly 0.6 the area of Lake Victoria in Africa, the second largest lake in the world. Like Victoria, Gosiute Lake owed its existence and long life to progressive, gentle downwarp of the crust, a downwarp that made room for successive increments of sediment.

Gosiute Lake passed through a complex and long series of changes of area and depth, but it had three major changes in size. During the first stage, which lasted roughly 1 million years, the lake was large and overflowed continuously, so that it was an entirely fresh-water lake. All during this stage it had a large central elliptical island made up of Upper Cretaceous rocks of the ancestral Rock Springs uplift.

The climate then became considerably more arid, and the lake shrank to about half its former size and ceased to overflow. This second stage also lasted about a million years. As all closed lakes do, it fluctuated frequently in area and depth. Many times it became extremely saline, and extensive beds of trona and mixed trona and halite were deposited. The beds of marlstone, dolomitic mudstone, oil shale, and bedded salts deposited in this closed lake have a maximum thickness of about 365 meters and make up the Wilkins Peak Member of the Green River Formation. Within this member is a saline facies, with which this report is primarily concerned.

The third, and last, major stage began when the climate became considerably moister so that Gosiute Lake again expanded, overflowed, and became a fresh-water lake with a large central island. In this stage, which lasted roughly 2 million years, the lake expanded to its maximum size of about 40,150 square kilometers (15,500 sq mi). The upper part of the sediments deposited in this large lake contains a great quantity of volcanic ash. The repeated influxes of volcanic ash, added to the normal limy sediment, may have filled the basin faster than the downwarp could accommodate them and so brought Gosiute Lake to its end.

It is useful to think of the saline facies of the Wilkins Peak Member as a great lens of sediments within the Wilkins Peak Member, laid down during the lowest stages of the closed lake. After each of the lowest stages, when the lake deposited the trona and mixed trona-halite beds, the lake expanded, and each time it expanded it deposited rather thick units of more or less saline, dolomitic mudstone, marlstone, and oil shale. These units extend laterally far beyond the limits of the trona beds but, of course, not nearly so far as the nonsaline sediments of the Wilkins Peak Member.

In addition to trona and halite, the saline facies also contains the following saline minerals: Shortite, northupite, pirssonite, gaylussite, nahcolite, thermonatrite, wegscheiderite, and tychite. Of these, shortite, which is found only in the Green River Formation, occurs in tremendous quantities. Northupite and wegscheiderite also occur in considerable quantities, but the others are rare.

The saline facies also contains an array of at least 27 nonsaline authigenic minerals, six of which are new species. Several others, acmite, magnesioriebeckite, labuntsovite, and leucosphenite, and probably several others, are remarkable because they had previously been known as minerals that formed only at rather high temperatures. All the nonsaline authigenic minerals occur sparingly except analcite, searlesite, stevensite, adularia, albite, and loughlinite, which have been found in considerable abundance. The adularia and albite are especially plentiful in the altered tuffs and tuffaceous beds. Nearly all the authigenic minerals formed after the sediments had been fully compacted. Analcite and pyrite, however, also formed, in part, just after deposition of the sediments.

New complete chemical analyses of seven typical rocks of the saline facies are given. From these analyses, and one analysis published by J. J. Fahey, and from microscopic and X-ray determinations, the mineralogy of the eight rocks has been calculated, or estimated. Limitations of the conclusions are discussed in the following paragraphs.

Beds of trona and mixed trona and halite underlie an area of roughly 2,600 km^2 (square kilometers) in the central and southern parts of the Green River Basin. Within this area are at least 27 beds of trona or trona and halite that range from about 1 m (meter) to more than 11.5 m thick at their thickest places. Between these beds are locally few to many thin trona layers, ranging in thickness from mere films to 0.3 or 0.6 m. Most of the trona beds contain brownish organic matter, pyrite, microgranular dolomite, fine silt particles, and thin partings of normal sediment, all of which indicate that these beds are chemical deposits laid down on the lake floor during very low stages of the lake.

The major trona beds range in area from less than 428 km^2 to at least 1,870 km^2. Very conservative estimates of the volumes of these beds indicate that 18 of them contain approximately

7.5×10^{10} metric tons of trona. Adjustments for the amounts of halite are not warranted.

We infer, from rather slender evidence, that the low level of Gosiute Lake during the Wilkins Peak stage, and particularly during the stage when the saline facies was being deposited, was caused by a change of climate, so that evaporation persistently exceeded the lake's supply of water. From formulas developed by Langbein and from hydrographic data from existing lakes, we calculated that the average annual rainfall at the level of Gosiute Lake when the lake was full, but not overflowing, was about 86 cm (34 in.) and that the rainfall decreased to about 48 cm (19 in.) during the salting stages. The latter calculation involves the plausible assumption that the net evaporation from the lake surface, at salting level, was 100 cm (40 in.) and the much less plausible assumption that the average annual temperature did not rise.

At salting stages Gosiute Lake was still a large, though shallow, lake, possibly never less than 10,000 km^2 in area. It then occupied much of the Green River Basin and had a large arm that extended around the south end of the Rock Springs uplift; this arm expanded to the east and southeast into a large bay. Bedded salts accumulated only in the Green River Basin part of the lake because two large rivers freshened the large eastern bay. To account for the localization of the trona beds in the southern half of the Green River Basin we postulate the existence of a shoal or bar running westward across the center of the Green River Basin and another extending southward or southwestward from the south end of the Rock Springs uplift. The part of the lake partly isolated by these bars, being poorly nourished by streams, must have lost more water than it received and so served as a sink and a concentrating basin for somewhat saline water that flowed in from the northern part of the lake and from the great eastern arm. This permitted progressive concentration of brine in one part of the lake without significantly decreasing the volume of the lake. Precisely this mechanism operates in some existing saline lakes and was artificially created in Great Salt Lake by the construction of the Southern Pacific's causeway.

We have no evidence that even in this part of the basin, the lake never became dry, though the surface of the brine may have sunk below the surface of the trona, or trona-halite, beds, as in Searles Lake, Calif., or in Lake Magadi, Kenya, Africa, today.

Rather late in the history of the saline facies, the locus of trona deposition gradually shifted northward from the southern part of the Green River Basin nearly to the center of that basin. This shift was apparently in response to a change in the pattern of downwarp.

Rhythmic alternations of lake level are recorded at several places in the saline facies by alternating kinds of sediment.

The saline facies contains, in the aggregate, such great quantities of sodium salts that it is pertinent to ask if some unusual source of sodium is necessary to account for them or if they were brought into the closed basin over a long interval of time by normal arid-climate streams. We first show that simple reduction in volume of the lake, even postulating extreme change, is not adequate to account for the total salinity necessary to precipitate the earliest trona bed. It is necessary, then, to conclude that all the constituents in the brines from which trona and halite precipitated were brought in by streams, were leached from new falls of volcanic ash, and were derived from the mineral springs known to have existed in the watershed.

Very rough estimates of the amounts of sodium, magnesium, sulfur, and chlorine brought into the (saline facies) basin in runoff of an assumed composition during the 8×10^5 years required to deposit those sediments are compared with the total amounts of those elements found in the saline facies. All but sulfur are of the same order of magnitude (all values in grams $\times 10^{16}$): Mg (found) 9.6, (calculated) 6.9; Na (found) 6.3, (calculated) 15.0; S (found) 1.4, (calculated) 13.4; and Cl (found) 1.25, (calculated) 6.0. Perhaps the correspondence is as close as could be expected in view of the fact that certainly great quantities of magnesium, sodium, sulfur, and chlorine must ultimately have been lost by overflow at the end of the Wilkins Peak stage. The loss would have been largely in the form of solutions containing magnesium, sodium, potassium, sulfate, and chloride.

The loci of several mineral springs that were active during the Green River epoch have been found by others on the southwest flank of the Rock Springs uplift. Overflow from these springs surely ran into that part of the basin where the trona beds formed. Bleaching of the country rock and the numerous veins of silica and calcite around the outlets suggest that the springs were warm and probably alkaline. We know of no way to estimate how much sodium, or other constituents, these springs contributed. Nevertheless, simply by analogy with warm, alkaline springs now active in other parts of the world, it is reasonable to think that their contribution may have been large, or perhaps even the dominant source of sodium salts. Thermal springs bring in daily about 4,300 tons of Na^{+1} and CO_3^{-2} into Lake Magadi, in Kenya. It is worth remarking that these African spring waters are predominantly sodium carbonate waters and are poor in sulfates.

Because volcanic ash falls were fairly common during the accumulation of the saline facies, we speculate that much sodium may have been leached from the ash that fell directly in the lake or, more importantly, from ash that blanketed the watershed.

After the last trona bed was deposited, we infer that there must have been a large body of brine, rich in the most soluble salts. Some of this brine was trapped in the sediments that overlie the uppermost trona bed, but most of it must have persisted as a saline hypolimnion while the lake level rose at the end of the Wilkins Peak stage. As the lake became larger and more dilute, this huge tonnage of salts must have eventually mixed with the fresh-water epilimnion and have been lost to the lake by overflow.

Phosphate in the Wilkins Peak Member poses a problem because it is concentrated in about 20 rather thin zones; all the rest of the sediments are extremely poor in phosphate. We conclude that phosphate came to be concentrated in such zones because it accumulated for long intervals in calcium-poor hypolimnetic brine and then precipitated during relatively much shorter intervals when calcium bicarbonate-rich mixolimnetic water precipitated minute crystals of calcite, which caused the phosphate to come down, probably as hydroxylapatite. We conclude also that, as the phosphate mineral formed, it competed with dolomite for new supplies of Ca^{+2} ions, with the result that the amounts of dolomite and phosphate mineral are inversely related in the phosphorite zones. The excess calcium brought into the hypolimnion accumulated as calcite.

The Green River trona beds accumulated at an average rate of 4.75 cm^{-1} yr. At this rate, nearly 14 times as much sodium would be required as was estimated for the annual delivery rate of sodium to the whole lake in stream and spring water. This difference, however, could easily have been drawn from the huge reservoir of sodium dissolved in the saline water of the northern and eastern parts of the lake.

In estimating the total time required to deposit the thickest trona bed (11.5 m), allowance was made for the slow rates of accumulation of the dolomitic marlstone partings. According to these estimates, it required about 3,900 years for the trona itself to deposit and about 7,450 years for the accumulation of the aggregate thickness (1.15 m) of dolomitic marlstone partings, the total elapsed time being on the order of 11,000 years. This apparent large drain on the reserves of sodium in the lake was continuously made up by the annual supply from streams, springs, and possibly new falls of volcanic ash.

Data are now available to determine from the phase relations of the system $NaHCO_3$–Na_2CO_3–H_2O several possible mechanisms by which trona may precipitate from brines and to evaluate quantitatively the effects of changes in temperature, solution composition, and P_{CO_2}. Eight phase diagrams and three tables of data are presented. The most important factor that emerges is the incongruent solubility of trona with respect to the HCO_3^{-1}:CO_3^{-2} ratio. Solutions in equilibrium with trona have lower bicarbonate contents than trona itself. Hence, the precipitation of trona impoverishes the brine in HCO_3^{-1}, unless CO_2 is added from a reservoir. Evaporation in a closed system eventually must lead to trona+natron assemblages. However, if an external reservoir, such as the atmosphere, buffers the activity of CO_2, and thus replenishes the bicarbonate content of the brine, trona may continue to precipitate until dryness. The amount of trona resulting can be calculated from the amount of sodium present in the original brine. The thick trona beds of the Green River Formation probably did form by this mechanism.

The solubilities of trona and nahcolite are much less affected by changes of temperature than they are by changes in P_{CO_2}. The magnitude of P_{CO_2} is reflected in the HCO_3^{-1}:CO_3^{-2} ratio of the brines. The effect of changes in P_{CO_2} can be shown more conveniently by using the bicarbonate quotient, defined as

$$\frac{gHCO_3}{gHCO_3+gCO_3}.$$

The bicarbonate quotient of a saturated solution equilibrated with present-day air is approximately 0.15 and is well within the range of natural brines in equilibrium with trona. Permissible ranges of the bicarbonate quotient between 25° and 50° C are given in a table in which the sodium contents of a solution are shown in equilibrium with trona and one other solid.

Three different mechanisms are discussed in detail by which an undersaturated solution may reach saturation with respect to trona and continue to precipitate trona: (1) isothermal evaporation with no loss of CO_2, (2) with some loss of CO_2, and (3) in equilibrium with a CO_2 reservoir.

Inasmuch as brines with as much as 12 weight-percent sodium can still be undersaturated at 30°C, considerable amounts of trona may crystallize simply by addition of CO_2. This mechanism probably is most important for precipitation of trona from interstitial brines, or from brines in the hypolimnion of a stratified lake. In both these environments, biogenically produced excesses of CO_2 are to be expected.

The most important mechanism for the deposition of thick trona beds is obviously evaporation in equilibrium with the atmosphere. Equilibration between brine and air does not, of course, have to be maintained perfectly and continuously, as long as the exchange is sufficiently fast and sufficiently large to replace the CO_2 lost to the brine through precipitation of trona. Evaporation is a slow process and there is probably ample time for CO_2 exchange, particularly in shallow, well-stirred lakes. If this were not so, we should find bedded deposits of trona + thermonatrite or trona + natron. We do not, and it is unlikely that recrystallization would have eliminated all traces of such assemblages, well buffered with respect to changes in P_{CO_2}.

The occurrence of halite in some of the trona beds shows that the Gosiute Lake brines were not simple carbonate-bicarbonate brines; therefore, the effects of the presence of other ions in the brines on the precipitation of trona are also evaluated.

For the precipitation of trona a simple carbonate-bicarbonate brine must have a bicarbonate quotient of about 0.15. Assuming a temperature of 30°C, such a brine must contain about 104,000 parts per million Na to be saturated with respect to trona. As a model of the Gosiute Lake brine at trona salting level, we have chosen a sample of Lake Magadi brine collected at the surface. This brine has a bicarbonate quotient of 0.14 and is slightly undersaturated with respect to trona. In Lake Magadi the brine is derived from the evaporation of water from adjacent saline springs. We have chosen a sample from one of these hot springs as a model of Gosiute Lake brine at a much more dilute stage.

A consideration of the phase equilibria in the system $NaHCO_3$–Na_2CO_3–$NaCl$–H_2O shows that the addition of NaCl decreases the solubility of nahcolite somewhat and the solubility of trona markedly. As a result, trona becomes a stable phase at temperatures as low as 0°C where it can crystallize from chloride-rich brines. Nine phase diagrams and four tables are considered in detail. Calculations are given for two paths that represent the extremes of two possible fates of Gosiute Lake brines during the formation of bedded trona. Intermediate between these two must lie the path, or paths, followed by the Gosiute Lake brine.

Undoubtedly, the most significant result of these studies is the fact that they show conclusively that if a brine continuously evaporates in equilibrium with air and has a bicarbonate quotient of 0.15, 80 percent of the total potential trona crystallizes out before halite saturation occurs. Furthermore, in sites within the pores of a trona bed, the greater the depth below the surface and the less access it has to the atmosphere, the less likely the occluded brine will ever become saturated with halite. Trona, however, will continue to crystallize out if biogenic CO_2 is supplied. These two findings seem to be adequate to account for the thick monomineralic beds of trona in the Green River Formation.

Disseminated crystals of trona in the marlstone beds are abundant and must have precipitated from interstitial brines after burial and mostly after the beds were fully compacted.

Shortite is by far the most common authigenic saline mineral in the saline facies of the Wilkins Peak Member. To learn more about the conditions under which shortite formed, its thermal stability was investigated experimentally. The phase relations of the system $NaHCO_3$–Na_2CO_3–$CaCO_3$–H_2O are shown graphically. Shortite forms from pirssonite + calcite by an increase in temperature, a decrease in the activity of H_2O, or by a decrease in pressure, or any combination of these. Addition of NaCl decreases the activity of H_2O and therefore favors the transformation of pirssonite to shortite. It is concluded that pirssonite formed in the marly sediments and that upon reaching a burial depth of about 1,650 meters and a temperature of about 90°C, pirssonite reacted with calcite to form shortite.

Northupite is the only authigenic chlorine-bearing mineral in the Green River Formation. A schematic isothermal-isobaric, a_{H_2O}, a_{CO_2} diagram expressing the stability relationships of northupite is given. In general, northupite forms in response to a decrease in either a_{H_2O} or a_{CO_2} or both.

No experimental data are available on the conditions under which loughlinite will form, but it seems clear that it can form wherever silica-bearing solutions come in contact with trona and dolomite. The fact that it is rare or absent above trona bed 17 suggests that the depth of burial may be a controlling factor.

Analcite is common in the saline facies, especially in altered tuffs. Its stability relations are already in the literature. Of interest is the fact that above a temperature of about 190°C, analcite and quartz are replaced by albite. In the presence of brine this transition temperature is lowered. The analcite-albite reaction defines an upper temperature limit for the diagenesis of the sediments of the Wilkins Peak Member.

The most plausible source of the constituents for all the authigenic minerals is the occluded brine. Assuming that the occluded brine contained 8.0 g Na/100-g solution, simple calculations show that the volume of brine occluded per unit of sediment contained more than enough sodium to form all the sodium-bearing minerals found. Other constituents in the brine, either by themselves or by reacting with minerals in the sediment, doubtless provided for the formation of all the authigenic minerals.

The silica regimen of Gosiute Lake must have been different from that in most existing lakes because there was no diatom flora and apparently no sponge fauna. The silica that entered the lake must have precipitated directly or reacted with other constituents to form some of the authigenic minerals.

The iron in Gosiute Lake, which was trapped in the sediments as the abundant mineral pyrite, may have been distributed through the lake water or the brine in the form of the very stable yellowish organic complex.

Possibly other metallic elements, such as titanium, zirconium, niobium, zinc, and manganese, were also mobile in the pore solutions because they all occur in one or another of the authigenic minerals. All these metals, except possibly zinc, form anion radicals in an alkaline environment.

In many of the more homogeneous beds of more or less organic dolomitic marlstone in the saline facies, the isolated euhedral crystals of shortite have a surprisingly uniform distribution, which is independent of the size of the crystals. A frequency histogram representing the distribution of about 1,700 crystals is given. The standard deviation of the histogram is 2.5. We believe that these shortite crystals formed after compaction ceased.

In any sedimentary deposit the increasing load of successive increments of new sediment expresses the pore water upward into successively younger layers. As the pores decreased to a critical size they served as a filter that permitted water to pass but not all of the salts. Such a mechanism may account, in part at least, for the observed concentration of saline minerals in zones. The great volume of occluded solution that passes upward during compaction was shown by Emery and Rittenberg in 1952. For a shale that had been buried to a depth of 1,524 meters and that had a porosity of about 5 percent, they calculated that 32,000 milliliters of pore water had passed through each square centimeter since it was originally deposited.

Because much of the mud that originally made up the sediments of the saline facies contained organic matter, the occluded water and brine probably contained H_2S and therefore had a low Eh. Even though the anaerobic bacterial activity that produced the H_2S ceased after moderate depth of burial, the pore solutions probably retained this characteristic to great depths.

INTRODUCTION

The trona beds and the associated saline minerals of the Green River Formation of Wyoming are restricted to the saline facies of the Wilkins Peak Member; this member has a lesser areal extent than the other members of the Green River Formation (pl. 1; fig. 1). The lithology of the Wilkins Peak Member and the stratigraphic relations of the member to the rest of the Green River Formation have been described rather fully in another report (Bradley, 1964b). Culbertson (1966) has described and discussed the stratigraphy of the trona and trona-halite beds. Also, the limnology of the Wilkins Peak Member has been outlined in a brief discussion of the paleolimnology of the Green River Formation (Bradley, 1963, p. 629–644). From these three accounts, the following brief summary of the Wilkins Peak Member and its history is drawn to serve as a setting for this report on the saline deposits of the Green River Formation.

Eugster is responsible for the discussion of the physical chemistry of the saline minerals and that of several of the authigenic nonsaline minerals. Bradley is primarily responsible for the rest of the report. Nevertheless, both authors worked over the whole report so many times that it can be regarded as a fully cooperative effort.

It is a pleasure to express our gratitude to colleagues and friends who have given this manuscript their searching criticisms. In its penultimate draft, Don Deardorff, of the Diamond Alkali Co., Prof. D. A. Livingstone, of Duke University, and W. C. Culbertson, of the U.S. Geological Survey, read the manuscript and made many useful suggestions. We are grateful to the Diamond Alkali Co., which generously supplied us with subsurface information during their long and remarkably successful trona exploration program. G. I. Smith, Blair Jones, and A. H. Truesdell, all of the U.S. Geological Survey, served as critics of the completed manuscript. Their extreme thoroughness and professional competence qualify them to rank among the most effective of critics. Indeed, G. I. Smith and Blair Jones have each reoriented or clarified the reasoning in so many places and each has made so many constructive suggestions that they probably should have been made joint authors.

GEOLOGIC SETTING

The Green River Formation, of early and middle Eocene age, is a great lens of lacustrine beds enclosed within a matrix of generally fine-grained fluviatile sediments that belong to the Wasatch Formation below and the Bridger Formation above. The generalized relationships between these formations and the Green River Formation and its several members and tongues are shown in figure 2.

Gosiute Lake, in which the sediments of the Green River Formation accumulated, formed by gradual and progressive downwarp of the earth's crust, a downwarp that made room for successive increments of sediment.

Although Gosiute Lake passed through a complex series of changes in area and depth during its roughly

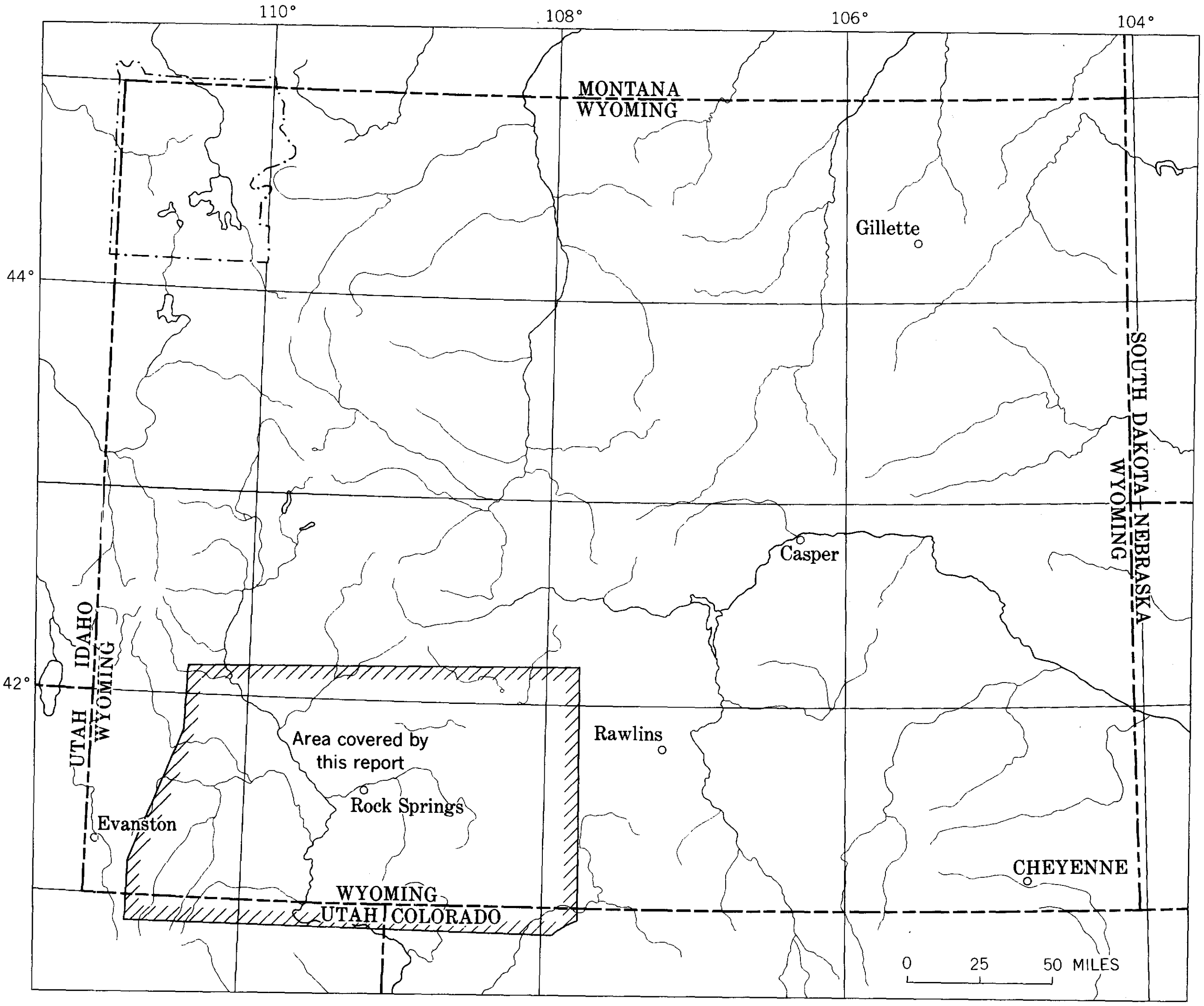

FIGURE 1.—Location of the area discussed in this report.

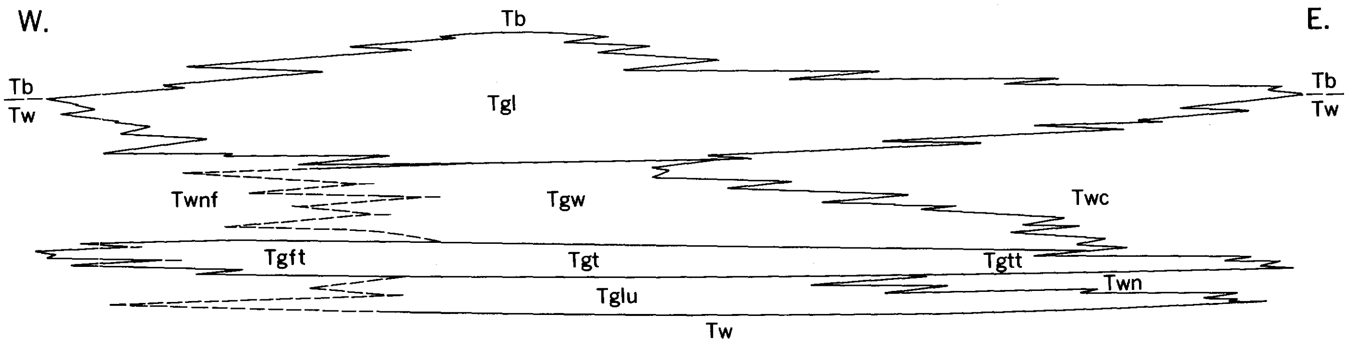

FIGURE 2.—Schematic section of the Green River Formation showing approximately the relative size and extent of each lithologic member of the Green River Formation and its relation to the Wasatch and Bridger Formations. Tw, Wasatch Formation; Twnf, New Fork Tongue, Twn, Niland Tongue, and Twc, Cathedral Bluffs Tongue, all of the Wasatch Formation. Tglu, Luman Tongue, Tgt, Tipton Shale Member, Tgtt, Tipton Tongue, Tgft, Fontenelle Tongue, Tgw, Wilkins Peak Member, and Tgl, Laney Shale Member, all of the Green River Formation. Tb, Bridger Formation.

4-million-year life, it had three major changes in size. During the first, or Tipton plus Luman stage, which lasted about 1 million years, it had a maximum area of some 32,400 km^2 (12,500 sq mi) and was a fresh-water lake with an outlet. It occupied much of the Green River Basin, all Washakie Basin, and extended far northeastward into the Great Divide Basin. Presumably, there was a large central island made by the Upper Cretaceous rocks of the ancestral Rock Springs uplift.

At the end of the Tipton stage the climate became considerably more arid, and Gosiute Lake shrank to about a third, or less, of its former area. It then occupied only a part of the Green River Basin and an area south and east of the Rock Springs uplift (pl. 1). It had no outlet and became, at times, very saline. During this stage, which also lasted about a million years, the Wilkins Peak Member formed. As all closed lakes do, Gosiute Lake fluctuated frequently in area and depth. It ranged from a probable maximum area of 20,700 km^2 (8,000 sq mi) to a minimum of perhaps about half that size (fig. 3). Within the Wilkins Peak Member is a saline facies with which this report is primarily concerned.

When the arid climate, which had produced the Wilkins Peak stage, reverted to a moister climate, Gosiute Lake expanded to its maximum size of about 40,150 km^2 (15,500 sq mi), and again became a fresh-water lake with an outlet. Even at this stage, however, it probably lost much more of its water by evaporation than by overflow. This most extensive stage of Gosiute Lake was the longest—roughly 2 million years—and during this stage the Laney Shale Member of the Green River Formation was deposited. The upper part of the Laney Shale Member, which was apparently deposited in a very shallow lake, contains much volcanic

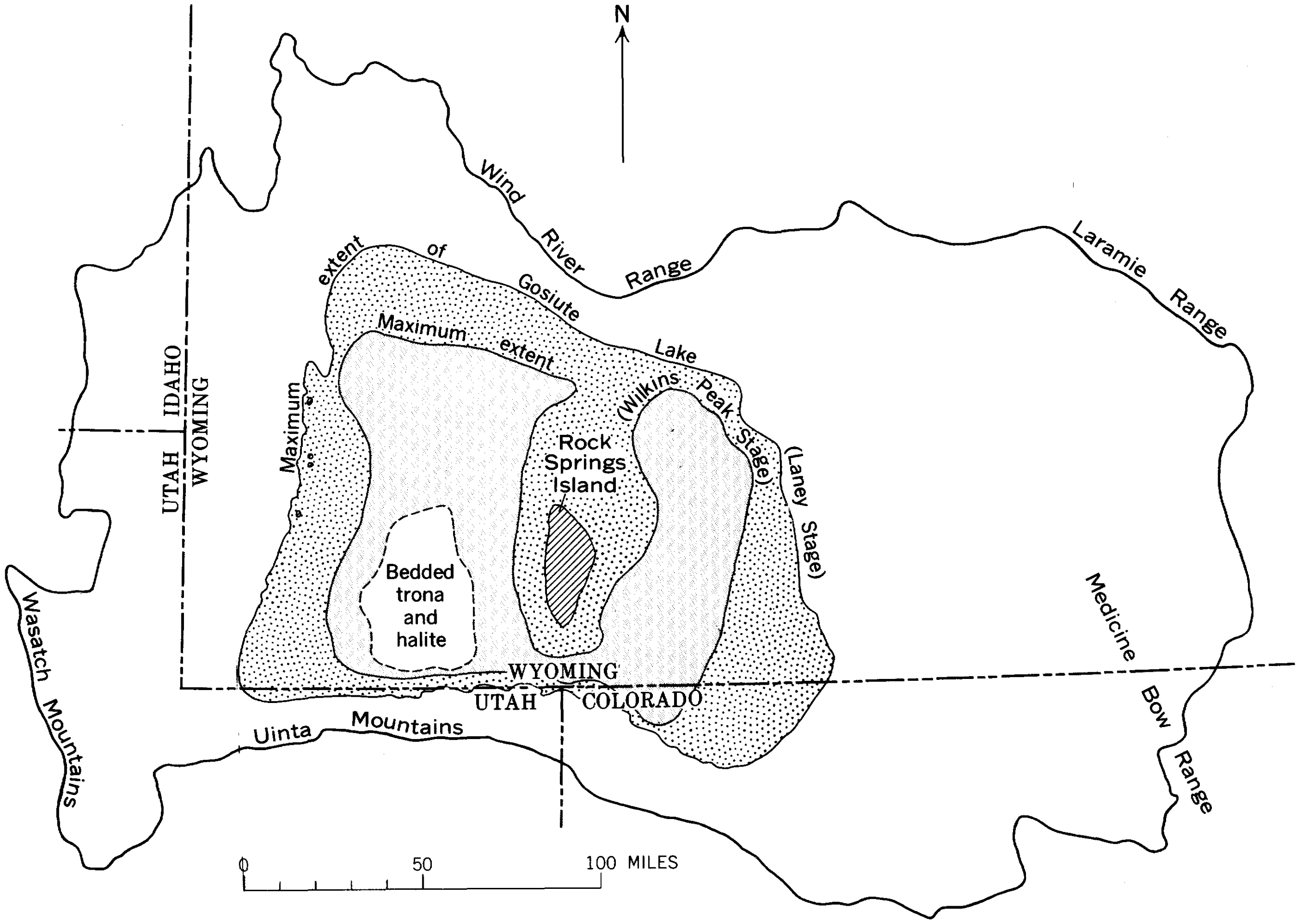

FIGURE 3.—Inferred outline of the hydrographic basin of Gosiute Lake. Within the hydrographic basin are shown the inferred maximum extent of Gosiute Lake during the Laney stage, the inferred maximum extent of the Wilkins Peak stage, and the inferred maximum extent of the area underlain by beds of trona and halite. Also shown are the inferred outline (ruled pattern) of the island in the Laney stage lake created by the ancestral Rock Springs uplift and the approximate locations of the principal mountain ranges bordering the hydrographic basin.

ash; it may well be that these repeated influxes of volcanic ash filled the basin faster than downwarp could accommodate them and so brought Gosiute Lake to its end, some 4 million years after it came into being.

STRATIGRAPHY AND COMPOSITION OF THE WILKINS PEAK MEMBER OF THE GREEN RIVER FORMATION

The Wilkins Peak Member consists predominantly of gray to greenish-gray dolomitic and somewhat tuffaceous marlstone, mudstone, muddy sandstone, a moderate number of lean to rich beds of oil shale, and a considerable number of rather thin volcanic ash beds. It is about 940 feet thick at its type locality, Wilkins Peak, in the southern part of T. 18 N., R. 106 W., Sweetwater County. The configuration of that part of the member in the Green River Basin is shown by contours in figure 4. It thins laterally and intertongues with, and grades into, either carbonaceous marsh deposits or fluviatile mudstone of the Wasatch Formation in one or another tongue of the Wasatch Formation. Southward, it presumably grades into near-mountain facies of undifferentiated Tertiary sediments.

The Wilkins Peak Member is not restricted to the Green River Basin but extends around the southern end of the Rock Springs uplift, across the Hiawatha Basin, up along the west side of Washakie Basin, and far northward through the central part of the Great Divide Basin. In all this area outside the Green River Basin the member had long been lumped with the Tipton Tongue of the Green River Formation until H. W. Roehler (oral commun., 1963) discovered its proper identity. Roehler gives three thicknesses for the Wilkins Peak Member, one of 536 feet south of the Rock Springs uplift (center of T. 13 N., R. 102 W.), and two along the west rim of Washakie Basin: 291 feet in the northern part of T. 14 N., R. 100 W., and 256 feet near the west-center of T. 17 N., R. 98 W. In the Great Divide Basin, Pipiringos (1961, p. A29–A30) gives the thickness of the upper part of the Tipton (now Wilkins Peak Member) as 100–120 feet. In that area the member consists of "loosely cemented sandstone and lesser amounts of clay shale, fine-grained calcareous sandstone, and algal reefs" (p. A29).

It may be useful to think of this member as a great lens of sediments laid down in a closed lake, which, like all closed lakes, fluctuated considerably and repeatedly in area and volume during its long history. We know from the fabulous quantities of bedded trona and lesser amounts of halite found in these lakebeds that the lake at this stage repeatedly became so concentrated that trona and halite precipitated. The known great lateral extent of the trona, and trona-halite, beds, shows that even at these lowest stages the lake was still large, but following each of these low stages the lake expanded very considerably. During each of these expanded stages, beds of dolomitic mudstone, marlstone, and oil shale were deposited. These make up the great bulk of the Wilkins Peak Member. It may be simpler to think of this member as a great lens of lacustrine sediments, which contains within it another comparable, but smaller, lens of saline sediments. This smaller internal lens consists not only of trona beds, but also of beds of dolomitic marlstone and mudstone that contain a very considerable quantity and variety of other saline minerals, which are discussed in the present report (p. B7–B12, B16–B60).

That part of the member enclosing the saline facies can be thought of as a less saline facies, which, of course, has a greater lateral extent. It also has a greater vertical range because nonsaline beds both underlie and overlie the beds of the saline facies.

SALINE FACIES OF WILKINS PEAK MEMBER

The saline facies of the Wilkins Peak Member can be defined as the group of beds lying between the stratigraphically lowest and highest occurrence of saline minerals, or their molds. Most of the beds within this bracket contain some saline minerals. The saline minerals range in abundance from sparsely scattered crystals to solid beds of trona and trona mixed with halite that are locally as much as 38 feet thick. (See pl. 2.)

We believe that the most reliable saline mineral to use in defining the top and bottom of the saline zone is shortite. The argument for this, however, is not particularly strong. In many of the cores that penetrate the thickest sequence of trona-halite beds in the south-central part of the Green River Basin, thin laminae, veinlets, and rosettes of trona were found in marlstone or oil shale beds 5 to more than 20 feet below the lowest observed occurrences of shortite crystals. These veinlets and rosettes of trona suggest that they formed, long after diagenesis, during a period when the lithified sediment of the basin was being uplifted and deformed. Trona, being more soluble than shortite, may have been more susceptible to postdiagenetic downward migration and recrystallization.

At the top of the saline facies, shortite seems to be the highest saline mineral, except locally, as at the outcrop west and southwest of the town of Green River where molds of radial aggregates of saline crystals are found in a zone a few feet thick, 25–30 feet up in the Laney Shale Member above the top of the Wilkins Peak

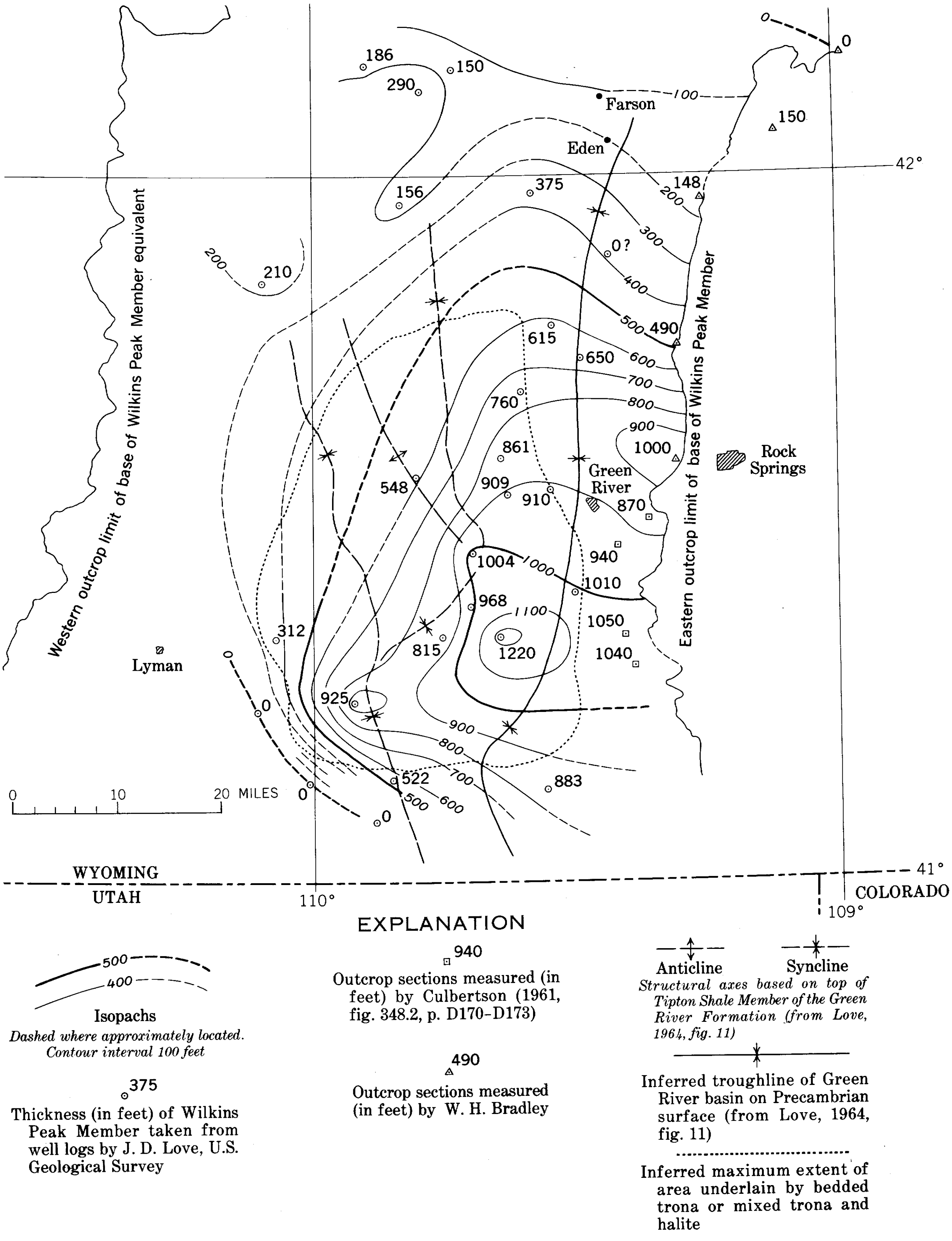

FIGURE 4.—Isopach map of the Wilkins Peak Member of the Green River Formation in a part of the Green River Basin, Wyo.

Member. These radial molds, from a few inches to nearly 1 foot in diameter, strongly resemble molds formed by aggregates of nahcolite crystals in the Green River Formation south of the Uinta Mountains. If these were formed by nahcolite, they represent a different lacustrine environment from that which gave rise to most of the other saline minerals that formed at the bottom or in the muds of Gosiute Lake. Like the other authigenic minerals, those that formed the radial molds crystallized in the sediments after compaction.

In spite of these uncertainties, the records from the cores taken from 21 exploratory boreholes show that the saline facies in the central part of the basin is only a little thinner than the Wilkins Peak Member itself and that, in general, the thickness of the saline facies varies with the thickness of the Wilkins Peak Member. The saline facies thins more rapidly toward the basin margins, however, and is, of course, considerably less extensive areally (fig. 4).

AUTHIGENIC MINERALS

In his study of the core from the John Hay, Jr., well 1, Joseph J. Fahey (1962, p. 6–12), of the U.S. Geological Survey, estimated the abundances of the various saline minerals throughout the whole saline facies, which there is 555 feet thick. Shortite ($Na_2CO_3 \cdot 2CaCO_3$) occurs predominantly as isolated crystals disseminated through the rocks. Commonly, however, they are concentrated along bedding planes (fig. 5). At some horizons, shortite crystals are so numerous that they make up thin beds of interlocking crystals. At other levels, the crystals are widely separated. Most of the shortite crystals are idiomorphic. They range in size from almost microscopic to 3 centimeters across.

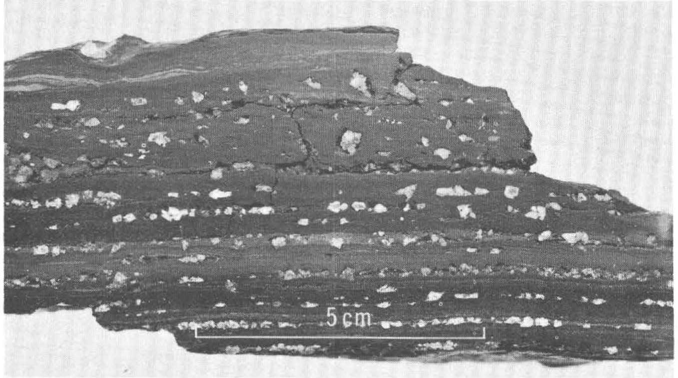

FIGURE 5.—Molds of shortite crystals (partly filled with calcite) concentrated along bedding planes of rich oil shale from the outcrop of the Wilkins Peak Member west of the town of Green River, Wyo.

Fahey (1962, p. 22) estimated that shortite makes up about 10 percent of the 555 feet in the saline facies and calculated that, if this percentage holds laterally, at least 125 million tons of shortite occurs under each square mile of land in that area.

Closely associated with the shortite crystals through much of the saline zone are crystals of northupite ($Na_2CO_3 \cdot MgCO_3 \cdot NaCl$). Although northupite crystals are disseminated through the rocks, they tend to be bunched in somewhat irregular masses of interlocking crystals. Unlike shortite, the northupite crystals are rarely euhedral. Fahey (1962, p. 31) estimated that northupite makes up about 2.2 percent of the saline zone. He observed also that northupite occurs only above the trona bed presently being mined by the Intermountain Chemical Co. and, indeed, most of it occurs in a zone about 160 feet thick (Fahey, 1962, fig. 7). According to Don Deardorff, of the Diamond Alkali Co. (oral commun., 1961), however, it occurs also in lower parts of the saline facies farther south. According to Fahey, it is found invariably in dolomitic rocks that contain relatively little organic matter. In at least one bed, however, rather large northupite grains are embedded in a matrix of secondary microgranular quartz. Shortite, on the other hand, occurs indiscriminately through the whole spectrum of rock types in the saline facies.

The authigenic mineral next in order of abundance in the saline facies is trona. These trona crystals, which occur singly or in aggregates scattered through the dolomitic marlstone and mudstone, evidently grew, as the shortite crystals did, from brine occluded in the mud and during late stages of diagenesis, and surely after compaction. They are not to be confused with the layers of trona that precipitated on the lake bottom at low stages of the lake. The authigenic crystals of trona range in size from microscopic to several centimeters across (fig. 6). Most of them occur as aggregates or small pods, though discrete small crystals are locally numerous. Idiomorphism is much less common among them than it is among the shortite crystals. Fahey (1962, p. 7–11) reports authigenic trona as making up as much as 15 percent of certain marlstone beds and reported shortite crystals in various stages of being replaced by trona.

In addition to shortite, trona, and northupite, Fahey found, in lesser amounts, halite ($NaCl$), pirssonite ($Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$), gaylussite ($Na_2CO_3 \cdot CaCO_3 \cdot 5H_2O$, nahcolite ($NaHCO_3$), thermonatrite ($Na_2CO_3 \cdot H_2O$), wegscheiderite ($Na_2CO_3 \cdot 3NaHCO_3$), and tychite ($2Na_2CO_3 \cdot 2MgCO_3 \cdot Na_2SO_4$).

According to Fahey (1962, p. 39), all these other minerals formed later than the shortite, as they replace shortite. For a fuller discussion of the occurrences of these minerals and their paragenesis, one should consult Fahey's report (1962, p. 38–44) on the saline minerals

FIGURE 6.—Authigenic crystals of trona in dolomitic marlstone of the Wilkins Peak Member of the Green River Formation.

he found in the core of the John Hay, Jr., well 1, Sweetwater County, Wyo. Also, in the present report (p. B59–B60), evidence is presented that indicates that pirssonite may also have been formed in very large quantities before the shortite.

Besides these saline minerals the following other authigenic minerals have been identified in the saline zone by Bradley (1929a, 1964a), Fahey (1941, 1950), Fahey, Ross, and Axelrod (1960), Milton, Chao, Fahey, and Mrose (1960), Milton, Mrose, Fahey, and Chao (1958), Mrose, Chao, Fahey, and Milton (1960), and Regis and Sand (1957).

TABLE 1.—*Authigenic minerals (other than saline minerals already discussed) found in the saline zone of the Wilkins Peak Member of the Green River Formation in Wyoming*

Acmite	$NaFeSi_2O_6$
Adularia	$KAlSi_3O_8$
Albite	$NaAlSi_3O_8$
Analcite	$NaAlSi_2O_6 \cdot H_2O$
Barytocalcite	$CaBa(CO_3)_2$
Bradleyite	$Na_3MgCO_3PO_4$
Burbankite	$Na_2(Ca,Sr,Ba,Ce)_4(CO_3)_5$
Chlorite	approx $Mg_5Al_2Si_3O_{10}(OH)_8$
Collophane	(carbonate apatite)
Ferroan northupite	$Na_2CO_3 \cdot (Mg,Fe)CO_3 \cdot NaCl$
Fluorapatite	$Ca_{10}(PO_4)6F_2$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Labuntsovite	$(K,Ba,Na,Ca,Mn)(Ti,Nb)(Si,Al)_2(O,OH)_7H_2O$
Lazurite	$Na_4(NaS_3 \cdot Al)Al_2(SiO_4)_3$
Leucosphenite	$CaBaNa_3BTi_3Si_9O_{29}$
Loughlinite	$(Na_2,Mg)_2Si_3O_6(OH)_4$
Magnesioriebeckite	$Na_2(Mg,Fe)_3(Fe,Al)_2Si_8O_2(OH)_2$
Marcasite	FeS_2
McKelveyite	$(Ba,Ca,Sr)_5(Y,Gd,Dy,Er,etc.,U,Th)_2(Na,K)_2(CO_3)_9 \cdot 5H_2O$
Norsethite	$BaMg(CO_3)_2$
Pyrite	FeS_2
Pyrrhotite	$Fe_{1-x}S$
Quartz	SiO_2
Searlesite	$NaBSi_2O_6 \cdot H_2O$
Siderite	$FeCO_3$
Stevensite	$Mg_3Si_4O_{10}(OH)_2$
Talc	$Mg_3Si_4O_{10}(OH)_2$
Vinogradovite	Na-Ti-Silicate
Witherite	$BaCO_3$
Wurtzite	ZnS
Unnamed	Na-Ti-Zr-Silicate

Of these authigenic minerals, analcite, loughlinite, searlesite, and stevensite, have been found in considerable abundance. In the saline facies, analcite is common. It occurs not only as the dominant mineral in many beds of tuff, in some of which it makes up 60–75 percent of the rock, but it is also scattered through many other beds of organic marlstone and oil shale that have widely differing admixtures of tuffaceous material. (See Bradley 1929a.) Some of the analcite appears to have formed very late in the diagenesis of these beds. This latest analcite forms overgrowths on, or replaces, northupite; these secondary growths are completely free of inclusions, whereas the earlier analcite crystals contain abundant inclusions.

Authigenic feldspars are abundant in many of the tuffaceous beds. Idiomorphic crystals of albite are not uncommon in many of the Wilkins Peak sediments, and Charles Milton, of the U.S. Geological Survey, has reported (oral commun., 1963) fairly sizable granules of adularia that form pseudomorphs after analcite crystals. A common habit in rocks that originally contained volcanic glass is a microperthitic or antiperthitic intergrowth of the two feldspars. Such patterns of intergrowth grade into cryptocrystalline areas, but the outlines of glass or pumiceous shards are discernible in some of the more nearly pure tuff layers. Hay and Moiola (1963, p. 323) have described aggregates of potassium feldspar grains in one of the thin tuff beds in the Searles Lake sediments which are very small and which are intergrown so as to have the texture of finely crystalline chert. Hay and Moiola suggest that these potassium feldspar grains may have replaced shards and pumice fragments.

Authigenic quartz is another distinctive feature of the rocks in the saline facies, particularly in the central part of the Green River Basin. This secondary quartz ranges from almost cryptocrystalline to grains nearly 0.2 millimeter across and is somewhat more common in the tuffaceous layers. In some beds it occurs as small, rather imperfectly formed, bipyramidal prisms.

In the saline facies of the Wilkins Peak Member, a considerable number of beds contain loughlinite $[(Na_2,Mg)_2Si_3O_6(OH)_4]$ (Fahey and others 1960), which occurs as veinlets and as beds locally as much as 1 foot or more thick. More generally, it is only one of several constituents distributed through the rock.

Searlesite is about as common as loughlinite. Fahey (1962, p. 44) reported that subhedral crystals of searlesite as much as 25 centimeters long have been found sparsely disseminated throughout the trona bed being mined by the Intermountain Chemical Co. Searlesite also occurs as isolated crystals, or groups of them, in the beds of organic marlstone and mudstone in the saline facies. Fahey also reported isolated minute euhedral crystals of bradleyite in this trona bed.

Whether dolomite should be regarded as an authigenic or primary mineral is uncertain. Alderman and Skinner (1957) and Alderman and Von der Borch (1961) suggest that dolomite precipitates directly from warm, strong brine. Peterson, Von der Borch, and Bien (1966) believe that for the most part magnesian calcite is the solid phase that precipitates, and that subsequently, in the sediment, this recrystallizes, takes up more magnesium, and becomes dolomite. Jones and Van Denburgh (1966, p. 441) report that at "Deep Springs Lake the inflow springs are heavily supersaturated with respect to dolomite, and primary dolomite composes a large proportion of the lacustrine muds." Clayton, Jones, and Berner (1968) concluded from isotope studies that dolomite crystallizes directly from solutions at Deep Springs Lake.

Most of the authigenic minerals (shortite, for example) formed, we believe, from entrapped brine after rather deep burial and after essentially the maximum state of compaction had been reached by the sediment, which, however, was still plastic. The reasoning that leads to this conclusion is derived almost wholly from the relations between shortite crystals and the laminated sediment that they displace (fig. 7). With few exceptions, the shortite crystals are euhedral, and well formed, and the interfacial angles (32°57′ and 57°26′) (Fahey, 1939, p. 515) make sharp chisellike edges. Between the crystals the varved or laminated oil shale is much contorted as though it had been pushed aside while still plastic. Indeed, the lengths of some of these varves between crystals (fig. 7) were measured and found to be long enough, if straightened out, to make continuous flat laminae across the photograph. The inference seems inescapable that these varves were, in fact, laid down as essentially flat laminae and that the crystals grew to their present size later. The contorted varves across the center of the photograph clearly had been compacted to virtually their present thickness before they were deformed. Otherwise, they would show thinning and thickening as they accommodated to the shape of the crystals during compaction. One other aspect of these contorted varves leads to this same conclusion. The varves in a number of the folds are steeply inclined. In fact, some of these steeply inclined folds have rather sharp apices. (See *a* in fig. 7.) Very little compaction could have taken place after these folds were formed without flattening them perceptibly.

Although most of the space for growth of these crystals was obtained by crowding aside the plastic mud, in a few places the crystals seem to have replaced the mud without detectable distortion. Despite this appearance, when these areas are examined critically under high magnification, it is evident that most, but not all, of the layers have actually been much compressed in a thin zone against the shoulder of the crystal as though responding to considerable shearing stress. In nonlaminated or massive marlstone, which is made up almost wholly of microgranular dolomite and some organic matter, it is not always possible to tell whether the shortite crystals grew by pushing aside the carbonate mud or by replacement. Wherever any lamination, or zonation is discernible, however, it shows distortion around the crystals; it seems reasonable, therefore, to infer that the beds of nonlayered carbonate mud also probably yielded to the growing shortite crystals by flowage. Blair Jones

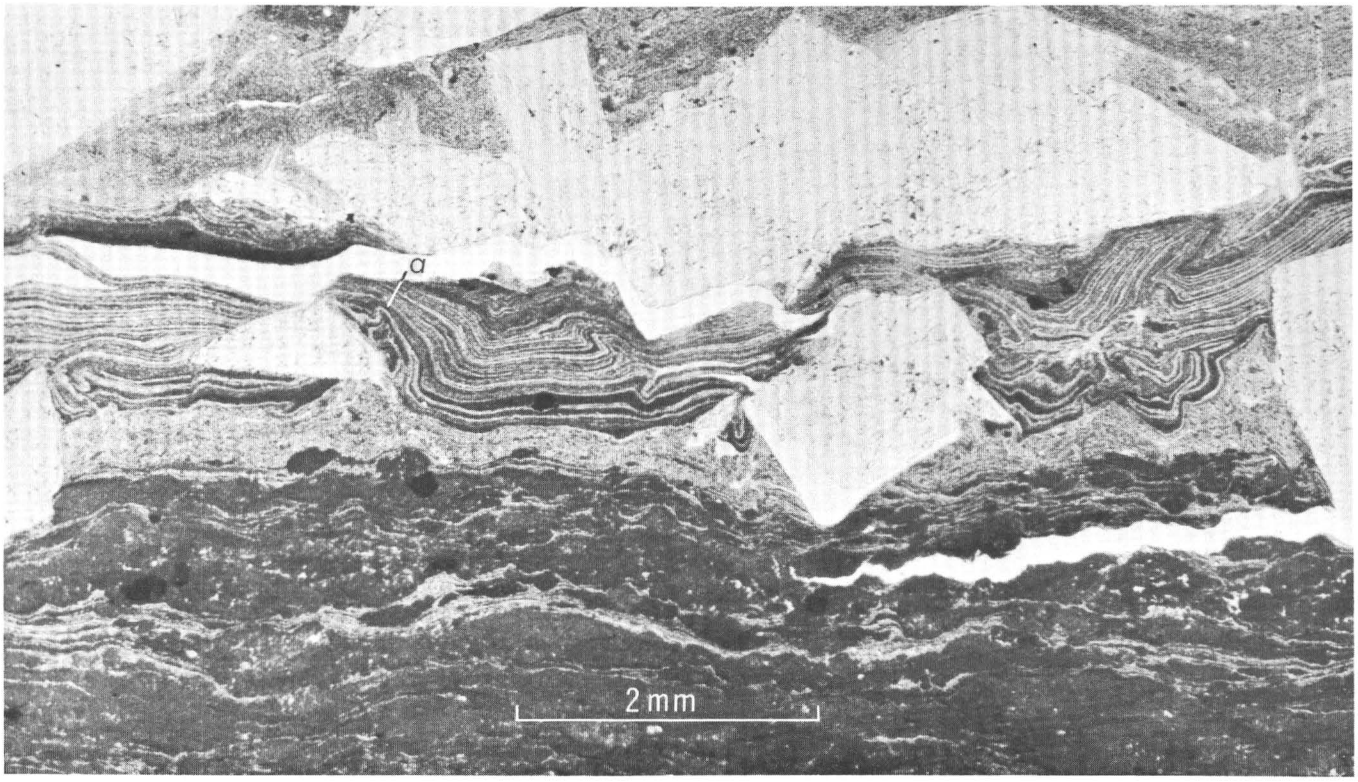

FIGURE 7.—Photomicrograph of thin section of varved oil shale. Varves were compacted and then deformed by the growth of large shortite crystals. Sharp folds in these varves, as at *a*, show that no significant compaction of the sediment could have occurred after they formed. Plane-polarized light.

(oral commun., 1965) points out, cogently, that the chemistry of this process requires a simultaneous concentration of Na_2CO_3-rich pore fluid and reaction with solid $CaCO_3$.

What has been described for shortite crystals applies rather generally to most of the authigenic crystals found in the Green River Formation. Nearly all are idiomorphic, and many contain inclusions of the microgranular carbonate mud in the form of minute grains of dolomite and calcite or organic matter, or both. In some of these authigenic crystals the occluded material makes a pattern that reflects the internal structure of the crystal; in others, the occluded particles are arranged in an irregular and rather vague netlike pattern, which suggests that these crystals replaced an aggregate of subhedral crystals.

Some crystals, or crystal aggregates, on the other hand, clearly formed in the very early stages of compaction. Pyrite is a conspicuous example. Some finely crystalline aggregates of pyrite, and also pyrrhotite, are much flattened in the plane of the bedding. Moreover, some oil-shale beds contain a great abundance of minute spherules of pyrite. These spherules probably formed a little below the mud-water interface at the bottom of Gosiute Lake. This inference is based on analogy with the closely similar, or identical, minute spherules of iron sulfide that form today below the surface of hydrogen sulfide-saturated organic muds in many lakes. On the other hand, both pyrite and pyrrhotite undoubtedly also formed later after much, or all, of the compaction had taken place. This is shown by wholly undistorted euhedral crystals of pyrite and delicate feathery aggregates of pyrrhotite crystals (fig. 8). These euhedral crystals, of course, may represent late reorganization of earlier, smaller crystals or spherules.

CHEMICAL COMPOSITION OF THE SEDIMENTARY ROCKS

Fahey (1962, p. 15) gives 14 complete chemical analyses of the rocks, including their contained saline minerals, in the saline zone of the Wilkins Peak Member. These analyses are of fresh rocks from the core of the John Hay, Jr., well 1 in the central part of the Green River Basin. One of Fahey's published analyses is repeated here as analyses 4 of table 2.

In addition to these analyses of Fahey, we now have seven more analyses of rocks from the saline facies. These are given below in table 2. An interpretation of the mineralogy of each of these analyzed rocks is given in table 3. The minerals were determined from inspection of thin sections, from examination of fresh

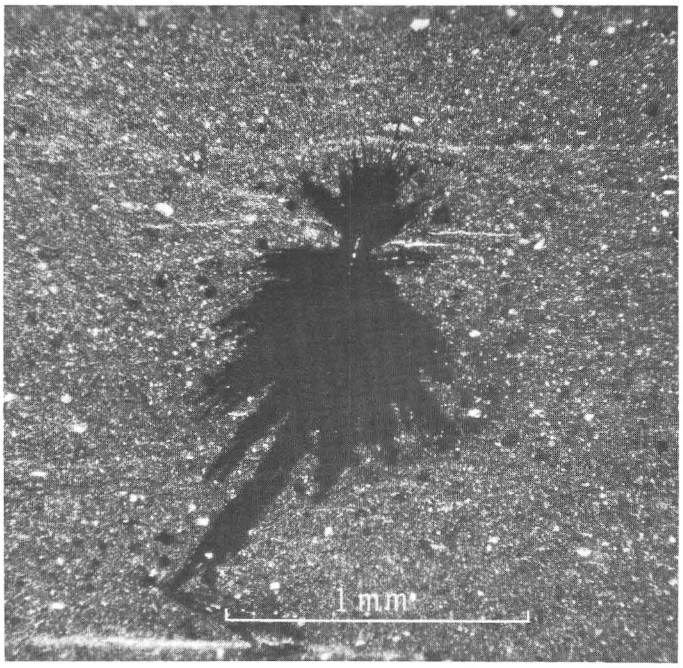

FIGURE 8.—Photomicrograph showing a bundle of iron sulfide crystals (pyrrhotite?) in organic marlstone from the Wilkins Peak Member of the Green River Formation. Such delicate crystals, cutting the bedding virtually at right angles, must have grown in the sediment after all compaction had ceased. Plane-polarized light.

and acid-leached fragments in index oils, from X-ray analyses, and from the chemical constituents in the analyses themselves.

Some of the kinds of errors inherent in these statements of the mineralogy should be made clear. In each one the amount of quartz is based on the amount of SiO_2 left after calculating out all the other minerals. The amounts of quartz (or opal) so determined are almost surely too large because some of the SiO_2 probably should have been combined with some of the constitutents not accounted for in the minerals listed. For example, there are small bits of sodic amphiboles in most of the rocks, though these are reported for only analysis 4. Other errors are revealed by the fact that rather small amounts of as many as 10 constitutents were left uncombined after calculating the mineralogy of each rock. Many of these errors arise from the fact that the simplest composition for each mineral was chosen for these calculations. The same, or comparable, errors are revealed by the fact that in none of these rocks does the sum of the weight percents of the minerals add up to 100.

To make these analyses and the respective mineralogical interpretations more meaningful, the following comments on the petrology of each analyzed rock are given.

1. In this oil shale the orthoclase and quartz are present as small sharply angular fragments characteristic of the crystal tuffs so common in the Green River Formation. They may have fallen into the lake directly as volcanic ash, but as they are not concentrated in layers, it is more likely that they were brought in as windblown dust from a tuffaceous terrane. The rather large amount of Al_2O_3 left uncombined suggests that a clay mineral should have been included in the mineralogy.

   Because the shortite was introduced into this rock during diagenesis, its presence makes the other constituents seem disproportionately small. For example, if the 26.06 percent of shortite is calculated out, the rock would consist of 45.7 percent dolomite, 16.28 percent orthoclase, 8 percent quartz, and 21.5 percent organic matter. Incidentally, this organic matter contains 2.4 percent nitrogen. J. W. Smith (1961, p. 13), of the U.S. Bureau of Mines, found 2.39 percent nitrogen in organic matter that he isolated from the Mahogany zone oil shale in the Green River Formation of Colorado.
2. This extremely fine-grained pale-greenish-gray dolomitic marlstone is a common rock type in the saline facies of the Wilkins Peak Member. Most of the minute sharply angular grains of potassium feldspar and quartz are concentrated in thin obscure laminae, which also contain other volcanic debris, evidently in large part devitrified volcanic glass shards. The stevensite is thought to be an authigenic mineral, and the exceedingly fine-grained dolomite may have been deposited directly from the warm, strong brine, or it may have formed by a diagenetic process soon after burial (p. B11). The anatase(?) occurs as exceedingly minute, essentially equidimensional grains (commonly 1 micron or less across) as inclusions in the potassium feldspar and quartz grains. The largest of these anatase(?) grains suggest very obtuse octahedra. Although this rock contains only 0.20 percent MnO, this is worth remarking, as it is 5–10 times as much MnO as has been found in any of the analyzed rocks from the saline zone.
3. This buff carbonate-rich marlstone is a crystal tuff rather characteristic of many of the thin zones described by J. D. Love (1964), of the U.S. Geological Survey, as being abnormally rich in P_2O_5. This particular sample, however, missed the rich phosphatic zone and contains only 0.02 P_2O_5, a value characteristic of the great bulk of the Wilkins Peak Member of the Green River Formation in Wyoming. This outcrop sample, which is

TABLE 2.—*Chemical analyses of rocks from the saline facies of the Wilkins Peak Member of the Green River Formation, Sweetwater County, Wyo.*

[nd, not determined]

	1	2	3	4	5	6	7	8
Laboratory No.	148,350	I.W.C.-537	151,513	148,139	153,922	158,259	160,238	155,841
Field No.	(2-56)	G.I.S. 56-7-30A	(5-57)	Fahey (1962, p. 15)	(17-58)	Butler well 1 at 549 ft	"Big Island" tuff	(18-58)
SiO_2	13.60	27.58	45.83	29.88	52.59	50.69	69.1	45.24
Al_2O_3	3.30	2.20	10.81	4.06	13.58	14.68	9.3	.81
Fe_2O_3	(1)	(1)	3.09	1.34	4.24	4.38	.17	.56
FeO	1.46	1.72	2.25	.90	.63		.28	.08
MgO	7.32	14.00	5.03	7.42	2.54	2.63	.1	22.95
CaO	20.84	15.32	8.37	9.35	7.78	3.56	.5	5.16
Na_2O	5.28	2.29	[2] 3.25	12.03	3.69	5.60	5.2	.24
K_2O	2.02	2.20	[2] 3.06	2.75	3.19	5.69	8.4	.02
H_2O+	nd	1.68	5.13	6.76	3.34	1.95	2.8	7.42
H_2O-	nd	1.66	.41	4.40	1.80	1.62		8.42
TiO_2	.14	1.60	.42	.13	.61	.56	.04	.08
P_2O_5	.02	.02	.02	.00	.12	.04	nd	nd
MnO	nd	.2	.07	.05	.07	nd	.005	.02
CO_2	28.98	26.55	10.47	14.44	5.64	5.25	4.61	5.95
SO_3	nd	nd	.61	.00	nd	nd	nd	nd
Cl	nd	nd	.09	2.38	nd	.11	nd	nd
F	nd	nd	nd	----------	nd	.17	.01	.77
S	1.68	.07	None	.08	nd	1.83	nd	nd
BaO	nd	None	1.14	.00	nd	[4] .1	.011	nd
Li_2O	nd	nd	[3] .02	.03	nd	nd	nd	nd
B_2O_3	nd	nd	nd	----------	nd	[4] .08	.084	nd
Organic matter	15.76	2.76	.04	4.78	nd	nd	nd	2.78
	100.40	99.85	100.11	100.78	99.82	98.94	100.61	100.50
Oxygen correction for S, Cl, and F	—.42	—.02	—.02	—.56	----------	—.77	----------	—.32
	99.98	99.83	100.09	100.22	----------	98.17	100.61	100.18
Rock density	2.289	2.261	2.678	----------				2.042

[1] Total iron calculated as FeO.

[2] Determined by Laura Reichen, U.S. Geol. Survey, using ion-exchange method.

[3] Determined by Janet Fletcher, U.S. Geol. Survey, by means of visible spectrum.

[4] Quantitative spectrographic determinations.

1. Moderately rich oil shale underlying trona bed in Intermountain Chemical Co.'s mine in sec. 15, T. 19 N., R. 110 W. J. J. Fahey, U.S. Geol. Survey, analyst.
2. Dolomitic marlstone, pale-grayish-green, immediately overlying trona bed in Intermountain Chemical Co.'s mine in sec. 15, T. 19 N., R. 110 W. J. J. Fahey, analyst.
3. Tuffaceous marlstone, buff, lower part of Wilkins Peak Member, sec. 6, T. 18 N., R. 105 W. J. J. Fahey, analyst.
4. Saline mineral-rich brownish-gray tuffaceous mudstone from the core of the John Hay, Jr., well, sec. 2, T. 18 N., R 110 W. Depth below surface in core 1,390 ft 0 in. to 1,391 ft 0 in. J. J. Fahey, analyst.
5. Tuffaceous and dolomitic mudstone, greenish-gray, from high in the Wilkins Peak Member, sec. 31, T. 19 N., R. 105 W. Vertie C. Smith, U.S. Geol. Survey, analyst.
6. Tuffaceous and dolomitic mudstone, greenish-gray, from the saline facies of the Wilkins Peak Member; Diamond Alkali Co.'s Butler well 1 (at 549 ft), NW¼ sec. 12, T. 18 N., R. 108 W. J. J. Fahey and Harry Rose, U.S. Geol. Survey, analysts.
7. Tuff, white; the "Big Island" tuff from the Stauffer mine; sec. 15, T. 20 N., R. 109 W. Harry Rose and J. J. Fahey, analysts.
8. Stevensite clay layer from the upper half of the Wilkins Peak Member; sec. 31, T. 19 N., R. 105 W. J. J. Fahey, analyst.

more porous than most of the rocks in the saline zone, is weathered, as is shown by the fact that the iron is present as ferric hydroxide and the TiO_2 as leucoxene. Furthermore, virtually all the feldspar grains, both potassium and sodium, have been considerably altered to montmorillonite(?). The large content of analcite is characteristic of these altered tuffs, but the high BaO content (1.14 percent) is distinctly unusual. The barytocalcite is apparently authigenic. Presumably much, or all, of the residual FeO and MgO should have been combined in the biotite. The composition, in percent, of biotite assumed for all these calculations was: SiO_2, 39.92; Al_2O_3, 17.22; FeO, 8.58; MgO, 22.23; K_2O, 7.90; H_2O, 4.15. These values were obtained by slightly simplifying the average of analyses 1–3 given by Rosenbusch (1927, p. 573).

4. This brownish-gray tuffaceous mudstone is rather typical of many of the saline mineral-rich beds in the saline facies. Its analysis is repeated here because the rock represents the rather clay-rich beds that contain considerable organic matter. We believe that the stevensite, northupite, shortite, and nontronite(?) are all authigenic. Only the orthoclase, albite, calcite, and organic matter are original constituents, and, indeed, the calcite may be authigenic rather than a precipitate from the lake water. Both the large quantity of stevensite and the saline minerals suggest that the original mud was saturated with strong brine, probably for a long time during diagenesis. The low summation of the mineral list, the fact that no quartz was observed in thin sections, and the rather large residual amounts of CaO and FeO suggest that the constituents are in part wrongly combined and that probably another silicate (clay?) mineral was missed.
5. This massive greenish-gray tuffaceous mudstone is a common rock type in the Wilkins Peak Member. The original tuff consisted predominantly of

TABLE 3.—*Calculated mineralogy of rocks from the saline facies of the Wilkins Peak Member of the Green River Formation, Sweetwater County, Wyo.*

[Chemical analyses for these rocks are given in table 2]

1	2	3	4	5	6	7	8
Dolomite 33.50	Dolomite 46.80	Analcite 20.50	Stevensite 18.16	Albite 28.90	Albite [4] 34.70	Potassium feldspar [1] 49.1	Stevensite 73.85
Shortite 26.06	Stevensite 13.30	Potassium feldspar [1] 17.20	Northupite 16.70	Potassium feldspar [1] 16.08	Potassium feldspar [1] 32.30	Quartz [2] 36.8	Dolomite 7.30
Potassium feldspar [1] 11.95	Potassium feldspar [1] 11.95	Quartz [2] 15.30	Potassium [1] 16.26	Montmorillonite 15.80	Dolomite 9.17	Trona 11.85	Calcite 5.20
Quartz [2] 5.86	Quartz [2] 11.72	Dolomite 13.90	Shortite 15.12	Calcite 12.80	Halloysite(?) 3.98	Biotite .45	Organic matter 2.78
Pyrite 2.44	Trona 4.08	Montmorillonite 7.92	Albite [4] 5.49	Quartz [2] 8.82	Pyrite 3.43		
Calcite 2.04	Shortite 3.00	Calcite 7.15	Calcite 4.57	Biotite 6.00	Biotite 2.88		
Anatase(?) .14	Siderite [3] 2.61	Ferric hydroxide 3.08	Quartz [2] 4.38	Ferric hydroxide 4.24	Quartz [2] 2.59		
Organic matter 15.76	Anatase(?) 1.61	Biotite 3.00	Nontronite [3] 2.85	Analcite 2.00	Shortite 2.00		
	Organic matter 2.76	Albite [4] 3.00	Organic matter 4.75	Anatase(?) .61	Riebeckite .89		
		Barytocalcite 2.21					
		Leucoxene .42					
		Organic matter .04					
97.75	97.83	93.72	88.28	95.25	91.94	98.2	89.13
Constituents not accounted for							
Al_2O_3 1.11	K_2O 0.16	FeO 1.99	CaO 1.25	CaO 0.60	CaO 0.04	Al_2O_3 0.08	Al_2O_3 0.81
CO_2 .86	FeO .10	MgO .73	Feo .90	FeO .12	Feo .26	CaO .5	Fe_2O_3 .56
P_2O_5 .02	MnO .20	P_2O_5 .02	TiO_2 .13	Al_2O_3 .49	BaO .10	Fe_2O_3 .17	TiO_2 .08
	P_2O_5 .02	MnO .07	MnO .05	P_2O_5 .12	TiO_2 .56	Na_2O .32	SiO_2 .14
		Cl .09	P_2O_5 .04	MnO .07	Cl .11	TiO_2 .04	MnO .02
		Li_2O .02	Li_2O_3 .03		F .17	MnO .005	Na_2O .24
			S .08		P_2O_5 .04	BaO .011	K_2O .02
					B_2O_3 .08	B_2O_3 .084	Li_2O .11
							CO_2 .18
							F .77

[1] Includes orthoclase from volcanic (or clastic) sources and authigenic potassium feldspar.

[2] Quartz includes that from volcanic (or clastic) sources and authigenic quartz and opal.

[3] Siderite in analysis 2 and nontronite in analysis 4; presence inferred only; not identified microscopically or by X-ray.

[4] Albite includes that from volcanic (or clastic) sources and authigenic albite.

fragments of albite and potassium and some quartz, along with an unusually large amount of biotite. Most of the feldspar grains have been partly altered to montmorillonite. This is an outcrop sample and, although apparently fresh, must have been weathered, to judge by the abundance of ferric hydroxide and absence of pyrite. Why this and many other rocks in this member have such a marked greenish color is not evident, unless the clay minerals contain appreciable amounts of ferrous iron.

6. This light-gray tuffaceous mudstone has a slight greenish cast and is typical of many beds in the saline facies of the Wilkins Peak Member. It is a mixed lithic and crystal tuff in which the lithic fragments greatly predominate. These fragments are very small (20–50 microns across) and generally equidimensional or nearly spherical. Many of them consist of microperthitic intergrowths of albite and adularia, which presumably developed during diagenesis. Both the lithic and crystal components contain many very fine grained inclusions. Conspicuous among these are minute biotite flakes and pyrite. Pyrite is exceptionally abundant for a rock that has no detectible organic matter. The riebeckite and biotite fragments are crystal constituents of the original tuff. Halloysite, which was identified only by its index of refraction, is an uncommon constituent of rocks in this member of the formation.

   The presence of TiO_2 and BaO in the residual constituents suggest that leucosphenite may be present, but none could be found. Many of the other residual constituents probably belong in either the amphiboles or the biotite.

7. This rock is a massive white tuff—the "Main" or "Big Island" tuff of Mannion and Jefferson (1962, fig. 3). It is a conspicuous marker bed a few feet above the top of the lower Big Island trona bed in the Stauffer trona mine (sec. 15, T. 20 N., R. 109 W.) The sample was collected by Charles Milton, of the U.S. Geological Survey. In thin sections the shard structure is very clear, though most of the glass has been altered to a fine mosaic of quartz and feldspar grains. The small amount of biotite is in very small black flakes. Mixed with the shards is a matrix of fresh and altered potassium feldspar, a few grains of plagioclase, and sharp angular grains of quartz. Some of the feldspar crystals have good crystal boundaries, but the interiors consist of a mosaic of smaller feldspar grains. Scattered through the rock are minute grains of trona.

   The calculated amount of biotite is consistent with the small amount estimated by inspection, and the calculated amount of trona agrees well with the amounts visible in thin sections and in small powdered samples examined in index liquids. X-rays indicate the presence of rather large amounts of both potassium feldspar and quartz. The calculted amount of potassium feldspar seems to be higher than we would have estimated from thin sections. If this calculated amount is correct, much of the potassium feldspar must be extremely fine grained.

8. This brown waxy clay occurs in widely separated thin layers in the saline facies of the Wilkins Peak Member. Four of the residual constituents (Al_2O_3, 0.81 percent; Fe_2O_3, 0.56 percent; Na_2O, 0.24 percent, and Li_2O, 0.11 percent) were included in the structural formula for stevensite in a published report on this mineral (Bradley and Fahey, 1962) but were not included in this calculation of the mineralogy of the rock. The amount of fluorine in this rock (0.77 percent) is noteworthy, but how it is combined mineralogically is unknown. It is not unreasonable to speculate, however, that it also belongs in the stevensite, for two closely related minerals, ghassoulite and hectorite, contain, respectively, 3.22 and 5.96 percent F. (See Faust and others, 1959, p. 344.)

THE TRONA BEDS

Beds of trona and mixed trona and halite underlie an area of roughly 2,850 km² (1,100 sq mi) in the central and southern parts of the Green River Basin (fig. 3). Within this area are at least 25 beds of trona or of trona and halite ranging in thickness from a little more than 3 feet to more than 38 feet. Between these major beds are locally few to many thin trona layers, ranging in thickness from mere films to 1 or 2 feet. The lateral extent of these thinner layers is unknown. Bedded trona consists of interlocking crystals of trona, which differ greatly in size from place to place (fig. 9). Most trona beds are brownish, owing to their content of organic matter and other impurities. The color ranges, however, from dirty white to rather deep brown. In addition to the thinner beds just mentioned, there are some layers that are pure white and have a fibrous structure. The crystal fibers in these beds are normal, or almost normal, to the bedding planes. In some beds the fibers are so fine that they give the material a silky luster. All the fibrous layers are virtually free of impurities of any kind and seem to have been wholly recrystallized after diagenesis of the sediments.

The fact that the brownish granular trona beds contain not only organic matter but also microgranular dolomite, pyrite, and fine silt particles (Fahey, 1962, p. 43–45) leads us to believe that they are chemical deposits laid down as beds on the lake floor during very low stages of the lake.

FIGURE 9.—Transverse section of a trona bed showing the interlocking bladed crystals of various sizes.

The major trona beds differ greatly in areal extent, ranging from less than 427 km² (165 sq mi) to at least 1,870 km² (723 sq mi). Each bed differs in thickness from place to place, some having a good deal of variation, some rather little. Isopach maps for three separate trona and trona-halite beds are shown in figures 10–12. Owing to the small number and distribution of the boreholes, much of the configuration of each of these three beds is inferred. Because many of the trona and trona-halite beds are overlain (and less commonly underlain) by a few to many irregularly spaced thin trona layers, the bed thickness is uncertain, locally by as much as 1 foot. In consequence, the contours on all the isopach maps (figs. 10–12) have been arbitrarily smoothed to give a general picture rather than a precise map. Very little is known about the margins of these trona beds. They may thin gradually to a featheredge, or, more probably they split into many thin wedges that die out between shoreward-thickening wedges of lacustrine and mudflat sediments,

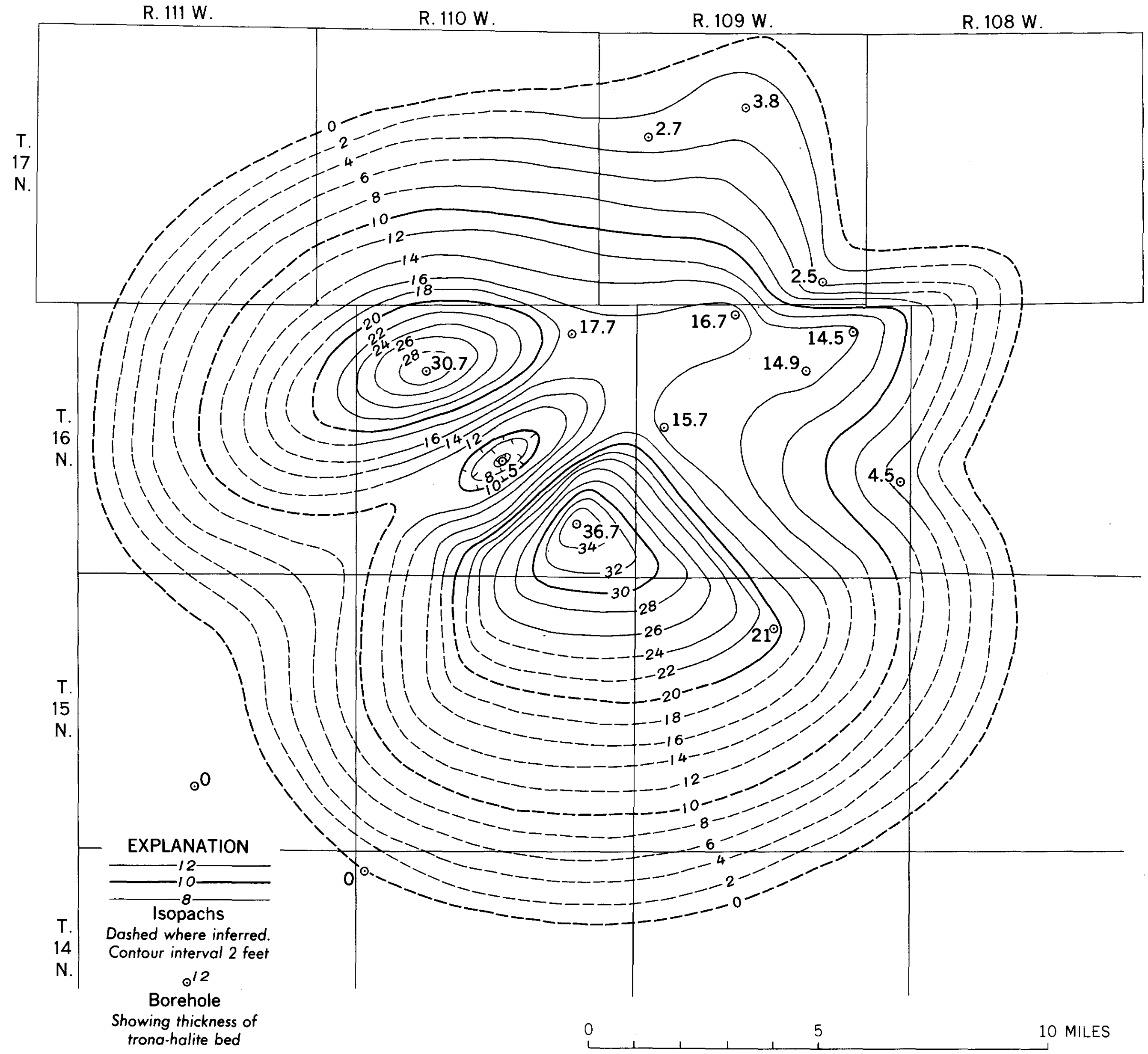

FIGURE 10.—Generalized isopach map of the lowest thick trona-halite bed 1 (see pl. 2).

that is, for the most part dolomitic mudstone and fine-grained muddy sandstone. Locally, most of the trona beds contain several to many partings of dolomitic marlstone, organic marlstone, or oil shale.

The trona beds are not centered one over the other. Beds are more numerous and thicker in the southern part of the basin, and they are scattered rather evenly through the lower part of the Wilkins Peak Member. Stratigraphically upward, the successive beds extend progressively farther northward. The beds highest in the section, the Lower and Upper Big Island beds, are restricted to the northern part of the trona area (pl. 2).

One of the most remarkable of these trona beds is the one numbered 17 on plate 2. This is the bed being actively mined by the Intermountain Chemical Co. in T. 19 N., R. 110 W. This bed has an inferred areal extent (fig. 12) of 1,870 km^2 (723 sq mi). It is reasonable to think that this is one of several trona beds known from drill holes to exist in the Church Buttes gas field (T. 16 N., Rs. 112 and 113, W., and T. 17 N., R. 112 W.), but means are not presently available to make such a correlation. If bed 17 does extend that far west, the actual areal extent is very considerably more than 1,870 km^2. Presumably, some of the other beds below bed 17 may also extend that far west. In drawing the

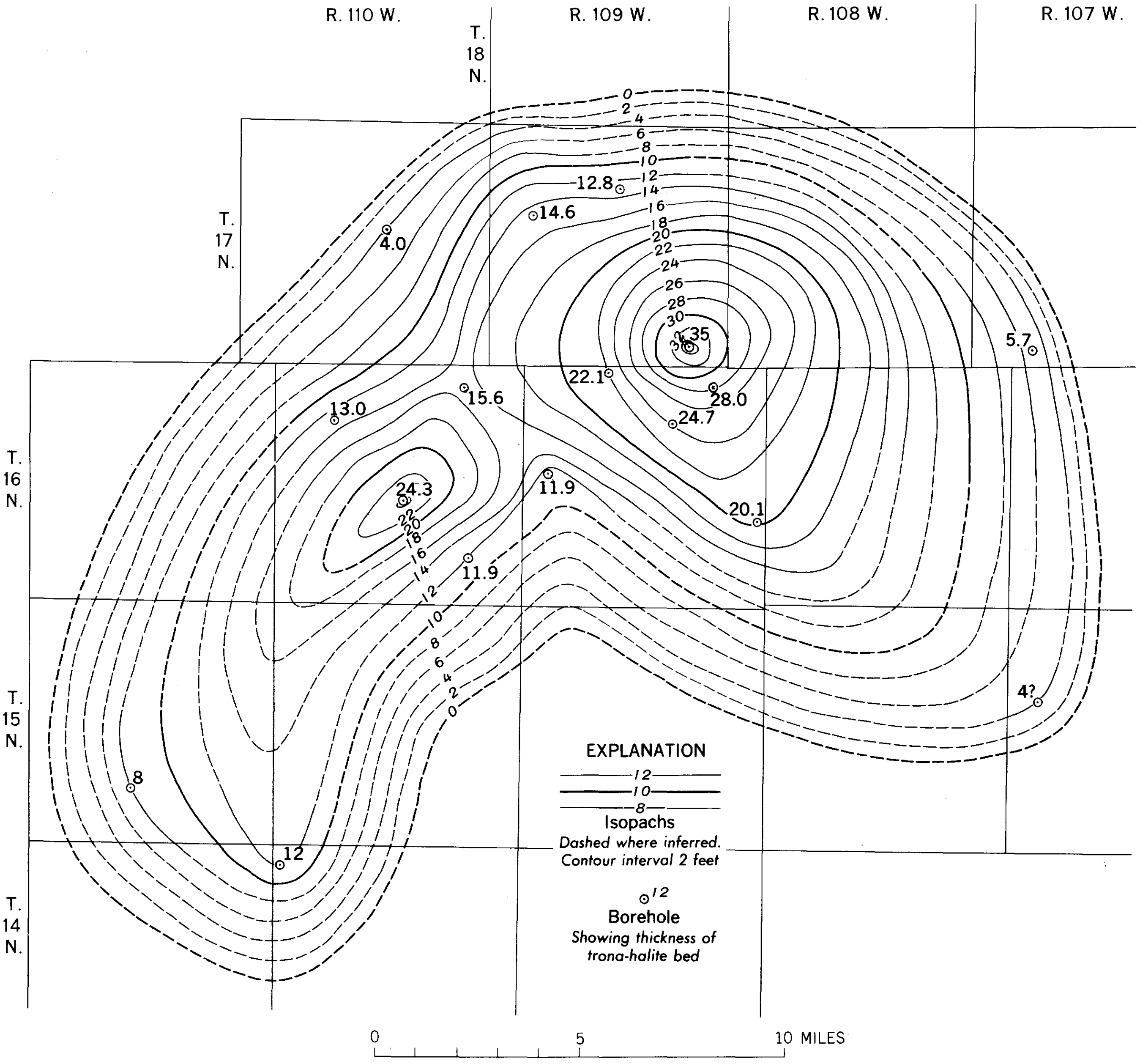

FIGURE 11.—Generalized isopach map of trona-halite bed 2 (see pl. 2).

outline of the area inferred to be underlain by bedded trona, we have assumed that some of the trona beds are coextensive with some of those found in the Church Buttes gas field.

Exploratory boreholes are numerous enough and so spaced that we have made generalized isopach maps of 18 of the trona beds, only three of which are reproduced here as figures 10–12. Casual inspection of these maps shows extensive areas in each bed where the contours have been sketched in freely for lack of data, especially around the margins. In the marginal areas of each bed, a uniform, rather steep rate of pinch-out has been assumed. Despite the inadequacies of these maps, and despite the fact that their vertical scale is enormously exaggerated, we can see that the basins in which the beds accumulated were not featureless. Perhaps the most interesting thing about these irregularities is the rough reciprocal relationship between the thick and thin areas in beds 1 and 2 (figs. 10, 11). This suggests that lenslike thickenings of trona in the lower bed were not much compacted and consequently made rather high areas on the lake bottom by the time bed 2 was laid down. Or, stated conversely, thin areas in bed 1 permitted the accumulation of a considerable

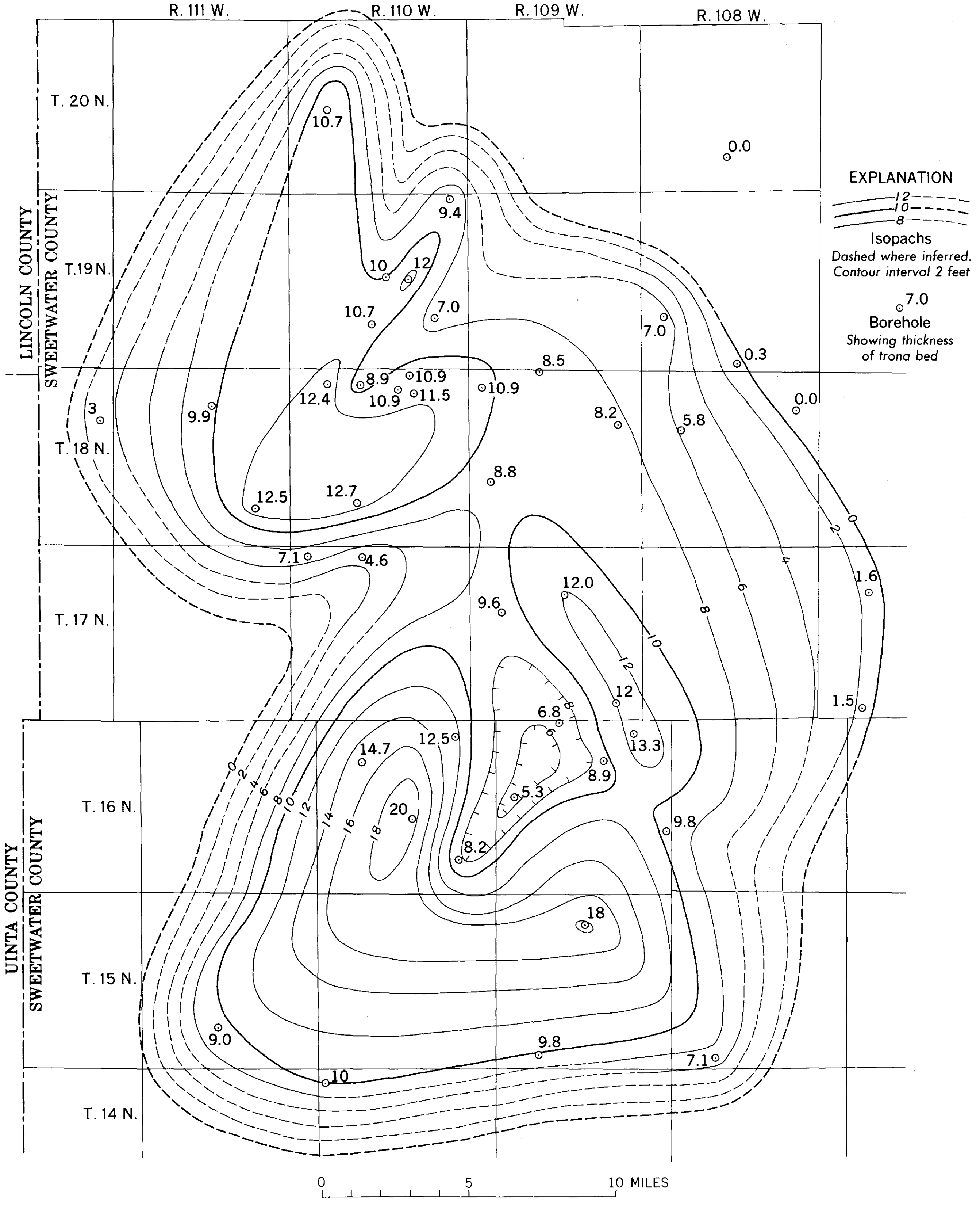

FIGURE 12.—Generalized isopach map of trona bed 17 (see pl. 2). This is by far the most extensive of the saline beds in the Wilkins Peak Member. The area shown probably is a minimum. Trona beds are known in the Church Buttes gas field (Tps. 16 and 17 N., R. 112 W.), and although there is no satisfactory correlation between them and the beds in the area shown on plate 2, it is rather probable that bed 17 is represented there.

thickness of fine-grained lacustrine mud, which compacted greatly under the weight of trona being deposited in bed 2, so that the thick areas of bed 2 overlie the thinner parts of bed 1.

VOLUME AND TONNAGE OF BEDDED TRONA

Using the isopach maps, the total volume within the contours and the number of tons of trona in each bed were calculated. These values are given in table 4. It was assumed that the beds consisted of pure trona, without partings and without inclusions of halite or wegscheiderite, though we know that most of the beds do contain partings of dolomitic mudstone, marlstone, and oil shale and that locally, many of the beds in the deeper part of the basin contain significantly large percentages of halite (Culbertson, 1966) and also some wegscheiderite (Fahey and Yorks, 1963, p. 400). The data available to us are not adequate to evaluate the amounts of trona displaced by these and other impurities, but such errors are probably overshadowed by deficiencies in the data used for computing the volumes of the beds. We believe that the volumes stated are conservative and that the tonnages given are correspondingly conservative.

Using additional data from the latest borehole, Culbertson (1966, p. B161) estimated that 24 beds, each more than 3 feet thick, contained about 6.7×10^{10} tons of trona. Excluded from this estimate are the zones, or beds, of mixed trona and halite, which aggregate an additional 3.5×10^{10} tons. The total, 10.26×10^{10} tons, exceeds considerably our estimate of 7.5×10^{10} tons given in table 4.

ENVIRONMENTAL CONDITIONS RESPONSIBLE FOR THE DEPOSITION OF THE SALINES

Gosuite Lake remained large and fresh during the Luman and Tipton stages, which we estimate lasted about 780,000 and 350,000 years respectively, or together a little more than 1 million years.[1] During most of this long interval, the lake must have overflowed continuously; but during the latter part of the Tipton stage it may have overflowed intermittently, and during the last few thousand years of the Tipton stage it probably did not overflow at all. By the beginning of the Wilkins Peak stage, Gosuite Lake was certainly a closed lake and had shrunk to about 20,700 km^2 (8,000 sq mi), roughly two-thirds of the area it had during the Tipton stage (pl. 1). During the early part of Wilkins Peak time, Gosuite Lake maintained virtually this size, though like all closed lakes, its surface area and depth must have fluctuated considerably. Gradually it decreased in area as its easternmost shore migrated westward and was followed by an expanding sheet of alluvial deposits that were to make up a part of the overlying Cathedral Bluffs Tongue of the Wasatch Formation (H. W. Roehler, oral commun., 1963). The minimum size of Gosiute Lake is not known, but probably even at its smallest size it had a considerable extent in the Green River Basin and a large arm or bay south and east of the Rock Springs uplift.

Table 4.—*Maximum areas, volumes, and tons of trona*[1] *in 18 principal beds*

[Three of the isopath maps drawn on those beds are given in figures 10-12. The beds are numbered in stratigraphic sequence from the lowest in the series, as on pl. 2]

Bed	Area (km^2)	Volume (m^3)	Tons (metric)
19	596	1.2×10^9	2.62×10^9
18	430	$.67 \times 10^9$	1.44×10^9
17	1, 870	4.6×10^9	10.2×10^9
16	1, 170	2.2×10^9	4.15×10^9
15	1, 270	2.7×10^9	5.98×10^9
14	1, 530	4.0×10^9	8.68×10^9
13	1, 110	2.5×10^9	5.42×10^9
12	1, 060	2.3×10^9	4.88×10^9
11	832	1.3×10^9	2.89×10^9
10	814	1.7×10^9	3.79×10^9
9[2]			
8	800	$.75 \times 10^9$	1.62×10^9
7	546	$.5 \times 10^9$	1.09×10^9
6	730	1.1×10^9	2.35×10^9
5	837	1.5×10^9	3.25×10^9
4	728	1.4×10^9	3.07×10^9
3	632	$.88 \times 10^9$	1.90×10^9
2	915	3.1×10^9	6.70×10^9
1	744	2.5×10^9	5.44×10^9
Totals		3.5×10^{10}	75.4×10^9 7.5×10^{10}

[1] Sp gr 2.147 (Fahey, 1962, p. 29).

[2] Insufficient data.

The large decrease in the size of Gosiute Lake is attributed to climatic change, which is discussed in the section below. An alternative possibility is that a considerable part of the drainage basin might have been lost by stream capture or tectonic movements, but this seems less likely for the reasons that follow.

The fact that about a million years later (at the beginning of the Laney stage) Gosiute Lake expanded again and to even greater size than it had during the Tipton stage poses some difficulty for the hypothesis that the low levels of the lake during the Wilkins Peak stage resulted from the loss of a significant part of the catchment basin. Although such a loss by stream capture is entirely plausible, it becomes much less so when one has to postulate that later the lost tributary must be recaptured and returned to its former pattern

H. B. S. Cooke (1957, p. 21–28) has presented persuasive evidence and arguments from his own studies and those of many of his colleagues and predecessors that tectonic movements in the late Tertiary

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[1] These and other estimated rates of accumulation used below are based on a study of rates of accumulation of similar sediment in modern lakes.

and early Quaternary of central Africa have radically changed the major drainage pattern. Some of the changes have increased the water supply of certain lake basins and left others starved for water, so that they shrank and become saline or actually dried up completely. None of these changes thus far recognized seems to have reversed itself after a long interval to return a water-starved lake to its original size, or larger.

CLIMATIC CHANGE

Compelling evidence for a climatic change would, at first sight, seem to be provided by the fact that the great contemporary Lake Uinta, south of the Uinta Mountains, also became saline at about the same time as Gosiute Lake. The weakness of this argument, however, is that there are good reasons for believing that Gosuite Lake overflowed for a long time into Lake Uinta (Bradley, 1931, p. v, 14) and, plainly, if Gosiute Lake lost a significant part of its inflow, the deficiency would promptly be felt in Lake Uinta.

A climatic change seems to be a more reasonable way to explain the low level and saline stage of Gosiute Lake. We are unable, however, to offer any explanation of what may have caused such a climatic change. Changes of apparently comparable magnitude occurred during the pluvial and postpluvial stages of the Pleistocene and Holocene and, like the postulated changes during the Eocene, we have no satisfactory explanation for them.

Some support for the inferred drier climate during the Wilkins Peak stage comes from a florule discovered by H. W. Roehler then of the Mountain Fuel Supply (oral commun., Aug. 1962), on the west flank of Little Mountain. These leaves and seeds were found near the top of the Wilkins Peak Member. Dr. H. D. MacGinitie of Napa, Calif., has studied this florule and regards it tentatively (written commun., Feb. 6, 1964) as a subhumid savanna-type flora, which contrasts strongly with the "humid, large-leafed, river bottom flora" that is typical of the upper part of the Laney Shale Member. This fact leads him to conclude that there must have been climatic swings in the Eocene from moist (pre-Wilkins Peak stage) to subhumid (during the Wilkins Peak stage) back to moist again during the Laney stage.

The paleoclimatology of the Gosiute Lake area, the morphology of the hydrographic basin, and the paleolimnology of the lake have been treated in another report (Bradley, 1963, p. 629–644). A summary of the conclusions reached in that study will suffice here. Late in the Tipton stage, it is inferred that the hydrographic basin had an area of about 126,000 km² (48,500 sq mi), of which about 32,000 km² (12,500 sq mi) was covered by Gosiute Lake, leaving a watershed area of about 93,000 km² (36,000 sq mi). At that stage the lake, whose surface is inferred to have stood about 300 m (1,000 ft) above sea level, repeatedly passed through a critical stage when the lake was full but did not overflow, in other words, when the evaporation from the lake surface exactly balanced the total supply of rain on the lake and runoff from the watershed. For this critical, but transient, stage the following annual values were calculated, using formulas developed by Langbein (1961, p. 4).

	Centimeters	*Inches*
Precipitation at lake level	86	34
Evaporation from lake surface	132	52
Evapotranspiration from watershed	74	29
Precipitation on watershed	97	38
Runoff	22	8.5

The average annual temperature was estimated at 19°C (66.5°F) from two independent lines of evidence (Bradley, 1929b, p. 92–93).

Because it is pertinent to this study, the discussion mentioned above (Bradley, 1963, p. 635) of the means for determining the mean annual rainfall during the very low stages of Gosiute Lake when trona was depositing is repeated here in full.

> A very rough measure of the decrease in rainfall needed to balance evaporation with decreasing size of the lake, after it became closed and so strongly saline that trona began to precipitate, in other words, after it reached its salting level, can be obtained from data available. Now the salting level is peculiar to each individual lake but it depends more heavily on the ratio of the area of the lake to the area of its drainage basin than it does on the kind of climate and composition of the brine in the lake. Langbein has found that if two lakes are at salting level and occupy about the same percentage of their respective drainage basins they have in common a factor of aridity, which he calls "net evaporation." Net evaporation he defines as the evaporation from the lake surface minus the amount of rain that falls directly on the lake. It happens that Great Salt Lake in Utah is close to its salting level and that it also occupies just about the same percentage of its drainage basin as Gosiute Lake did at its maximum salting stage. Great Salt Lake has a net evaporation of about 100 cm (40 in.). If we make the bold, but not implausible, assumption that Gosiute Lake at salting level also had a net evaporation of 100 cm (40 in.) and that the average annual temperature stayed at 19°C (66.5°F), we can read from Langbein's graph [fig. 13] that the mean annual rainfall must have been about 60 cm (24 in.). Actually, in any shift of climate toward aridity it is likely that the temperature would rise appreciably, so the corresponding rainfall would have to be somewhat higher to keep the net evaporation constant. For example, if the temperature rose to 21°C (70°F) the graph shows a rainfall of 68 cm (27 in.). We have no way of estimating temperature changes, however, so the estimate of 60 cm (24 in.) for the mean annual rainfall at the time of maximum aridity will have to suffice. If this is of the right order it indicates a very marked change of climate during the Eocene, a change that lasted about one million years. After that, the climate again became more

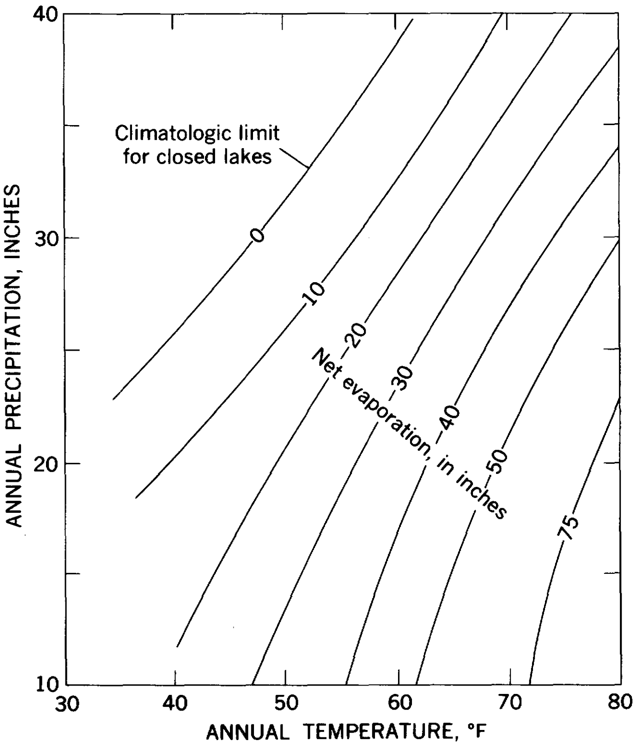

FIGURE 13.—Graph showing the dependence of net evaporation from the surface of a closed lake on the annual precipitation and the annual temperature. Net evaporation is defined as the difference between the gross evaporation and precipitation on the lake surface. From Langbein (1961, fig. 3).

humid and the lake enlarged to its maximum size (Laney stage) and overflowed for something like two million years before it filled with sediment and became extinct.

PALEOLIMNOLOGY OF TRONA DEPOSITION

The enormous tonnages of trona and halite found in more than a score of laterally extensive beds seems to compel the conclusion that Gosiute Lake repeatedly shrank to small size and that its waters repeatedly became a brine so concentrated that first trona and then halite precipitated out on the lake bed. The geology of the Wilkins Peak Member, however, argues rather strongly against this concept of extreme shrinkage. With relatively few exceptions, the beds of this member are of lacustrine origin and have far greater lateral extent than either the trona-halite beds or the more extensive beds that contain dispersed crystals, or molds, of saline minerals. Moreover, few breaks (disconformities) in the sequence of beds have been found, except, as we interpret the field relations, at the bases of the nine greenish-gray, muddy sandstone, or silty mudstone marker units described by Culbertson (1961).

The geologic evidence leads us to believe, then, that Gosiute Lake remained a large lake, one whose surface area was measured in thousands of square kilometers—possibly never less than 10,000 km^2—even at its lowest levels. Yet the bedded salts formed only in a much smaller area in the southern and central part of the Green River Basin.

These facts lead us to reconstruct the following picture of Gosiute Lake at one of the times when a bed of trona was forming. Although the lake had great lateral extent west, east, and south of the Rock Springs uplift, it was probably all rather shallow and all saline. The long eastern arm, or bay, however, was probably always somewhat less saline than that part of the lake in the Green River Basin because of the two large rivers that emptied into it, one at the northeastern end, which drained the Granite Mountains (Fremont and Natrona Counties, Wyo.), and the other entering the southern end in the vicinity of the present Canyon Creek (T. 12 N., R. 102 W., Sweetwater County, Wyo.). This second river evidently drained a large part of the eastern end of the Uinta Range. Furthermore, no salt crystals or salt crystal molds have yet been found in the Wilkins Peak beds that were deposited in this eastern and southern arm, though mud cracks are not uncommon.

In order to account for the localization of trona-halite beds in the southern part of the Green River Basin, it is necessary to postulate one shoal or bar running west across the central part of the Green River Basin, and another extending south or southwest from the south end of the Rock Springs uplift, despite the fact that we know of no certain field evidence to support this postulate. The inferred shoals must have partly isolated the southern half of the Green River Basin. No large rivers entered this southern half. We must assume that this part of the lake, not being well nourished with stream water, must have lost more water by evaporation than it received and, consequently, that this loss must have been offset by a flow of less saline water from the northern part of the lake and also from the eastern arm. Any such supplement of saline water must have also included underground seepage. Continuation of this process would inevitably have led to progressive concentration of the brine in the southern part of the Green River Basin and, probably, gradual depletion of salts from all the rest of the lake. This mechanism would have permitted the progressive concentration of the brine in one segment of Gosiute Lake without significantly decreasing its total volume. Under these conditions, trona and, at times, halite would have precipitated out on the bottom just as halite and mirabilite are doing today in a partly isolated segment of Great Salt Lake, Utah (Adams, 1964, p. 1027–1028).

Such a mechanism would permit the deposition of really thick beds of salts because of the enormous reservoir of dissolved salts in all the rest of the lake, which acted as a great generator of brine.

This mechanism for the deposition of thick salt beds is, of course, not new. Probably the classic, and most extreme, present-day example of such a hydrographic system is the Gulf of Kara on the east side of the Caspian Sea. The water surface of the gulf is now some 4 meters or more below the level of the Caspian Sea. Great volumes of salt are precipitating in the gulf from its concentrated brine. A much less extreme example of this system is the Mediterranean Sea, which loses more water by evaporation than it receives from direct precipitation and runoff from the land. Atlantic Ocean water flows into the Mediterranean to make up the loss. The water at the eastern end of the Mediterranean is nearly 8 percent more saline than is the Atlantic Ocean water (Schott, 1915).

A closer analogy with the regimen of Gosiute Lake (as we visualize it) is Great Salt Lake, Utah, in which a partly isolated bay has been created artificially by the construction of the Southern Pacific's causeway. Although this causeway has openings through it to allow free passage of water between the two parts of the lake, the flow is mostly northward into the northwestern bay (which is roughly one-third of the total area of the lake) because that bay is not so well supplied with runoff from the land as the rest of the lake. Consequently, evaporation from the water surface tends to make its level sink, and brine from the rest of the lake flows in to make up the loss (Adams, 1964). Virtually all Adams' article is pertinent, but the following passage (p. 1028) is especially so:

> About 30 or more centimeters of solid salt now covers the bed of the northwest water body and the band of adjacent dry lake bed. This quantity of salt is about 10^9 metric tons. Coincidentally, the main body of the lake, which before 1959 became saturated in the summer when the surface elevation reached -30 centimeters on the gage at Saltair, now (in 1963) does not become saturated until the surface elevation reaches about -140 centimeters. These observations of change in surface elevation at which salt saturation occurs may be used in conjunction with the known salt concentration at saturation and the change in the water volume with surface elevation to calculate that about 10^9 metric tons of salt have been removed from solution in the main body of the lake. This is one-quarter of the salt formerly in solution in this body. Five summer seasons, 1959 to 1963 inclusive, have passed since the railroad embankment was completed.
>
> The part of the salt layer above the present water level is an important part of the total solid salt. It results from stranding of salt by annual lowering of lake level as well as from progressive net lowering for several years, and from stranding of salt which has crystallized from the water brought to the otherwise dry area by wind tides.

Adams (1964) pointed out that the changed regimen of Great Salt Lake is not simple, and no such system would be expected to be. Storms and wind-generated seiches in the lake cause intermittent reversals of flow. Seasonal changes in the distribution of runoff and in rates of evaporation from the two parts of the lake also change the balance, so that brine occasionally flows southward into the main body of the lake. The net effect, however, in Great Salt Lake is decisive and results in the deposition of bedded salt on the bottom and at the margins of this partly isolated arm of the lake. It is this hydrographic mechanism which we visualize as the major factor to account for the bedded trona and halite in the Wilkins Peak Member.

This hydrographic system accords with the observed characteristics of the trona-halite beds in the Wilkins Peak Member, though it does not account for the sediments between salt beds. Nearly all the salt beds have partings of dolomitic marlstone or lean to rich oil shale whose upper and lower boundaries are sharp (fig. 14). These partings evidently began to deposit soon after the lake level rose above the shoals or bars and permitted a free interchange of water throughout the lake. The prime difficulty in explaining not only these partings but all the sediments between the salt beds is to account for their uniformly high content of calcite over areas measured, with few exceptions, in thousands of square kilometers. The most probable mechanism by which calcium could have been so widely distributed is for the lake to have become stratified by acquisition of either a perennial, or seasonal, mixolimnion that was rich in Ca^{+2} and HCO_3^{-1} ions. It is necessary to postulate that this overlying body of water, however long it persisted, was somewhat saline because it occupied a closed basin. Being somewhat saline it is properly designated a mixolimnion. Only this mechanism seems competent to distribute the large quantities of calcite so widely. Furthermore, only such mixolimnia could have provided water of low enough salinity for the algal growth necessary to account for the layers of oil shale. Finally, the fine clay particles in the dolomitic mudstone layers could also have been widely distributed in such mixolimnia, which, for areas that size, must have had active wind-driven internal circulation.

Prolonged stages of relatively high lake level not only produced the series of dolomitic marlstone and mudstone beds and beds of oil shale that make partings in the salt beds, but also those beds that lie between the trona-halite beds and that extend laterally far beyond the limits of the saline facies of the Wilkins Peak Member. These relatively high lake-level stages represent, we believe, intervals when the climate was somewhat less arid than at times when the lake level was low and the beds of trona and halite were deposited.

In the hydrography postulated, it would be expected that in the deeper part of the subbasin where trona had just been depositing there probably was a persistent body of strong brine, a monimolimnion, which, at times, was overlain by less saline surface water, a mixolimnion. At the other extreme, we imagine that at times the lake level fell so low that the southern part of the Green River Basin was cut off completely from the rest of the lake and that the mixolimnion evaporated from that isolated part. Indeed, at these lowest stages the lake level in this southern part of the basin may well have sunk below the upper surface of the trona-halite (or trona) bed and persisted as a body of wholly interstitial brine as at Lake Magadi, Kenya (Baker, 1958). or in Searles Lake, Calif., today.

We have no evidence to indicate that Gosiute Lake ever went to complete dryness during any of these lowest stages, even in this isolated part. If it did, we must assume that all the magnesium in the residual brine became fixed in such minerals as dolomite, stevensite, and northupite. The potassium in the Gosiute Lake brine may have been removed preferentially, as in other closed-lake waters, by complex interaction with silicate material, either by simple adsorption or by chemical combination (Jones and Van Denburgh, 1966, p. 443–444). Actually, the Gosiute Lake watershed may have been a low potassium, low magnesium province (B. F. Jones, oral commun., 1967). Sulfate may also have been low in the watershed, but if the lake went to dryness, none of it (other than the minute traces of tychite reported by Fahey (1962, p. 18) crystallized as a sulfate mineral. It could, however, all have been reduced by biogenically produced hydrogen sulfide and the sulfur fixed as one or another iron sulfide species, which are abundant in nearly all the sediments of the Green River Formation. If Gosiute Lake did go down to dryness, the fate of the potassium, magnesium, and sulfate might have been essentially the same as what happened to them in the brines that were occluded in the muds when the muds finally became dewatered by compaction and the crystallization of OH-bearing minerals. None of the very soluble potassium or magnesium sulfates or chlorides or complex sulfate-chlorides have yet been found in any of the salines of the Green River Formation. The most soluble magnesium mineral found in the Wilkins Peak Member is northupite. According to Smith and Haines (1964), northupite is the most soluble magnesium mineral yet found in the Searles Lake sediments. From this long argument we conclude that, during the Wilkins Peak stage, no part of Gosiute Lake, even in the partly isolated part of the Green River Basin, ever became more nearly dehydrated than Searles Lake is today.

Rather late in the Wilkins Peak stage, the locus of trona deposition shifted northward (pl. 2). This shift

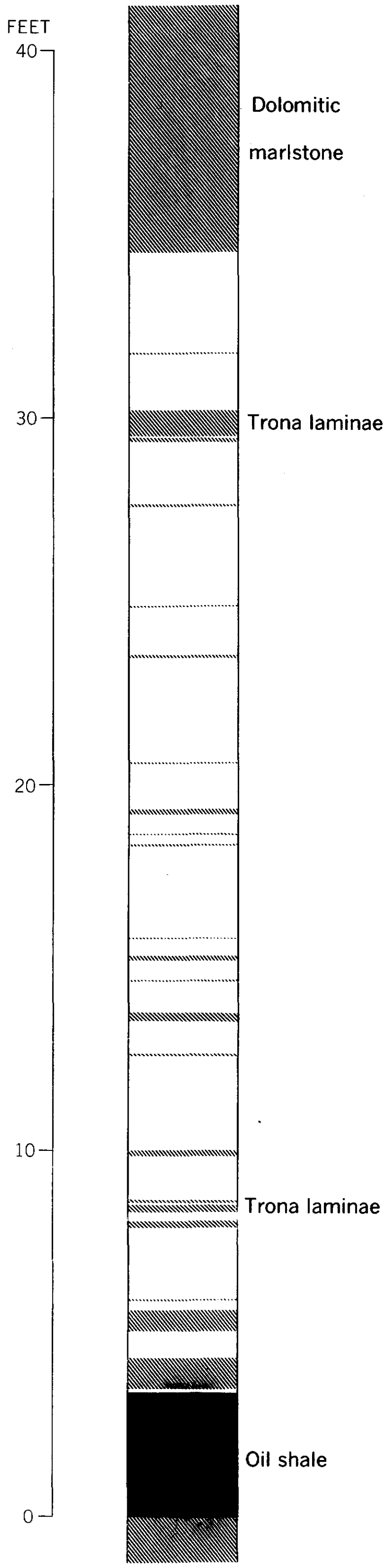

FIGURE 14.—Columnar section of a thick trona-halite bed from the southern part of the Green River Basin showing the thickness and distribution of partings. Unpatterned beds are trona-halite.

took place in time to extend the trona bed now being mined at Westvaco much farther north than any of the underlying beds. As plate 2 shows, the still younger trona beds have their centers offset progressively farther north. We infer that the hydrography of Gosiute Lake did not change significantly, only the geographic position of the partly isolated basin where the brines were concentrated and where the salt beds were deposited. This northward shift in the locus of trona depostition was discovered by D. L. Deardorff, of the Diamond Alkali Co., who has contributed so much to our understanding of the history of the salines in the Wilkins Peak Member (Deardorff, 1963).

REGIMEN OF LAKE-LEVEL CHANGES

The levels of closed lakes, as is well known, fluctuate about a mean that is characteristic for each particular lake and its prevailing climate. Gosiute Lake was no exception to this rule, and some of the fluctuations left rather clear records in the lake sediments, the lowest levels having given rise to the bedded salt deposits and the higher levels to beds of dolomitic marlstone, limy sandstone, mudstone, and oil shale.

Rhythmic alterations of more and less limy or dolomitic beds are characteristic of various parts of the Wilkins Peak Member. The beds in these sequences range in thickness from a few inches to several feet, but in any given sequence the pairs of beds are of roughly the same thickness. Two of these sequences are given below to illustrate the point.

Rhythmic sequence of beds from a zone 85 meters (280 ft) above the base of the Wilkins Peak Member in sec. 33, T. 21 N., R. 105 W.

	Thickness (cm)	(in.)
Sandstone, limy and muddy, fine-grained; crudely bedded	5.0	2
Shale, sage-gray, soft, flaky	7.5	3
Sandstone, limy and muddy, fine-grained; wavy bedding	5.0	2
Shale, sage-gray, soft, flaky	7.5	3
Sandstone, limy and muddy, fine-grained; wavy bedding	5.0	2
Shale, sage-gray, soft, flaky	10.0	4
Sandstone, limy; contains mud lumps	5.0	2

As will be seen from the sequences below, the limy and sandy beds represent the low-lake-level stages, and the less limy units, the higher water level stages. This distinction is shown by the fact that many of the most limy units are either mud cracked or contain mud lumps, whereas none of the less limy beds do. According to the rates of sedimentation given in an earlier report (Bradley, 1963, p. 632), the 5-cm (2 in.) limy sandstone beds required about 40 years to accumulate, and the 7.5-cm (3 in.) shale beds, about 500 years. The next rhythmic sequence is from a lower part of this same section of the Wilkins Peak Member, but the controlling cycle of weather or climatic changes were considerably longer.

Rhythmic sequence of beds from a zone 26 meters (85 ft) above the base of the Wilkins Peak Member in sec. 33, T. 21, N., R. 105 W.

	Thickness (cm)	(ft)	(in)
Marlstone, light-grayish-brown, platy; weathers nearly white; bedding planes mud cracked	30	1	0
Mudstone, greenish-drab; rather hard	107	3	6
Mudstone, light-greenish-dray; limy	30	1	0
Mudstone, greenish-drab, soft	107	3	6
Marlstone, light-grayish-brown, sandy; contains mud lumps	30	1	0
Mudstone, greenish-drab, soft	91	3	0
Marlstone, light-grayish-brown; weathers nearly white	25		10
Mudstone, greenish-drab, soft	91	3	0
Marlstone, light-grayish-brown; weathers nearly white	30	1	0

According to the rates of sedimentation mentioned above, the 30-cm marlstone beds required about 500 years to form, and the 90-cm mudstone beds, about 6,000 years (107-cm beds, about 7,000 yr). The whole cycle then seems to have recurred about every 6,500 years. This is a long enough interval to think of it as a fluctuation of climate rather than of weather.

Many other comparable sequences of alternating kinds of beds occur throughout the Wilkins Peak Member, and most of them reflect plainly significant fluctuations of lake level, as would be expected of a closed lake.

In the Green River Formation of Colorado, rhythmic sequences of lean and rich oil-shale beds occur (Bradley, 1929b, p. 105–106). The average length of that cycle (one bed of rich oil shale and one bed of lean oil shale) was 21,630 years, which perhaps may be explained by the changes of climate to be expected from cyclic changes in the eccentricity of the earth's orbit. Such climatic changes may have given rise to some of the longer rhythmic sequences of beds observed in the Wilkins Peak Member of the Green River Formation in Wyoming. Alternations of shorter duration have no satisfactory explanation.

It is highly probable that Gosiute Lake, while it was closed, also fluctuated about relatively long-term mean levels, but no record of these fluctuations is evident in the sediments, except the cyclic recurrence of the trona-halite and trona beds.

At the lowest levels, at and near the salting stages, Gosiute Lake must have continued to fluctuate in depth and area.

SOURCE OF COMPONENTS IN SALINE BEDS

In the aggregate, enormous volumes of sodium salts are contained in the saline facies of the Wilkins Peak Member. Such great quantities of the salts of one element, to be measured in cubic kilometers, makes it pertinent to ask if some unusual source of sodium is necessary to account for them, or if they can be accounted for by assuming that normal arid-climate streams brought them into the closed basin over a long interval of time.

CONCENTRATION OWING TO DECREASE OF GOSIUTE LAKE VOLUME ALONE

Only a small part of the trona and halite found in the Wilkins Peak Member could have been derived from simple decrease in the volume of Gosiute Lake. By far, the greater part must have been derived by another means, that is, by evaporation over long intervals of normal stream water, by leachates from new falls of volcanic ash, and by contributions from mineral springs known to have existed in the watershed. In the following pages these various possibilities are discussed and, where possible, assessed by quantitative estimates.

It is pertinent first to inquire how much of the dissolved salts in the earliest strongly saline lake stages of the Wilkins Peak may have been derived from simple decrease in volume of the lake. Such a calculation can be only a rough approximation because we have very little reliable information about the morphometry, and therefore the volumes of the lake, either at an overflow stage (late Tipton stage) or at the time, rather early in the Wilkins Peak stage, when the lowest trona bed was deposited. Moreover, we can only infer what the concentration of total dissolved solids may have been in the large lake at overflow stage. The assumptions used are these: (1) that Gosiute Lake, at its last overflow stage, near the end of the Tipton stage, had a volume of about 1.2×10^{12} m^3; (2) that the concentration of the lake water, at that stage, was 116 ppm of total dissolved solids; and (3) that the lake shrank to a minimum volume of only 2.5×10^9 m^3.

The first assumption is based on a reconstruction of the lake bottom compiled from depths inferred from the kinds of sediment in the upper part of the Tipton Shale Member and its lateral equivalents.

The second assumption, that the lake water at its last overflow stage contained only 116 ppm of total dissolved solids, is taken from the composition of the water in Lake Victoria, Africa (Hurst, 1925, p. 68). This large lake was chosen because it is analogous in several ways to Gosiute Lake, as we visualize it, late in the Tipton stage, when it was full but had just ceased to overflow (table 5).

TABLE 5.—*Comparison of Lake Victoria in Africa with Gosiute Lake as it is inferred to have been, late in the Tipton stage*

[Data on Lake Victoria from Hurst, 1925, p. 22–60]

	Lake Victoria	Gosiute Lake
Area of lake (exclusive of islands) kilometer^2	56, 450	32, 000
Area of watershed kilometer^2	193, 000	93, 000
Percentage of hydrographic basin occupied by lake surface	22. 6	34. 4
Rainfall on lake surface millimeter	1, 260	864
Evaporation from lake surface millimeter	1, 310	1, 320
Runoff reaching the lake millimeter	216	280
Percentage of total supply provided by rainfall on lake surface	79	80
Percentage of total supply lost by evaporation from lake surface	82. 4	100
Mean annual air temperature °C	±22	19

The assumed figure for the total dissolved solids (116 ppm) is the average of three determinations taken only a day or two apart in April 1923 (Hurst, 1925, p. 68). They range from 112 to 120 ppm. Later and better analyses (table 6) indicate that the dissolved solids probably total somewhat less, but, considering all the other uncertainties involved, such a difference is not significant. The essential thing is that the water (pH 8.0–8.5) is dilute and high in sodium and carbon dioxide species and very low in sulfate.

We wish to make it quite clear that in assuming water as dilute as this for Gosiute Lake, we are deliberately implying that that lake full of water accumulated while the rainfall was appreciably greater than it was subsequently during the Wilkins Peak stage. As we shall see, in the section below we assume that the runoff from the watershed then was considerably more concentrated, as would be appropriate for the drier climate we postulate for the Wilkins Peak stage of Gosiute Lake.

TABLE 6.—*Average of several analyses of Lake Victoria water*

	Parts per million (except P and N, in micrograms per liter)		*Parts per million (except P and N, in micrograms per liter)*
Ca	5. 6	Cl	4. 0
Mg	2. 6	SO_4	2. 3
Na	10. 2	SiO_2	4. 0– 4. 5
K	3. 7	P	20–60
HCO_3+CO_3	[1] 55. 5	Nitrate N	10

[1] Calculated from 0.91 me/l by J. F. Talling (written commun., Nov. 19 and Dec. 8, 1962), on the assumption that only HCO_3 is present. See also analyses from Talling and Talling (1965, p. 426–427).

The third assumption, that the lake shrank to a volume of only 2.5×10^9 m^3 , is based on the inference that the volume of the lake was equal to the estimated volume of the lowest trona bed in the Wilkins Peak Member, which is surely an extreme minimum value.

The probable extreme shrinkage of Gosiute Lake from overflow stage near the end of the Tipton stage to a minimum early in the Wilkins Peak stage is from 1.2×10^{12} m^3 to 2.5×10^9 m^3, that is, by a factor of 480. If the total dissolved solids at the high lake stage were 116 ppm, then the apparent maximum concentration resulting from shrinkage alone would be $480\times116=55{,}680$ ppm. This is only a fraction of the more than 290,000 ppm, which it evidently reached, because about that concentration is required to precipitate trona. (See table 15.) We conclude, therefore, that not more than roughly one-fifth of the salts that became concentrated in the brine from which the first (oldest) trona bed precipitated, could have come from simple decrease in volume of the water as it shrank down from its last overflow stage in late Tipton time. The rest must have been brought in by streams of somewhat greater salinity than those of the Tipton stage during the several tens of thousands of years probably required for shrinkage to the first salting stage. To account for all the stratigraphically higher (later) trona and halite beds, we assume that all their constituents must have been brought in by streams, leached from new falls of volcanic ash, and derived from the mineral springs known to have existed in the watershed.

CALCULATED COMPOSITION OF WATER ENTERING GOSIUTE LAKE

There are, of course, several ways to estimate the amounts of dissolved constituents brought into Gosiute Lake during the long interval while the sediments were accumulating. We have chosen the following way. To compute the amounts of any constituent that may have been brought into the lake basin by streams and springs, it is necessary to have figures for the chemical composition of the average runoff from the watershed. As a first step, we assumed that the runoff might be expected to have approximately the composition and concentration of the Green River today, because the Green River drains a large part of the same hydrographic basin that Gosiute Lake occupied and under an essentially arid climate.

This assumption is tested by comparing the amount of calcium found now in the saline zone of the Wilkins Peak Member with that which streams having the present composition of the Green River could have supplied under the arid climate already inferred (p. B21–B22). Calcium was chosen for this test because, of all the elements brought into a closed basin in solution, it is the most likely to be trapped permanently.

Calcite and dolomite are abundant in most of the Wilkins Peak rocks. The best we can do is use a large sample of the Wilkins Peak Member—the saline zone—and assume that the amounts of calcium deposited in that zone are comparable with the total amount of calcium brought into the lake basin during that interval.

The amount of calcium in the rocks of the saline zone was estimated from the weighted average of 19 chemical analyses of 19 representative rocks distributed throughout the thickness of the saline facies. Most of the samples were taken from drill cores. We found that the saline facies (estimated volume 7.9×10^{17} cm^3) contained 2.05×10^{17} g Ca, but that runoff having the composition of the Green River today (41 ppm Ca) would have brought in only 1.37×10^{17} g Ca in the 8×10^5 years that we infer it took the saline facies to accumulate. To have supplied 2.05×10^{17} g Ca in that interval, the runoff would have had to contain almost 1½ times as much Ca, that is, 61.4 ppm Ca rather than 41 ppm.

To calculate the inferred composition of the water entering Gosiute Lake, the concentration of each constituent of the water of the Green River was therefore increased proportionately to that required to bring into balance the amount of calcium found in the saline facies and the amount supplied by runoff (table 7).

TABLE 7.—*Composite of 12 analyses of water from the Green River at Jensen, Utah, taken at regular intervals between June 1 and September 30 (weighted for river discharge) and the recalculated analysis inferred to represent the average composition of runoff (including springs) that fed Gosiute Lake during the Wilkins Peak saline stage*

[Chemical analyses in parts per million]

	Green River at Jensen, Utah [1]	Inferred composition
SiO_2	10.5	15.8
Fe	.1	.1
Ca	41.1	61.4
Mg	13.8	20.7
Na	29.8	44.5
K	2.2	3.3
HCO_3	152.2	227.0
SO_4	80.6	120.5
Cl	12.0	18.0
F	.3	.4
NO_3	1.0	1.5
BO_3	.2	.2
	343.8	513.4

[1] U.S. Geological Survey (1952, p. 613).

The compositions of other large rivers might be substituted for that of the Green River as a model, but uncertainties in the other assumptions are so large that such an attempt at refinement is not warranted. For example, the area of the Gosiute Lake watershed is not at all certain, and it may be off by a large factor. Moreover, there are the difficulties in reconstructing the Eocene geology, the detailed topography, and most importantly, the soils, local climate, and hydrologic properties. One would still have to draw analogies with one or another modern stream system and then extrapolate from available data on the discharge and time weighting of compositional data. Moreover, we have no way of knowing how large the discharge from the mineral springs may have been, and we can only speculate on what their compositions may have been. And, after all, new falls of volcanic ash repeatedly blanketed the lake basin and its catchment area. Leachates from the fresh and weathered ash must have modified the composition of the stream waters appreciably.

CALCULATED GEOCHEMICAL BALANCES FOR SODIUM, MAGNESIUM, SULFUR, AND CHLORINE

The amounts of sodium, magnesium, sulfur, and chlorine found in the saline facies were next compared with the respective amounts assumed to have been brought into the lake basin in 8×10^5 years in the runoff that had the average composition calculated in table 7.

The amounts of magnesium and sulfur in the rocks of the saline facies were estimated from the same chemical analyses that were used to determine the amount of calcium. The amount of sodium was estimated from the rather well-known volume of bedded trona (see table 4) and the estimated amounts of the sodium-bearing minerals halite, shortite, northupite, analcite, and authigenic albite. Most of these estimates were made by Fahey (1962, p. 6–12, 18–22) on the core taken from the John Hay, Jr., well 1. The estimates of the quantities of analcite and authigenic albite were made by W. H. Bradley from a study of many thin sections of rocks from the John Hay, Jr., well 1 and from other cores and outcrop samples. In these estimates it was assumed that essentially the same distribution of these authigenic minerals held, on the average, for all the rest of the saline facies. All these estimates are thought to be conservative. The amounts of chlorine were estimated in part from the amounts of northupite ($Na_2CO_3.MgCO_3.NaCl$) and from information on the amounts of halite found in the trona beds in cores taken from exploratory boreholes. The chlorine estimate is thought to be very conservative. Table 8 gives the amounts of these several elements found in the saline facies, together with the amounts estimated to have been brought into the basin in 8×10^5 years in the runoff, which includes all the streams, rills, and springs whether mineral rich or not. The average composition of this total runoff is given in table 7.

The volume of runoff into Gosiute Lake can be calculated from data on the hydrography of the lake developed over many years by Bradley and from formulas developed by Langbein (1961, p. 4), of the U.S. Geological Survey, in his study of various relations between temperature, rainfall, runoff, evaporation from the free water surface, evapotranspiration on one hand, and on the other, from the lake levels and salt accumulation in many closed lakes in various parts of the world. In a closed lake where the level fluctuates about a mean at which the loss of water by evaporation from the lake surface balances that received from direct precipitation on the lake and from runoff

$$A_L E_L = P_L A_L + r A_W. \qquad (1)$$

Applying this formula to Gosiute Lake, we find

A_L = area of the lake, 4.1×10^{13} cm^2

E_L = evaporation from the lake, per unit area, 150 cm yr^{-1}

P_L = precipitation on the lake, 48.3 cm yr^{-1}

r = runoff into the lake, per unit area per year

A_W = watershed; 1.215×10^{15} cm^2.

The runoff

$$r = \frac{A_L E_L - P_L A_L}{A_W} \qquad (2)$$

$$= 3.43 \text{ cm yr}^{-1},$$

and total volume of runoff for the interval during which the saline facies accumulated is

$$t r A_W,$$

where $t = 8 \times 10^5$ years, the estimated time required to deposit the saline facies. Using the values given above and converting to liters, r comes out to 3.34×10^{18} liters. Then the total weight of each element delivered to the closed lake during the saline interval is this volume times the weight of each element in a liter of runoff in mg liter^{-1} (=ppm). The calculated values are given in table 8.

TABLE 8.—*Amounts of several elements found in authigenic minerals in the saline facies of the Wilkins Peak Member compared with the amounts of the same elements calculated to have been brought into Gosiute Lake during the deposition of the saline facies* [1]

	Estimated amounts found in the sediments (in grams $\times 10^{16}$)	*Calculated amounts brought into the lake in runoff in* 8×10^5 *years (in grams* $\times 10^{16}$)
Ca	[2] 20.5	[2] 20.5
Mg	9.6	6.9
Na	6.3	15.0
S	1.4	13.4
Cl	1.25	6.0

[1] These values differ from those published earlier (Bradley, 1963, p. 638) because many more data are now available than there were then and because these values are based on the volume of the whole saline facies rather than on selected vertical profiles. Both sets of values, however, are subject to rather large, unknown errors.

[2] The values for Ca are set equal by definition, as explained on p. B27.

The great excess of S estimated to have been brought into the lake over the amounts found in the saline facies suggests the general observation for the Great Basin expressed by Jones (1966, p. 196) that sulfate decreases by reduction within the permanent lacustrine environment. It is easy to imagine very considerable losses of H_2S directly to the atmosphere from the extensive mudflats that must have encircled Gosiute Lake and that must have been intermittently exposed during the Wilkins Peak stage.

As mentioned above, the amounts of Ca were set equal to provide a basis for calculating the average concentration of runoff water. (See table 7.)

The fact that considerably more Mg was found in the rocks than was supplied by runoff suggests that the present-day Green River is poorer in Mg than was the runoff that nourished Gosiute Lake during its saline stage.

A supply of Na nearly 2½ times greater than that found in the rocks is not too surprising when we consider that the present-day Green River runs for many miles through the Na-rich Green River Formation and may, therefore, be abnormally rich in Na.

The discrepancies between the amounts of these five constituents found in the sediments and the amounts calculated to have been brought in suggests that the composition of the present-day Green River may not be the best model that could be found. On the other hand, we tried the compositions of several other rivers with no better results. Perhaps no better correspondence should be expected when one considers all the uncertainties inherent in any such exercise.

POSSIBLE ROLE OF THERMAL SPRINGS AS SOURCES OF SODIUM AND OTHER CONSTITUENTS

How much of the sodium and other constituents delivered to Gosiute Lake during its saline stage may have come from thermal springs is impossible to say. It is reasonable to assume that thermal springs were more numerous then than now along the major geologic lineaments in the hydrographic basin because those features were then still rather young geologically and because volcanism was then also rather common. Present-day thermal springs in the inferred hydrographic basin contain considerable quantities of dissolved solids, and some are rich in sodium and potassium (unfortunately, not analyzed separately). (See table 9.)

A group of spring deposits within the rocks of the upper part of the Wilkins Peak Member have been discovered independently by W. C. Culbertson of the U.S. Geological Survey, and H. W. Roehler, then District Geologist of the Mountain Fuel Supply Co., Rock Springs, Wyo. The largest one of these spring deposits in sec. 33, T. 13 N., R. 108 W., is about 76 m (250 ft) by 36.5 m (120 ft) in ground plan and stands about 15 m (50 ft) high, though it is obviously only partly exhumed from the more normal Wilkins Peak beds. It consists of pure white dense intensely brecciated marlstone and has numerous veins of silica and calcite. The whiteness of the marlstone and the fact that the whiteness is confined to the elliptical area of the spring deposit suggest that the rock may have been leached by warm or hot water.

Wiegman (1965) reported, from a study of airplane photographs, additional similar spring deposits in the adjacent secs. 32 and 31. W. C. Culbertson, of the U.S. Geological Survey, however, examined these deposits on the ground and reports (oral commun., 1966) that these small topographic features are erosional remnants that have none of the distinctive characters of the spring deposits described above.

Convincing evidence of warm or hot springs that might possibly have been active during the saline stages of Gosiute Lake has been cited by Love (1962). According to Love, the springs were active in post-Eocene time, and nothing actually is known about their exact age or whether they were even extant during mid-Eocene. The site of these inferred large hot springs is in sec. 26, T. 17 N., R. 104 W., along the south flank of Aspen Mountain.

We have no means of estimating how much sodium, or other constituents, these springs contributed, but simply by analogy with alkaline thermal springs in other parts of the world, notably those at Lake Magadi, Kenya, which Eugster observed in 1966, it is reasonable to assume that the contribution may have been large.

TABLE 9.—*Composition (in parts per million) of some present-day thermal spring waters in the inferred hydrographic basin of Gosiute Lake*

[Unpublished data from the files of the U.S. Geol. Survey. nd, not determined]

No.	pH	SiO_2	Fe	Ca	Mg	Na+K	HCO_3	SO_4	Cl	F	NO_3	Total dissolved solids	Temperature (° C)	Discharge (gph)
1	10	55.0	nd	3.2	0.2	97.0	30	16	78	7.0	0.0	301	18.3	50–100
2	7.5	20.0	nd	221	48.0	14	123	641	3.8	2.0	.8	1,010	29.4	75–100
3	8.2	9.7	nd	8.0	.7	171	141	51	132	15.0	1.0	458	------	250
4	7.8	8.6	nd	30	32	2,200	3,000	600	1,340	2.8	2.3	6,700	22.8	10
5	7.9	14.0	nd	29	31	2,320	3,140	637	1,420	2.8	1.9	6,000	25.6	10
6	7.9	42.0	nd	35	37	2,040	2,890	558	1,220	2.8	2.1	5,360	22.2	50
7	7.6	8.1	2.0	86	58	774	1,570	228	432	.5	1.2	2,360	------	5
8	7.9	54.0	nd	18	.5	302	104	145	310	12.0	.2	893	37.8	300

Sublette County, Wyo.:
1. Steele hot spring, sec. 8, T. 32 N., R. 107 W.
2. Unnamed, sec. 36, T. 39 N., R. 110 W.

Routt County, Colo.:
3. Unnamed, sec. 18, T. 7 N., R. 84 W.
4. Lithia spring, sec. 6, T. 6 N., R. 84 W.
5. Narcissus spring, sec. 6, T. 6 N., R. 84 W.
6. Sulfur spring, sec. 6, T. 6 N., R. 84 W.
7. Iron spring, sec. 6, T. 6 N., R. 84 W.
8. Heart spring, sec. 8, T. 6 N., R. 84 W.

TABLE 10.—*Mean values and ranges of constituents (expressed in grams per 100 grams liquor) of 24 thermal springs that feed Lake Magadi and Little Magadi, southwestern Kenya, and the temperature, specific gravity of the water, and estimated aggregate discharge of all the springs*

[Data from Baker, 1958, p. 51, 55]

	Temperature (°C)	Na_2CO_3	$NaHCO_3$	NaCl	Na_2SO_4	NaF	Total solids	Specific gravity	Discharge (cubic feet per day)
Means	45.7	0.659	1.100	0.694	0.024	0.019	2.102	1.018	9,680,000
Ranges	33 to 85	0.111 to 1.548	0.438 to 2.065	0.217 to 1.042	0.009 to 0.034	0.004 to 0.033	0.617 to 3.093	1.004 to 1.0275	

Indeed, they may even have been the dominant source of the salts that made up the trona and mixed trona-halite beds.

Lake Magadi, in southwestern Kenya, receives most of its enormous quantities of sodium carbonate from thermal springs (Baker, 1958, p. 44–55). This lake, one of the many African rift-valley lakes, has a surface area of 84 km^2. It occupies a closed basin and, except during the two rainy seasons of each year, has about 70 km^2 of trona exposed to the air. The remainder of the surface area is made up of irregular lagoons of strong brine distributed around the margins of the lake. These brine lagoons are fed by many warm to hot springs, which contain moderate to very high concentrations of sodium carbonate and other salts (table 10).

These spring waters, which Baker (1958, p. 55) estimates bring about 4,300 tons of Na_2CO_3 per day into Lake Magadi and Little Magadi, are remarkable in that they are so dominantly sodium carbonate waters and that they contain so little sulfate. They are amazing for their very high content of fluoride (40–330 ppm). The terrain from which these springs emerge is made up largely of alkali trachyte lava, which is cut by many faults, some of which have large displacement. These trachytes contain on the average 5.78 percent Na_2O.

POSSIBLE ROLE OF VOLCANIC ASH AS SOURCES OF SODIUM AND OTHER CONSTITUENTS

The sediments of the saline facies of the Wilkins Peak Member contains numerous volcanic-ash layers and many of the rocks contain small to large admixtures of clastic particles of evident volcanic origin. It seems reasonable to speculate, therefore, that much of the sodium and other constituents brought into Gosiute Lake may have been leached from volcanic ash that fell directly into the lake or, more importantly, from volcanic ash that blanketed the watershed.

Basharina (1958) showed that very considerable quantities of 16 chemical constituents were leached from newly erupted volcanic ash (pyroxene andesite) in distilled water and in a remarkably short time. The amounts and kinds of ions leached depended on the grain size of the ash because certain gases like chlorine, sulfur, bromine, fluorine, and boron were selectively adsorbed on the finest particles. He found, for example, that the amounts of chlorine and sulfur were, respectively, 63 and 50 times as much as occurred in the old volcanic rocks.

Each sample of 100 grams of newly fallen ash was leached in 500 milligrams of distilled water by shaking for 10 minutes and then letting it stand for 5 hours at 18°–20°C. Each sample was leached this way three times, and the three leachates were combined and analyzed by standard procedures. All the leachates were acid (pH 3.2–4.5).

All the ash came from the Bezymyanny Volcano in Kamchatka, Siberian RSFSR, which erupted violently on October 22, 1955, for the first time in historic times. Especially vigorous ash production occurred also on November 17, 1955, and March 30, 1956. Table 11 gives the results of these leaching experiments and the locations from which the samples were collected. Table 12 gives the size distribution of the ash particles in each sample.

RESIDUAL BRINE AND ITS FATE

During the thousands of years that the trona-halite and associated less saline beds were being deposited, we might expect that the saline waters of Gosiute Lake would have become progressively richer in such constituents as potassium, magnesium, and sulfate. Much of the potassium and magnesium, however, and some of the sulfur, must have been lost to the lake by occlusion of brine in the sediments and selective retention of the cations in the sediments during diagenesis. As mentioned previously, sulfate minerals are unknown except for a few traces of tychite. Iron sulfides, however, are rather common, and the sulfur in them almost certainly was derived from sulfates brought into the lake in solution. Sulfur may also have been lost to the atmosphere as hydrogen sulfide produced biogenically in the marginal mudflats (p. B28–B29).

Authigenic (or primary?) dolomite (p. B12–B16) is common in virtually all the rocks (other than the salt beds) of the Wilkins Peak Member. The deposition, or early formation, of such large quantities of dolomite means, beyond much question, that magnesium was being continuously abstracted from the lake and, of

TABLE 11.—*Chemical constituents leached by distilled water from newly fallen volcanic ash from the Bezymanny Volcano, Kamchatka, Siberian RSFSR*

[Data from Basharina, 1958. Results are in parts per million of the air-dried volcanic ash. nd, not determined; Tr., trace]

Sample	pH	SiO_2	Fe^{+2}	Fe^{+3}	Al	Ca	Mg	Na	K	HCO_3	Cl	SO_3	SO_4	S	F	Br	H_3BO_3
749–a	4. 0	1. 5	0. 65	0. 4	2. 1	18. 5	1. 73	3. 2	1. 15	10. 4	16. 7	0. 38	43. 8	1. 8	0. 67	0. 16	0. 35
749–b	4. 5	. 45	. 2	. 11	. 35	8. 4	2. 68	1. 0	. 3	1. 2	11. 5	. 62	35. 6	2. 56	. 15	. 21	. 15
749–v	3. 2	. 25	1. 10	. 29	1. 8	48. 9	3. 88	12. 4	3. 45	------	53. 0	------	93. 8	nd	. 35	. 12	. 36
751	4. 0	1. 0	. 28	. 20	. 80	18. 2	2. 77	4. 1	1. 0	1. 9	17. 8	. 48	49. 6	1. 79	. 45	. 19	. 30
752–d	4. 0	1. 20	. 22	. 14	. 6	17. 1	2. 68	1. 68	. 67	4. 6	19. 0	. 24	28. 9	2. 24	. 4	. 16	. 16
752–g	4. 0	. 9	. 26	. 15	. 9	23. 2	3. 7	2. 4	1. 3	5. 6	26. 7	. 21	65. 0	3. 2	. 35	. 12	. 36
753–a	4. 2	2. 0	. 26	. 32	. 65	10. 9	2. 1	1. 75	. 38	4. 2	13. 5	. 34	23. 7	2. 35	. 35	Tr.	. 28
753–b	4. 0	. 5	. 2	. 3	1. 1	18. 0	2. 5	1. 66	. 24	1. 8	19. 8	. 36	46. 4	2. 2	. 3	Tr.	. 24
755	3. 8	. 8	. 25	. 11	. 35	10. 2	2. 4	3. 5	1. 3	6. 0	7. 6	. 46	28. 6	1. 64	. 6	. 12	. 42

DATE OF COLLECTION AND LOCATION

Sample	Date of collection and location
749–a	Oct. 22–29, 1955, 16 km from the volcano.
749–b	Nov. 7, 1955, 16 km from the volcano.
749–v	Nov. 7, 1955, 16 km from the volcano.
751	Nov. 7, 1955, 12 km from the volcano.
752–d	Nov. 16–17, 1955, at Klyuch, 45 km from the volcano.
752–g	Nov. 9, 1955, at Klyuch, 45 km from the volcano.
753–a	Feb. 9, 1956, 16 km from the volcano.
753–b	Feb. 9, 1956, 16 km from the volcano.
755	Mar. 30, 1956, at Klyuch, 45 km from the volcano.

TABLE 12.—*Size distribution of ash particles in the samples whose analyses are given in table 11*

[Data from Basharina, 1958]

Sample	1 mm	1–0.25 mm	<0.25 mm	0.25–0.05 mm	0.01 mm	<0.01 mm
749–a		0. 9	99. 1	------	------	------
749–b		80. 6	19. 4	------	------	------
749–v		2. 6	97. 4	------	------	------
751		2. 0	--------	55. 6	9. 1	23. 3
752–d		. 5	--------	52. 3	25. 0	22. 7
752–g	------	------	100. 0	------	------	------
753–a		1. 7	98. 3	------	------	------
753–b		9. 9	90. 1	------	------	------
755	0. 5	2. 1	--------	69. 0	12. 9	15. 5

course, this helped to keep magnesium from increasing in the saline lake water. Other magnesium-bearing minerals, such as northupite, stevensite, loughlinite, and others, also trapped magnesium and likewise worked against the progressive enrichment of the brine in magnesium. Haines (1959, p. 146) reports that the brines pumped from Searles Lake, Calif., contain no detectible amounts of either calcium or magnesium.

In the same way, the occurrence of moderate to rather large amounts of authigenic potassium feldspar (adularia) worked against the progressive accumulation or potassium in the lake brines.

From what limited evidence we have, the composition of the saline water in Gosiute Lake after the known beds of salt had been deposited, or the salt trapped in the sediments, may not have been greatly different from what it was before the first trona bed was laid down. Certainly, some percentage of the soluble constituents not fixed in the sediments must have remained in solution regardless of the stage of the lake and the extremes of concentration or dilution. To this extent the residual brine had continuity. Indeed, the geology of the hydrographic basin is a powerful stabilizing factor on the chemical character of its waters. This generalization was developed in an important paper by Jones (1966, p. 191–197).

Langbein (1961) has discussed in some detail the general tendency for the salinity of closed lakes not to increase in pace with the total amounts of dissolved solids delivered to them over long intervals of time. He explains the apparent anomaly by showing that the lake waters progressively lose salts to the accumulating sediments.

Some thousands of years after the last trona bed formed, the lake level rose until it expanded to its maximum extent and again overflowed. For a long time during this last rise and expansion of the lake, a body of saline water persisted as a stagnant hypolimnion. This water was the residual brine of the Wilkins Peak stage of Gosiute Lake and part of the mixolimnion. In this quiet hypolimnion, the varved organic marlstone of the lowest part of the Laney Shale Member accumulated. Presumably, such bodies of hypolimnetic brine were in part, at least, occluded in the sediments and subsequently became concentrated enough during diagenesis to give rise to the globular molds of a bladed salt (nahcolite?) found locally at a horizon 7–9 meters above the base of the Laney Shale Member.

Eventually, the huge tonnage of salts still in solution mixed with the freshening mixolimnion and were lost by overflow. From then on, Gosuite Lake again became a homogeneous fresh-water lake, though one characterized by high calcium bicarbonate content. This is shown by the preponderance of marlstone in the Laney Shale Member throughout much of its great lateral extent.

THE PHOSPHATE PROBLEM

The amount of phosphate in most of the Wilkins Peak Member, in common with the phosphate in the sediments of Great Salt Lake, Searles Lake, and those in the borate basin at Boron, Calif., is surprisingly small; surprising because waters of lakes in closed basins are known to contain vastly greater quantities of phosphorus than the waters of lakes that have outlets (Hutchinson, 1957, p. 728). The phosphate in the Wilkins Peak Member, however, poses something of a problem because it is so very unevenly distributed stratigraphically.

Phosphorus is concentrated in rather thin zones in amounts that exceed the average in Wilkins Peak sediments by factors of as great as 600 or more. As discussed below, we conclude that phosphate came to be concentrated in such zones because it accumulated for long intervals of time in calcium-poor hypolimnetic brine and then precipitated during relatively much shorter intervals when calcium bicarbonate-rich mixolimnetic water precipitated minute crystals of calcite, which caused the phosphate to come down, probably as hydroxylapatite. We also conclude that as the phosphate mineral formed, it competed with dolomite for the new supplies of Ca^{+2} ions, with the result that the amounts of dolomite and phosphate mineral are inversely related in the phosphorite zones (fig. 15). The excess calcium brought into the hypolimnion accumulated as calcite.

J. D. Love (1964, p. E1-E40), of the U.S. Geological Survey, has made a systematic study of the rather thin zones in the Green River Formation of Wyoming that are abnormally high in phosphorus and uranium. According to him, there are 20 such well-defined phosphorite zones in the Wilkins Peak Member. They range in thickness from 3 inches to 6 feet. Their P_2O_5 content ranges from less than 1 to 18.2 percent, and their U content ranges from 0.003 to 0.15 percent. It is worth remarking, as Love's data show, that even within each phosphorite zone, the P_2O_5 and U values differ considerably from layer to layer. On the average, these phosphate-rich zones contain about 2.7 percent P_2O_5, whereas 30 analyses of all the other rocks in the Wilkins Peak Member average only 0.06 percent P_2O_5. If all the P_2O_5 in the Wilkins Peak Member were uniformly distributed through its whole thickness, the average content of P_2O_5 would be 0.09 percent. This fact alone suggests that phosphorus may have been supplied to Gosiute Lake at a rather uniform rate, but that it was stored and then precipitated in more than average amounts at irregular intervals.

By contrast, eight analyses of marlstones from various parts of the underlying Tipton Shale Member and the overlying Laney Shale Member of the Green River Formation range from 0.12 to 0.36 percent P_2O_5 and average nearly 0.24 percent.

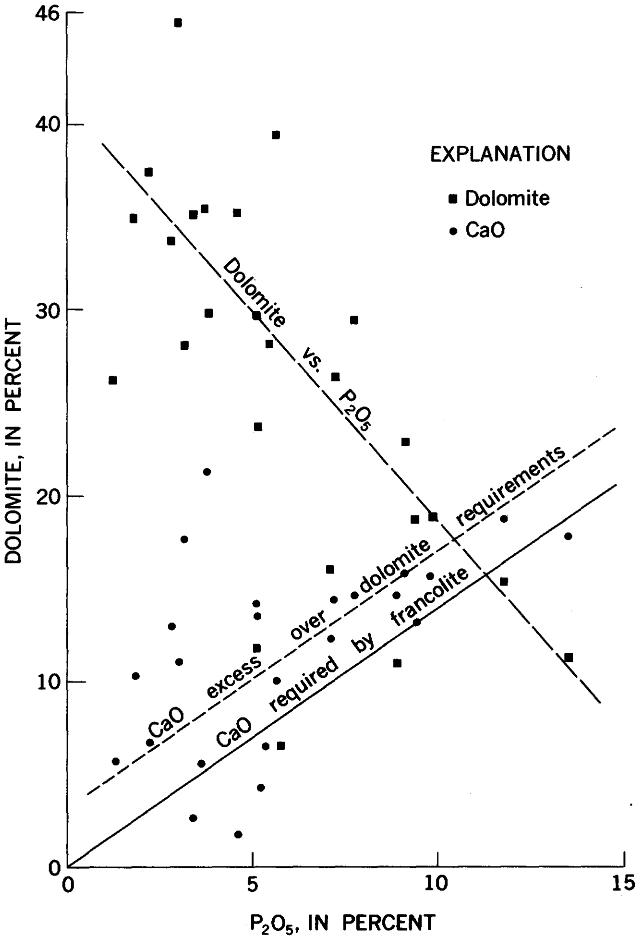

FIGURE 15.—Graph showing the decreasing amounts of dolomite plotted against increasing amounts of P_2O_5 and calculated from the amounts of P_2O_5 and MgO reported in analyses of phosphorite zones (Love, 1964, table 4) in the Wilkins Peak Member, and, from the same analyses, the respective excesses of CaO over those required for the dolomite. The great scatter in the points calculated as excess CaO is expectable. But the six of these points that fall below the line stating the CaO requirements for francolite indicate some factor that has not been considered. Such a factor could be, for example, the presence of another magnesian mineral besides dolomite. Three possibilities are northupite ($Na_2CO_3 \cdot MgCO_3 \cdot NaCl$), stevensite [$Mg_3Si_4O_{10}(OH)_2$], and loughlinite [$(Na_2,Mg)_2Si_3O_6(OH)_4$].

The sediments of two Pleistocene to present-day salt lakes, Great Salt Lake, Utah, and Searles Lake, Calif., illustrate the low phosphorus content rather typical of most of the beds in the Wilkins Peak Member of the Green River Formation.

Generally typical greenish-gray dolomitic mud from a depth of 1.7 meters in the central part of the Great Salt Lake Desert contains only 0.03 percent P_2O_5, which is comparable with the average P_2O_5 content of most of the beds in the saline facies of the Wilkins

Peak Member. This sample from the Great Salt Lake Desert was kindly sent us by Prof. Armand Eardley, University of Utah, and the P_2O_5 determination was made by J. J. Fahey, of the U.S. Geological Survey.

The mud units in the beds of Searles Lake, Calif., contain very small amounts of P_2O_5. The mean of eight analyses of the "parting mud" weighted according to the length of the core sampled gives 0.05 percent P_2O_5, which is very close to the average content (0.06 percent P_2O_5) of the beds of the Wilkins Peak Member, exclusive of the thin phosphate-rich zones. Twelve analyses of the "overburden mud," weighted as above, show the P_2O_5 to be significantly lower even than the "parting mud." The mean is 0.012 percent P_2O_5; but in one core of the "overburden mud" the P_2O_5 averages 0.102 percent—twice as high as the "parting mud" values and nearly 10 times as high as the other analyses from the "overburden mud." No satisfactory explanation of the rather high P_2O_5 values in this one core sample is at hand. All the chemical analyses of cores from Searles Lake sediments were sent to us by G. I. Smith, of the U.S. Geological Survey. The analyses were made by the American Potash & Chemical Corp., and the data taken from them are published with the corporation's permission. (Written commun., Feb. 10, 1959, to George I. Smith from D. S. Dinsmoor, Vice-President, American Potash & Chemical Corp.)

Additional evidence that sediments formed in saline lakes are likely to be generally poor in phosphate, comes from a partial analysis of a shale sample collected by Bradley in the Western mine at Boron, Calif. This shale represents a marginal facies of the ancient saline lake in which the famous borate deposits of that area were deposited. This shale contains 0.02 percent P_2O_5.

Whatever phosphorus is now found in the sediments must at one time have been a constituent of the lake water. Phosphorus occurs in lake waters in at least four different forms: as phosphates (water soluble and acid soluble), as soluble (or colloidal) organic phosphorus, and as phosphorus still in particulate remains of organisms or in fecal matter (Hutchinson, 1957, p. 728). In lake waters, as in the ocean, most phosphorus is continuously recycled by life processes. It is assimilated by plants and returned to the water upon decay of the plants and of the bodies and the feces of animals that fed upon the plants. Much of the organic material that reaches the bottom arrives there as fecal material. Phosphorus is returned to the lake by diffusion from the mud as the particulate organic matter decays, especially in relatively shallow water.

The total phosphorus content of lake waters has a tremendous range—from less than 0.001 ppm in Traunsee, Austria, to 208 ppm in the saline Goodenough Lake, British Columbia (Hutchinson, 1957, p. 728)—a factor of more than 200,000. These values are for near-surface (epilimnetic) waters. In the stagnant hypolimnia of stratified lakes, the content of phosphorus is generally higher than it is in the surface waters.

Present-day brine lakes that are poor in calcium and magnesium contain large quantities of dissolved phosphorus and provide a good analogy with the chemical characteristics of the Gosiute Lake brine, which we postulate to account for the phosphorite zones. Blair Jones, of the U.S. Geological Survey, informed us (oral commun., Apr. 1964), that his studies of Deep Springs Lake, Calif., show that the brine contains 1,070–1,410 ppm PO_4 (349–460 g cm^{-3}) and that certain small brine pools in Alkali Valley, Oreg., contain as much as 2,420 ppm PO_4 (788 g cm^{-3}). Abert Lake, Oreg., however, may provide an even closer analogy to the conditions that we have assumed for Gosiute Lake (table 13).

TABLE 13.—*Chemical composition of water in Abert Lake, Oreg., in 1963*

[Analyst: A. S. Van Denburgh, U.S. Geol. Survey. Density at 25° C=1.045; pH=9.6]

	Parts per million		*Parts per million*
SiO_2	144	Cl	19, 300
Ca	1. 4	F	7. 5
Mg	. 6	NO_3	1. 0
Na	22, 000	PO_4	74. 0
K	752	B	80
HCO_3	5, 930	Br	93
CO_3	9, 460	I	3. 2
SO_4	990		

Phosphorus may be trapped in the sediments of saline lakes as apatite, or more likely at the time of formation, as a mineral of the carbonate apatite family. Indeed, apatite has been identified in the phosphorite zones of the Wilkins Peak Member by X-ray patterns, but the crystals are too minute to be seen in a light microscope. The phosphorite zones also contain dolomite and calcite.

We visualize the following sequence of events in the paleolimnology of Gosiute Lake to account for the phosphorite zones. We have postulated (p. B23–B24) that while the bulk of the sediments between the trona, or trona-halite, beds were being laid down, the lake was meromict, and had a strongly saline hypolimnion overlain by a mixolimnion that was characterized by an abundance of calcium bicarbonate in solution. In common with most meromictic lakes, we infer that, for long periods of time, the hypolimnion became progressively richer in phosphorus by the continuous influx of particulate organic matter from organisms grown in the overlying waters. Eventually, a change in the regimen of the mixolimnion came about, and minute calcite particles began to precipitate because of large losses of carbon dioxide from the surface of the lake. Such large losses of carbon dioxide occur through the photosynthesis of larger than usual growths of planktonic algae, or through progressive warming of the water, or both. Such "rains" of calcite particles—enough to make the lake water milky—have long been known in existing lakes (Nipkow, 1920, p. 100–112; Minder, 1923).

Actually, changes in the surface waters of any lake that start calcite precipitating are not necessarily sudden events. They may start gradually and are usually intermittent with the seasons, but once started, the calcite precipitation may continue for tens or hundreds of years. In lakes as large as Gosiute Lake, one would not expect the regimen to change abruptly. The important thing, however, is that this mechanism provides a means of bringing new supplies of calcite, and hence Ca^{+2} ions, into the hypolimnetic brine where they can react with the phosphate.

Indeed, Gessner (1939) suggested this mechanism to account for the precipitation of calcium phosphate in lakes. He pointed out that when an abundance of calcite particles settled down through the water there was an excess of the Ca^{+2} ion, which further decreased the solubility product of $a^{3}_{\mathrm{Ca}}{}^{+2}\times a^{2}_{\mathrm{PO_4}}{}^{-3}$. Gessner believed, however, that the product he got in his experiments was tricalcium phosphate, but in this he must have been mistaken. K. J. Murata (written commun., Mar. 6, 1964), of the U.S. Geological Survey, called our attention to the fact that later work (Remy, 1956, v. 1, p. 639) has shown that "Tricalcium phosphate cannot be prepared in the pure state by precipitation from solution. The precipitates formerly regarded as such are variable mixtures of hydroxylapatite and secondary calcium phosphate ($CaHPO_4$), depending on conditions of deposition * * *."

Chemically, there seems to be an analogy between the precipitation of carbonate hydroxylapatite, dolomite, and calcite from sea water and from the brine of Gosiute Lake when these three minerals formed and gave rise to the phosphorites of the Wilkins Peak Member. Smirnov, Ivnitskaya, and Zalavina (1962) showed that in 3.5 percent NaCl solutions, the solubility of carbonate hydroxylapatite (and carbonate fluorapatite) was the smallest, dolomite next, and calcite the greatest of the three. It follows from this that, if there were "rains" of calcite particles from a mixolimnion, these calcite particles would react first with the phosphate ions to form carbonate apatite (or carbonate hydroxylapatite, or carbonate fluorapatite) and next with the magnesium (presumably present as bicarbonate in the mixoliminion) to form dolomite; finally, the excess calcite would be preserved as the final and residual mineral of the three. (See fig. 15.)

A simple calculation, supported by a few plausible assumptions, shows that the Gosiute Lake hypolimnetic brine might have held only a quite modest amount of phosphorus in solution and yet provided all that was necessary to account for the amount of phosphorus found in one of the richer phosphorite zones in the Wilkins Peak Member.

For this calculation we have chosen an analyzed sample from Love's (1964) Zone 3 (U.S. Geol. Survey lab. No. 274,006), which contains 9.1 percent P_2O_5, 7.4 percent organic matter, and is assumed by analogy with similar rocks to have a bulk density of 2.5. The rock is a brownish-olive-green compact dolomitic organic marlstone (CaO, 22.8 percent; MgO, 5.0 percent). Assume that this compacted sediment accumulated at about 2,000 years per foot (65.7 yr cm^{-1}), which is about the same rate of accumulation as that of greenish-gray dolomitic muds in the center of Great Salt Lake (Eardley and Gvosdetsky, 1960, p. 1339). Each year is represented by a layer of compacted rock 0.015 cm thick. As this has a bulk density of 2.5, each cm^2 of the layer that thick contains 0.0375 g of rock, which contains 9.1 percent of P_2O_5, or 0.0034 g P_2O_5 cm^{-2} yr^{-1}. Next, assume (really only a conservative guess) that the hypolimnion was only 5 m deep, and calculate how much phosphorus it would have to contain to yield 0.0034 g P_2O_5 cm^{-2} yr^{-1}. This comes out to 6.8 ppm P_2O_5 or about 3 ppm P. This is a far smaller amount than Hutchinson (1957, p. 728) cites for Owens Lake, Calif. (78 ppm P), and vastly less than has been found in the water of Deep Springs Lake, Calif. (349–460 ppm P). On the other hand, it is appreciably more than is found today in the waters of Great Salt Lake, Utah (about 0.4 to about 0.9 ppm). (Armand Eardley, Univ. Utah, written commun., Nov. 28, 1962; B. F. Jones, U.S. Geol. Survey, oral commun., 1966.)

From this calculation, it appears reasonable to believe that even the richest of Love's (1964) phosphatic zones (18.2 percent P_2O_5) can be accounted for by direct precipitation of carbonate apatite (or carbonate hydroxylapatite, or carbonate fluorapatite) from the hypolimnetic waters of Gosiute Lake during a meromictic stage when the mixolimnion produced "rains" of calcite particles through the photosynthetic activity of plankton algae, or warming, each year, or even every few years. At the rates of accumulation assumed, a 7.5–cm (3 in.) layer would represent an interval of about 500 years.

Although some of these phosphate-rich zones contain considerable uranium, as phosphorites go, there is only a crude relationship between the U and the

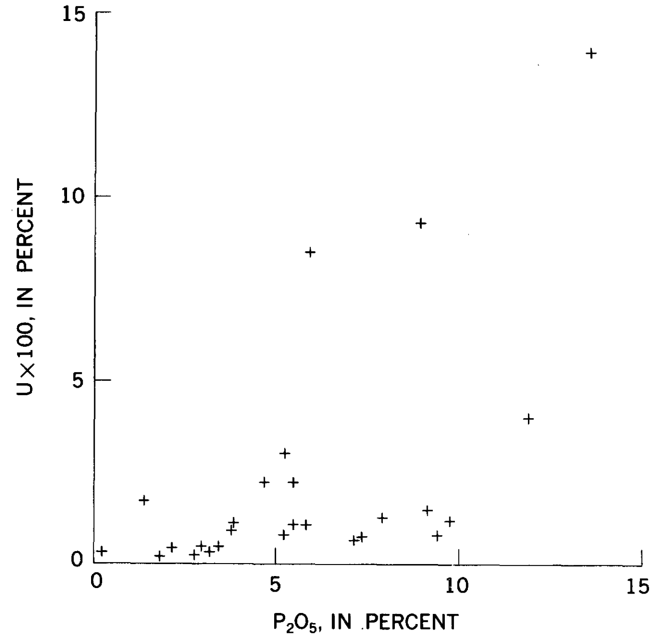

FIGURE 16.—Graph showing the relation of P_2O_5 to U in the phosphorite zones of the Wilkins Peak Member.

P_2O_5 content (fig. 16). About all one can say is that the highest U content is found in the rocks containing the most P_2O_5 and that the beds containing the least P_2O_5 contain the least U, but the scatter is great. McKelvey, Everhart, and Garrels (1955, p. 513–524) have shown that both organic matter and apatite will precipitate and hold U. They also cite the fact that certain alkaline uranyl carbonates and alkaline-earth carbonates are extremely soluble in water. Such salts [$Na_4(UO_2)(CO_3)_3$ or $Na_6(UO_2)_2(CO_3)_5$ or $Mg_2(UO_2)(CO_3)_3$] might be expected to have existed in the Wilkins Peak Member pore solutions, which were rich in Na^{+1}, Mg^{+2}, CO_3^{-2}, and Cl^{-1}. Inasmuch as both organic matter and apatite fix U (McKelvey, Everhart, and Garrels, 1955, p. 513–523), the scatter in the graph (fig. 16) showing the relationship between U and P_2O_5 might be accounted for by the assumption that in these U-P_2O_5-rich zones in the Green River Formation, some of the U is in the organic matter but most of it is in the apatite. Poor as the relationship between U and P_2O_5 is, it is better than the relationship between uranium and organic matter. In apatite, U substitutes for Ca. (McKelvey, Everhart, and Garrels, 1955, p. 521).

One might speculate that the conditions in Gosiute Lake that favored the precipitation of abnormal amounts of carbonate apatite might also have favored the simultaneous precipitation of U, most of which combined with the apatite by displacing Ca.

We are left, then, with the problem of how to account for the paucity of phosphorus in the greater part of the Wilkins Peak Member rather than how to explain the thin zones that are abnormally rich in P_2O_5. From the foregoing considerations it seems that the bulk of the Wilkins Peak sediments are poor in phosphorus because while they were being deposited, phosphorus was being stored in a calcium-poor saline hypolimnion, from which it was released only very sparingly by combining with the small amounts of Ca^{+2} ions available.

GEOCHEMISTRY OF THE TRONA DEPOSITS

RATE OF DEPOSITION

The rate at which various bedded salts accumulate, once crystallization starts, is rather rapid, according to the observations of H. P. Eugster at Lake Magadi, Kenya; G. I. Smith at Searles Lake and Owens Lake, Calif.; and Blair Jones at Deep Springs, Calif., and Great Salt Lake, Utah.

Baker (1958, p. 44) found layers about 1 inch (2.5 cm) thick in the upper part of the trona now forming in Lake Magadi, which he inferred to represent "seasonal growths." In 1966, Eugster observed layers there as thin as one-fifth inch (0.6 cm). G. I. Smith (oral commun., 1966) reports that when the hydrography of Owens Lake, Calif., was radically changed, salts (mostly trona) deposited at the rate of nearly 1 foot (30 cm) per year.

The average rate at which the trona accumulated in bed 17, now being mined by the Intermountain Chemical Co., has been estimated by Fahey (1962, p. 44–45) to be between 3.5 and 5.9 yr cm^{-1} (108 and 180 yr ft^{-1}), or an average of 4.75 yr cm^{-1}. For the following calculations we shall use 4.75 yr cm^{-1} (145 yr ft^{-1}) as a plausible average rate of accumulation for the solid beds of trona in the Green River Formation.

ADEQUACY OF SODIUM SUPPLY

It may be instructive to compare this rate of accumulation of sodium (in trona) with the estimated average annual rate of supply of sodium brought into the lake while the saline facies of the Wilkins Peak Member was being deposited. In table 9 we estimated, on the basis of salts found in the Wilkins Peak Member, that about 1.5×10^{17} g Na was brought into the lake in about 8×10^5 years, or 1.9×10^{11} g Na yr^{-1}. The area of bed 17, as presently known, is 1.9×10^3 km^2 (723 sq mi). If this much Na is distributed over 1.9×10^3 km^2, there would be only 0.01 g cm^{-2} yr^{-1}. If the trona accumulated at the average rate of 4.75 yr cm^{-1}, however, it would have required 0.137 g Na cm^{-2} yr^{-1}, or 13.7 times as much as the estimated average annual rate of supply.

If our concept of the hydrography of Gosiute Lake at the time the trona-halite beds were being deposited is right, the amount of sodium in the whole body of the moderately saline lake beyond the partly isolated salting-area should have been ample to supply this deficit for many years. Moreover, additional supplies of sodium were being brought in each year by the streams and springs, and finally, still more must have been added from time to time by leachates from new falls of volcanic ash and from salts already stored in the peripheral lake sediments at times when the lake level had been somewhat higher.

This mechanism seems to make it rather easy to account for the accumulation of even the very thick trona-halite beds.

In reckoning the time it took to deposit one of the trona-halite beds, allowance must be made for the much slower rates of deposition of whatever parting layers of marlstone or oil shale the salt bed contains. Consider, for example, the trona-halite bed illustrated graphically in figure 14. This bed has an overall thickness of 9.3 m (30.7 ft), but 1.15 m (3.78 ft) of this consists of partings of dolomitic marlstone. At 4.75 yr cm^{-1} (145 yr ft^{-1}), the trona-halite part of the bed required 3,900 years to form, whereas the dolomitic marlstone partings at 65 yr cm^{-1} (2,000 yr ft^{-1}) required almost twice that many years (about 7,450). Consequently, the total time required to deposit this thick bed with its contained partings may have been on the order of 11,000 years.

So long a drain on the reserves of sodium salts in the main body of the lake may have significantly diminished the salt mass in solution. New supplies of salts were continuously being brought in, however, and, more important, during the 7,000 or 8,000 years that the lake level was somewhat higher and that the dolomitic marlstone partings were being deposited, sodium salts were continuously accumulating in the lake water. Thus, the previous losses to the salt-depositing area were being replenished. Even though the lake level was higher at these times and the surface area was greater, it was still a saline lake whose level was dependent upon a balance between inflow and evaporation.

PHYSICAL CHEMISTRY OF TRONA DEPOSITION

As we have mentioned previously, trona occurs in two modes in the Green River Formation: as thick monomineralic beds and as individual crystals or groups of crystals disseminated in the dolomitic marlstone. We have indicated that we believe the beds to be direct precipitates from concentrated brine bodies and the disseminated crystals to be authigenic and to have crystallized from interstitial solutions after burial and compaction. We must now review the mechanisms that might yield these two types of deposits. For this reason, a rather detailed account of the stability and phase relations of trona, as determined in the laboratory, is necessary. We must begin with simple systems and gradually work towards the complexity of a Gosiute Lake brine. As we will attempt to show, the inferences drawn from the laboratory data are very revealing with respect to the paleolimnology and paleogeochemistry of the Gosiute Lake deposits.

Some studies have been published that bear on the physical and chemical conditions of trona precipitation. These studies make it possible to put limits on certain parameters, such as temperature and P_{CO_2}, which must have existed during the time trona was depositing. Most natural brines from which trona precipitates are complex in composition, but it is more convenient to discuss first the stability of trona in a pure system, in equilibrium with Na_2CO_3–$NaHCO_3$ solutions. The effect of additional constituents, particularly NaCl, in the brine can then be evaluated.

MINERAL EQUILIBRIA IN THE SYSTEM $NaHCO_3$–Na_2CO_3–H_2O

Compositions of saturated solutions in the system $NaHCO_3$–Na_2CO_3–H_2O were determined by Freeth (1923), by Hill and Bacon (1927), and by Wegscheider and Mehl (1928). The stability of the sodium carbonate-bicarbonate minerals was calculated from these data in terms of P_{CO_2} and T by Milton and Eugster (1959). Garrels and Christ (1965, p. 371, 372) give diagrams at 25°C calculated from thermochemical data by Alfred Truesdell and by Malcolm Ross. Eugster (1966) measured the CO_2 content of a gas phase equilibrated with saturated sodium carbonate-bicarbonate solutions between 20° and 70°C.

In combining these data, it is possible to arrive at several possible mechanisms by which trona may precipitate from brines; it is also possible to evaluate quantitatively the effects of changes in temperature, solution composition, and P_{CO_2}. The minerals which must be considered are nahcolite ($NaHCO_3$), trona ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$), natron ($Na_2CO_3 \cdot 10H_2O$), and thermonatrite ($Na_2CO_3 \cdot H_2O$). Wegscheiderite ($Na_2CO_3 \cdot 3NaHCO_3$), described by Fahey and Yorks (1963), forms from solutions only at higher temperatures and can be omitted in this discussion. Figure 17 gives the composition of solid phases known in the system $NaHCO_3$–Na_2CO_3–H_2O at 1 atmosphere pressure, as well as that of the saturated solutions at 25°C. Part of the system has been enlarged in figure 18 and distorted in order to show conveniently different possible evaporation paths. Figure 18 is an isobaric-isothermal section with two three-phase assemblages and three two-phase assemblages in addition to the region of undersaturated solutions. Compositions of all phases of any three-phase assemblage are fixed at

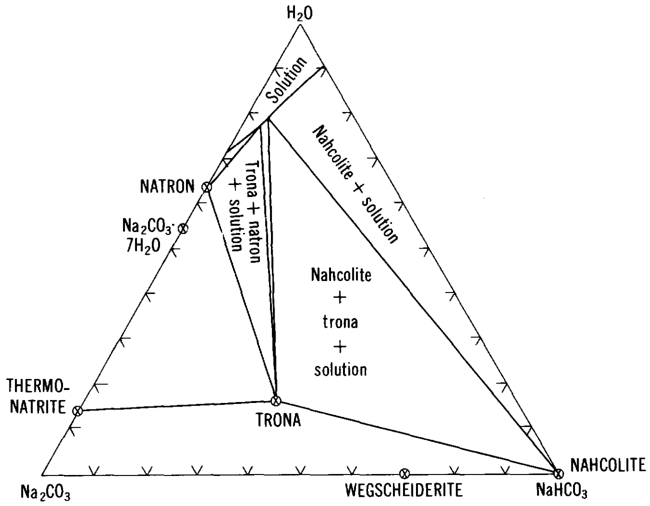

FIGURE 17.—Diagram giving the compositions, in weight percent, of solid phases known in the system $NaHCO_3$–Na_2CO_3–H_2O at 1 atmosphere pressure and the compositions of the saturated solutions at 25°C.

constant P and T in a three-component system. The saturated solutions of the three-phase assemblages have been designated with I and II, respectively. Three paths, 1, 2, and 3, have been indicated as examples for evaporation of undersaturated solutions; path 1 is for a bicarbonate-rich, and path 3, for a bicarbonate-poor, solution. In the undersaturated solutions the activity of CO_2, a_{CO_2}, decreases from right to left. During evaporation, the compositions of the solutions (that is, the plotted positions of the compositions) move away from the H_2O corner, and along straight lines, if the CO_2 content remains constant. These paths can be used to discuss evaporation under equilibrium conditions in a system closed with respect to all components except H_2O.

Path 1 has been so chosen that the bicarbonate: carbonate ratio of the solution is that of trona (1 mol HCO_3 for each mol CO_3). Because of the incongruent solution of trona, such a solution becomes first saturated with respect to nahcolite, at point *a*, if the CO_2 content remains constant. As evaporation continues, nahcolite precipitates, the compositions of the saturated solution moves along the solution boundary towards I, and the bulk composition moves through the nahcolite + solution field to the boundary between the nahcolite + solution field and the nahcolite + trona + solution field. Upon further evaporation, the composition of the solution remains at I, all the precipitated nahcolite is converted to trona, and additional trona precipitates from the solution, while the bulk composition moves through the nahcolite + trona + solution field towards trona. Evaporation is completed when the last remainder of nahcolite has been converted and the solution disappears; the system now consists of trona only. Relative amounts of phases and their compositions can be read quantitatively from figure 17.

A solution whose composition changes along path 2 becomes saturated with respect to trona at point *b*. As trona precipitates, the composition of the solution moves towards II; it reaches II at the moment natron joins trona as precipitate and remains at II until dryness. Similarly, a solution whose composition changes along path 3 will begin to precipitate natron at point *c;* as the bulk composition crosses from the natron + solution field into the natron + trona + solution field, trona also precipitates, and the composition of the solution moves towards II, its final composition.

In a system open to H_2O only, deposits consisting of trona alone can form during isothermal evaporation in one of two ways: (1) if the bicarbonate:carbonate ratio in the solution is near 1:1 (mol percent, path 1), perfect equilibrium between solids and solution must apply throughout, so that all of the nahcolite precipitated earlier may be converted to trona; (2) if the bicarbonate:carbonate ratio lies near path 2, trona precipitates first, and, if evaporation ceases before natron appears, a considerable amount of pure trona may accumulate.

The thick trona beds of the Green River Formation give no indication that some trona formed by conversion from nahcolite, nor are there any signs of subsequent natron deposition. It must be remembered that nahcolite + trona and trona + natron assemblages are well buffered with respect to changes in P_{CO_2}. Conversion of such assemblages to trona alone would require substantial losses of CO_2 for the former and gains for the latter assemblage. We feel that there is no evidence for such complete conversion in every single bed and believe that evaporation could not have taken place in a closed system (closed except with respect to H_2O).

The most obvious modification then is to assume that the overlying atmosphere acted as a reservoir of constant P_{CO_2}, keeping the bicarbonate:carbonate ratio in the brine well buffered. If we assume that this buffered equilibrium ratio is that of path 2, evaporation follows path 2, and no CO_2 is exchanged between the undersaturated solution and the atmosphere. Saturation occurs again at point *b*, and trona begins to precipitate. In a closed system this precipitation would have removed CO_2 from the brine, forcing it to move towards II. Now, however, CO_2 is being supplied by the atmosphere, and the solution remains at *b*, the bicarbonate:carbonate ratio being dictated by the atmosphere. As trona precipitates, the bulk composition (solution *b*+trona) moves towards trona until all solution is used up. Thus, a pure trona deposit

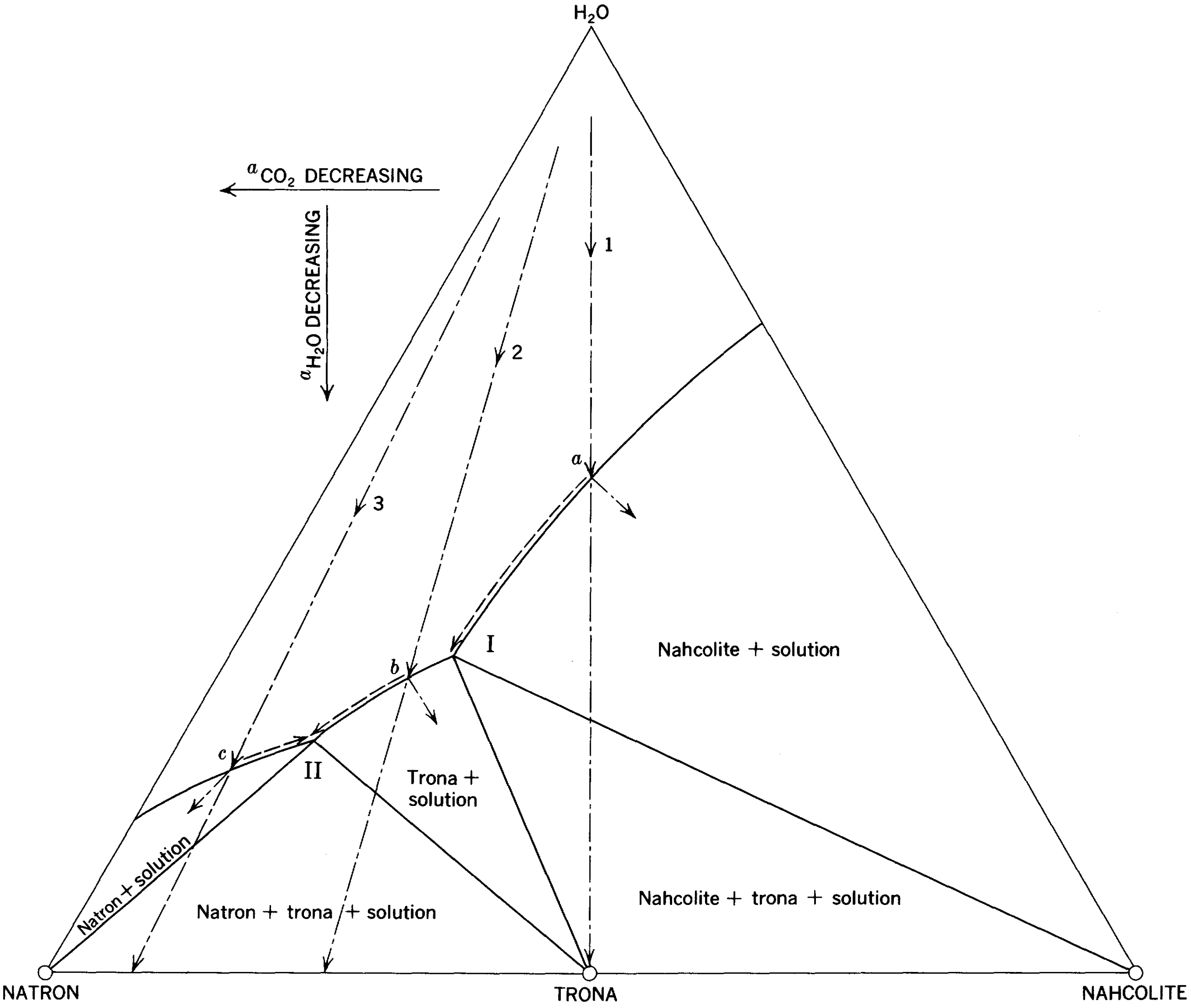

FIGURE 18.—Diagram showing a part of the system shown in figure 17 enlarged and distorted to show conveniently the different possible evaporation paths. The diagram is an isobaric-isothermal section with two three-phase assemblages and three two-phase assemblages in addition to the region of undersaturated solutions.

results. The amount of trona obtained can easily be calculated from the amount of sodium present in the original brine; the amount of CO_2 supplied by the atmosphere depends on the amount of trona formed and the bicarbonate content of that brine. It is likely that the thick trona beds of the Green River Formation did form by this kind of process.

Before we can analyze the relationships quantitatively, the effect of temperature shown on a diagram such as figure 17 must be evaluated. Rather than constructing a series of isothermal ternary sections, we can present the data in a single diagram by using temperature, bicarbonate:carbonate ratio, and total sodium as the parameters. Figure 19 was drawn from the data of Wegscheider and Mehl (1928) and Freeth (1923), using *T* and weight percent sodium of the solution as independent parameters, and contouring the bicarbonate quotient (b.q.), defined as $\frac{\text{g HCO}_3}{\text{g HCO}_3+\text{g CO}_3}$, on the surfaces of the plotted compositions of the saturated solutions. The two sets of data agree well with respect to the sodium contents; there is considerable discrepancy, however, in the bicarbonate quotients, the higher bicarbonate contents being reported by Wegscheider and Mehl (1928). It is difficult to prevent CO_2 loss during analysis, and the values of Wegscheider and Mehl (1928) are thought to be more reliable.

Undersaturated solutions exist below the boundary indicated at about 2 percent sodium at low temperatures

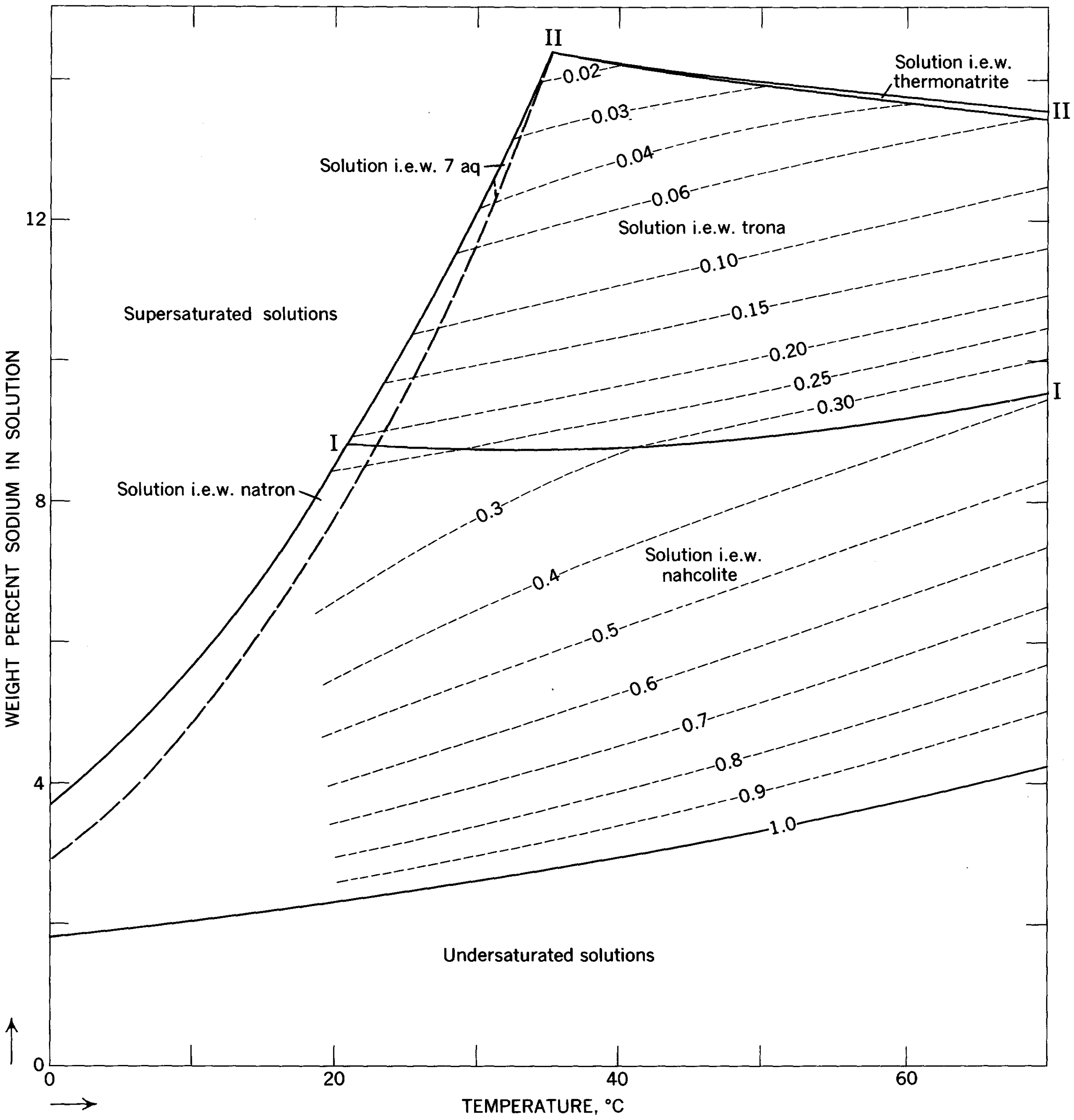

FIGURE 19.—Compositions of saturated solutions drawn from the data of Wegscheider and Mehl (1928) and Freeth (1923), using *T* and weight percent sodium in the solution as independent parameters, and contouring the bicarbonate quotient, $\frac{\text{g } HCO_3}{\text{g } HCO_3 + \text{g } CO_3}$, on the surfaces of the plotted compositions of the saturated solutions. See text for explanation of the 7 aq and natron fields. I and II, three-phase assemblages of figure 18; i.e.w., in equilibrium with; short-dashed lines, bicarbonate-quotient contours.

and at about 4 percent sodium at higher temperatures. Above this boundary, only saturated and supersaturated solutions can exist. Fields are shown for saturated solutions in equilibrium with (i.e.w.) nahcolite, trona, natron, $Na_2CO_3 \cdot 7H_2O$ (7 aq), and thermonatrite. Compositions of solids are omitted. Boundaries between fields represent saturated solutions in equilibrium with two solids. Intersections of such boundaries form three invariant points, representing the assemblages:

natron + trona + nahcolite + solution at about 20°C
natron + 7 aq + trona + solution at about 32°C
7 aq + thermonatrite + trona + solution at about 35°C.

Because of the parameters chosen, a small area of figure 19 is ambiguous in terms of phase assemblages: the solution + natron and the solution + aq fields; they have been drawn as lying behind (in terms of the bicarbonate quotient) the solution + nahcolite and solution + trona fields (dashed curves). The maximum sodium contents for saturated solutions is reached with the natron + nahcolite + solution, natron + trona + solution, trona + 7 aq + solution, and thermonatrite + solution assemblages (curves II–II). By far, the largest areas of the diagram are occupied by solutions in equilibrium with nahcolite and with trona; this makes figure 19 particularly suitable for the purposes of our discussion. Bicarbonate quotients have been calculated for these two fields and have been contoured. They vary from 1.0 (no CO_3^{-2} in solution) to 0.0 (no HCO_3^{-1} in solution). There is a striking dependence of the solubility (as represented by percent sodium) on the bicarbonate quotient. Thus, the solubility of nahcolite can, at a given temperature, be increased nearly fourfold by a suitable decrease in the bicarbonate quotient. This can be accomplished simply by a loss of CO_2 to the atmosphere. Inversely, an undersaturated solution with a given bicarbonate quotient and temperature can become saturated at that temperature and without loss of H_2O, simply by an increase in the bicarbonate quotient, that is, by an addition of CO_2. Deposition of trona or nahcolite by such a mechanism may be very important in subsurface environments, where evaporation is excluded. For a more detailed discussion, see pages B53–B54, B57.

In contrast to nahcolite and trona, the solubility of natron and thermonatrite show little dependence on the bicarbonate quotient; in fact, the solubility of natron decreases slightly with increasing CO_3^{-1} content of a solution at constant temperature.

The effects of changes in temperature and the bicarbonate quotient on the deposition of trona and nahcolite can be read quantitatively from figure 19. The two effects are most conveniently compared by constructing isothermal sections from figure 19. Six such sections are presented in figure 20, in 10°C steps. The intersections of the isotherms with the ordinate on the left represent solubilities in the system Na_2CO_3–H_2O and intersections on the right those in the system $NaHCO_3$–H_2O. The isotherms are curved, and breaks in curvature occur where two solids coexist with a saturated solution; the series of points, I, again represent the assemblage trona + nahcolite + solution. The bicarbonate quotient of solid trona is indicated at 0.505, again demonstrating the fact that solutions coexisting with trona are much poorer in HCO_3^{-1}. The bicarbonate quotient of a saturated solution equilibrated with present-day air is approximately 0.15 and well within the range of solutions in equilibrium with trona (p. B44).

The solubilities of trona and nahcolite are much less affected by changes in temperature than they are by changes in the bicarbonate quotient. This is already apparent in figure 19 by the slopes of the bicarbonate-quotient contours. The bicarbonate quotients permissible for solutions in equilibrium with trona range from a minimum of 0.02 at 35°C (a solution practically free of HCO_3^{-1}) to a maximum of 0.39 at 70°C. The permissible ranges between 25° and 50°C are given in table 14, in which the sodium contents of a solution in equilibrium with trona and one other solid are also given.

TABLE 14.—*Composition of saturated sodium carbonate-bicarbonate solutions*

[Data from Wegscheider and Mehl, 1928]

Temperature (°C)	Solids in equilibrium with solution	g Na/100-g solution	Bicarbonate quotient
25	Trona + nahcolite	8.81	0.23
30	do	8.76	.25
40	do	8.80	.29
50	do	9.07	.33
70	do	9.62	.39
25	Trona + natron	10.23	.12
30	do	12.33	.04
40	Trona + thermonatrite	14.21	.02
50	do	13.96	.03
70	do	13.50	.06

Mechanisms by which trona may precipitate can now be discussed in detail. Three isotherms such as those of figure 20 have been drawn schematically in figure 21, T_1 and part of T_2 and T_3, where $T_2 > T_1 > T_3$. I again stands for a solution saturated with trona + nahcolite, and II may now stand for a solution saturated with trona + thermonatrite, as temperatures are more commonly above 20°C. Three different mechanisms have been indicated by which an undersaturated solution may reach saturation with respect to trona and continue to precipitate trona: (1) isothermal evaporation, (2) addition of CO_2, and (3) decrease of temperature. Path 1 has been subdivided into 1*a*, 1*b*, and 1*c*, depending upon whether evaporation is accompanied with no loss of CO_2 (1*a*), some loss of CO_2 (1*b*), or proceeds in equilibrium with a reservoir with a fixed P_{CO_2} (1*c*).

POSSIBLE CRYSTALLIZATION CONDITIONS

The data given in figures 19 and 20 form the quantitative framework within which possible crystallization paths can be discussed quantitatively.

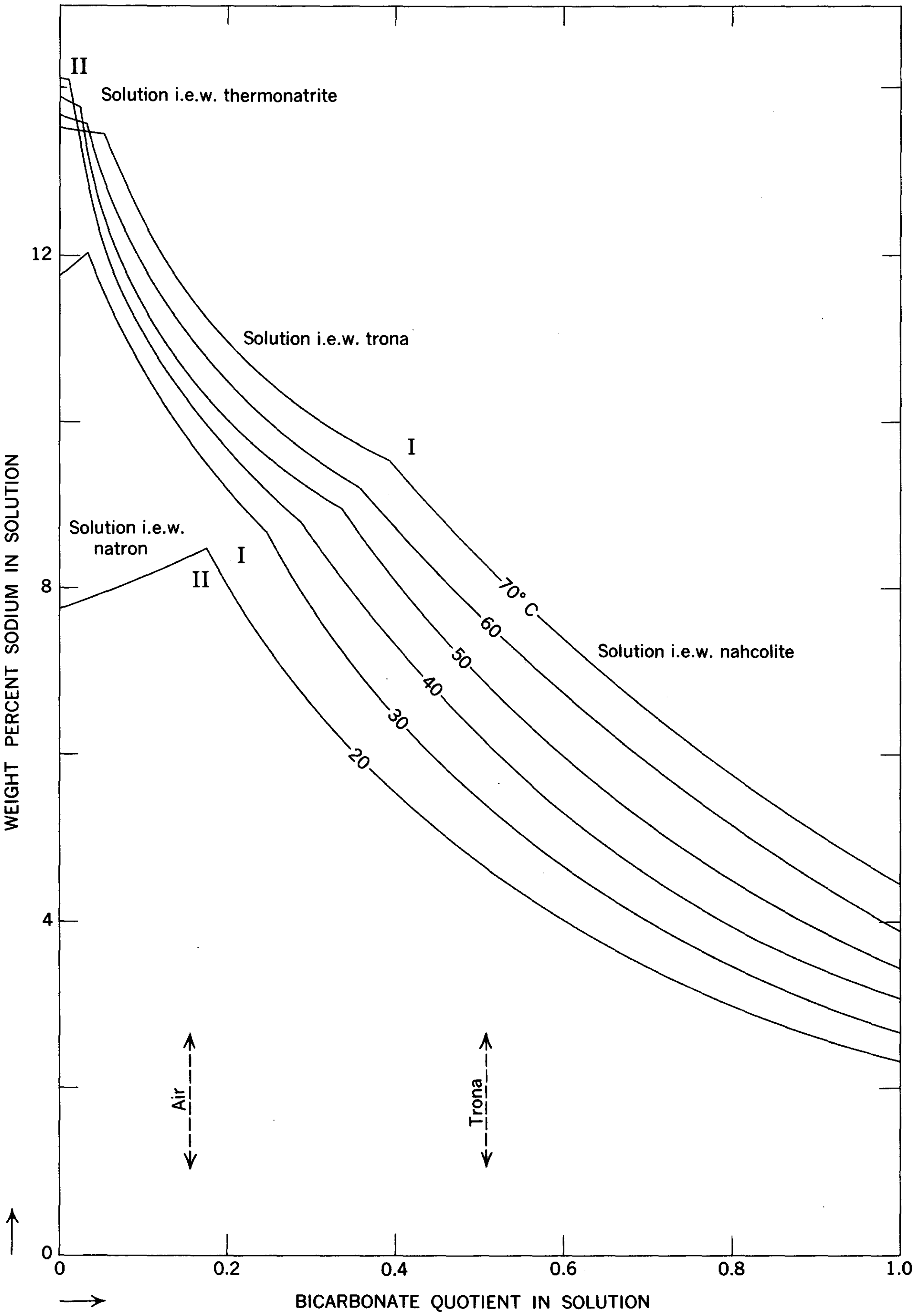

FIGURE 20.—Isothermal sections constructed from figure 19 presented in 10°C steps. The intersections of the isotherms with the ordinate on the left represent solubilities in the system Na_2CO_3–H_2O, and the intersections on the right, those in the system $NaHCO_3$–H_2O. i.e.w., in equilibrium with.

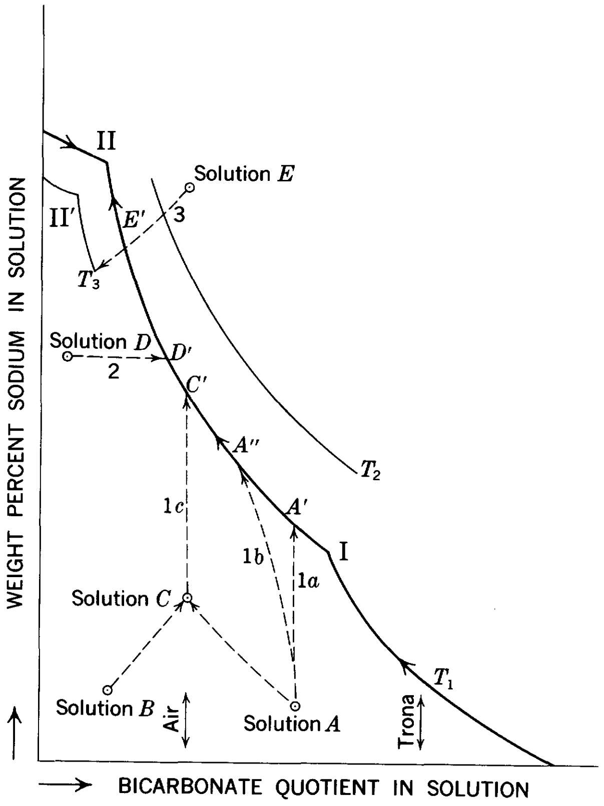

FIGURE 21.—Diagram showing three isotherms such as those of figure 20 drawn schematically. T_1 and a part of T_2 and T_3 where $T_2 > T_1 > T_3$. I stands for a solution saturated with trona and nahcolite, and II and II′ stand for a solution saturated with trona + thermonatrite, as temperatures are more commonly above 20°C. Three different mechanisms are indicated by which undersaturated solution may reach saturation with respect to trona and continue to precipitate trona: (1) with isothermal evaporation, (2) addition of CO_2, and (3) with decrease of temperature. Path 1 is subdivided into 1*a*, 1*b*, and 1*c*: 1*a*, evaporation without CO_2 loss; 1*b*, some CO_2 loss; 1*c*, CO_2 exchange with a reservoir of constant P_{CO_2}. Point *A* is the starting point for 1*a*, 1*b*, and that example of 1*c* which represents a solution with a P_{CO_2} initially higher than that of the reservoir. Points *A′* and *A″* and *C′* are the respective points of trona saturation. *B* is a solution with a P_{CO_3} lower than that of the reservoir, and *C* is a solution with P_{CO_2} equal to that of the reservoir. *D* and *E* are the initial brines for paths 2 and 3, respectively, and *D′* and *E′* are the corresponding points of trona saturation. I and II are the points indicated in figures 17–20. The bicarbonate quotient of solid trona and of a solution in equilibrium with air have also been indicated on the abscissa.

CRYSTALLIZATION BY ISOTHERMAL EVAPORATION

1. No loss of CO_2

If an undersaturated solution represented by *A* (fig. 21) is subjected to isothermal evaporation at temperature T_1 and the CO_2, content remains unchanged, the composition of the solution follows path 1*a* in figure 21, showing no change in the bicarbonate quotient and an increase in percent Na. Evaporation proceeds until saturation is reached at *A′*, the intersection of 1*a* with the solution + trona boundary (I–II) for the specified temperature. The higher the bicarbonate quotient, the earlier this occurs. If evaporation continues, again without loss or addition of CO_2 to the system, trona precipitates, while the composition of the solution moves towards II and becomes progressively impoverished in bicarbonate. This path is inevitable because the precipitating solid has a bicarbonate quotient of 0.505. Trona continues to precipitate while the solution becomes more and more concentrated in sodium, until at point II, thermonatrite coprecipitates with trona. The solution composition then remains at II until dryness. The final trona to thermonatrite ratio is determined by the bicarbonate quotient of the original solution *A*.

Arrows on the isotherm T_1 in figure 21 indicate direction of changes in composition solutions during isothermal evaporation. All solutions with a bicarbonate quotient between 0 and 0.505 go to dryness at point II and crystallize mixtures of trona and thermonatrite. All solutions with bicarbonate quotients between 0.505 and 1.0 (except for the value of 1.0 itself) go to dryness at point I and crystallize to a mixture of nahcolite + trona. Solutions with bicarbonate quotients between 0.505 and that of point I for the respective temperature (0.39, 0.33, 0.26 for 50°C, 40°C, 30°C, respectively) first crystallize nahcolite while the composition of the solution moves towards I. At I, upon further evaporation (again no loss of CO_2), nahcolite is converted to trona. When the conversion is complete, the composition of the solution moves from I to II and remains there until it solidifies to a mixture of trona + thermonatrite.

2. Some CO_2 *lost*

Evaporation rarely will be restricted to a loss of H_2O only. CO_2 will, in general, also be lost during evaporation. In this case, the path of the changing compositions of the solution is curved from *A* towards *A″*, the curvature depending upon the relative losses of H_2O and CO_2. Saturation occurs at *A″*, the intersection with the respective isotherm, and trona begins to crystallize as the composition of the liquid moves to II. The final ratio of trona + thermonatrite after solidification at II depends not only on the bicarbonate quotient of the original solution, but also on the amount of CO_2 lost during evaporation. Furthermore, solutions with bicarbonate quotients greater than 0.505 may now move beyond point I to II and crystallize trona + thermonatrite rather than nahcolite + trona, as for the case without CO_2 loss.

3. Evaporation in equilibrium with a CO_2 *reservoir*

Because of the presence of the atmosphere during evaporation and its capacity to act as a CO_2 reservoir, the case of evaporation in equilibrium with a reservoir of constant P_{CO_2} must also be considered. The atmospheric CO_2 will, under equilibrium conditions, impose a bicarbonate quotient upon the brine which is fixed for a given temperature. This quotient has been marked schematically in figure 21 and labelled "Air." An evaporating undersaturated solution, whose composition is represented say at A or at B, will lose H_2O and will adjust its CO_2, by exchange with the reservoir, to reach the equilibrium bicarbonate quotient, say at C. Further evaporation results only in a loss of H_2O, until saturation occurs at C'. Trona begins to precipitate, but the composition of the solution remains as at C', because the excess CO_2 required for the formation of trona is continuously being supplied by the reservoir, until evaporation is complete. The last solution, just before dryness is reached, still has the bicarbonate quotient of C. Under such conditions all the sodium of the original brine will be contained in trona, and the amount of trona deposited will depend only on the amount of sodium contained in the original brine.

This is probably the mechanism by which the thick monomineralic trona beds have accumulated. For this reason, path 1*c* will be discussed quantitatively under the section "Crystallization path of brines in equilibrium with P_{CO_2} of the atmosphere."

CRYSTALLIZATION BY ISOTHERMAL ADDITION OF CO_2

Consider an undersaturated solution represented by point D at temperature T_1. If CO_2 is added at constant temperature and no evaporation occurs, the composition of the solution moves parallel to the abscissa and saturation occurs at point D'. If addition of CO_2 continues after the solution has reached point D', trona must precipitate. This impoverishes the brine in sodium, and its plotted composition therefore moves from D' towards I. The amount of trona precipitated depends directly upon the amount of CO_2 added. If sufficient CO_2 is added, the brine may reach point I and precipitate nahcolite. As figure 20 shows, point II lies between 8.6 and 9.0 percent Na. As brines with as much as 12 percent Na can still be undersaturated at 30°C, considerable amounts of trona may crystallize simply by addition of CO_2. This mechanism is probably most important for the precipitation of trona from interstitial brines that are removed from surface evaporation, or from brines in a stratified lake, in which the brine is overlain by fresher water. CO_2 produced by organic activity, either in the epilimnion or in the muds, can cause a considerable amount of trona to be precipitated. Furthermore, trona alone precipitates by this mechanism, even if the interstitial brines are complex in composition.

CRYSTALLIZATION BY DECREASE OF TEMPERATURE

A solution represented by point E in figure 21 is saturated with respect to trona at temperature $T(T>T_2)$. As the temperature decreases, trona precipitates, and the composition of the solution moves towards E', which it reaches at T_1. Upon further temperature decrease, say to T_3 $(T_3<T_1)$, trona continues to precipitate, and the composition of the solution moves from E' towards the isotherm for T_3. The temperature effect on the solubility of trona is not very large. A solution with a bicarbonate quotient of 0.15, for instance, changes its sodium concentration from 10.1 percent at 40° to 9.9 percent at 30°, only 0.2 percent Na being contributed to the precipitation of trona. If the temperature is decreased to 20°C, however, much natron precipitates, and the solution contains only 8.2 percent Na, the difference being incorporated into the precipitation of natron.

Decrease of temperature within the range of ambient temperature, therefore, may, by itself, cause only a small amount of trona to precipitate. If the decrease is large enough, however, natron becomes stable and precipitates in very substantial amounts.

CRYSTALLIZATION PATH OF BRINES IN EQUILIBRIUM WITH P_{CO_2} OF THE ATMOSPHERE

The most important mechanism for the deposition of thick trona beds is obviously evaporation in equilibrium with the atmosphere. Equilibration between brine and air does, of course, not have to be maintained perfectly and continuously, as long as the exchange is sufficiently fast and sufficiently large to replace the CO_2 lost to the brine through precipitation of trona. Evaporation is a slow process (p. B35), and there is probably ample time for CO_2 exchange (for studies of exchange kinetics see, for instance, Barnes, 1965), particularly in shallow, well-stirred lakes. If this were not so, we should find bedded deposits of trona+thermonatrite or trona+natron. It is not likely that recrystallization would have eliminated all traces of such deposits. (See also p. B37.)

CO_2 contents of a gas phase equilibrated with sodium carbonate-sodium bicarbonate brines have been determined by Eugster (1966), and the data are summarized in figure 22. The experimentally determined CO_2 contents are considerably higher than those previously calculated (see Milton and Eugster, 1959, p. 129). Trona +solution occupy a broad range, spanning about two orders of magnitude in percent CO_2 or P_{CO_2}. Present-day air has CO_2 contents varying between 300 and 400 ppm (see, for instance, Keeling, 1958, 1960; Bischof, 1960,

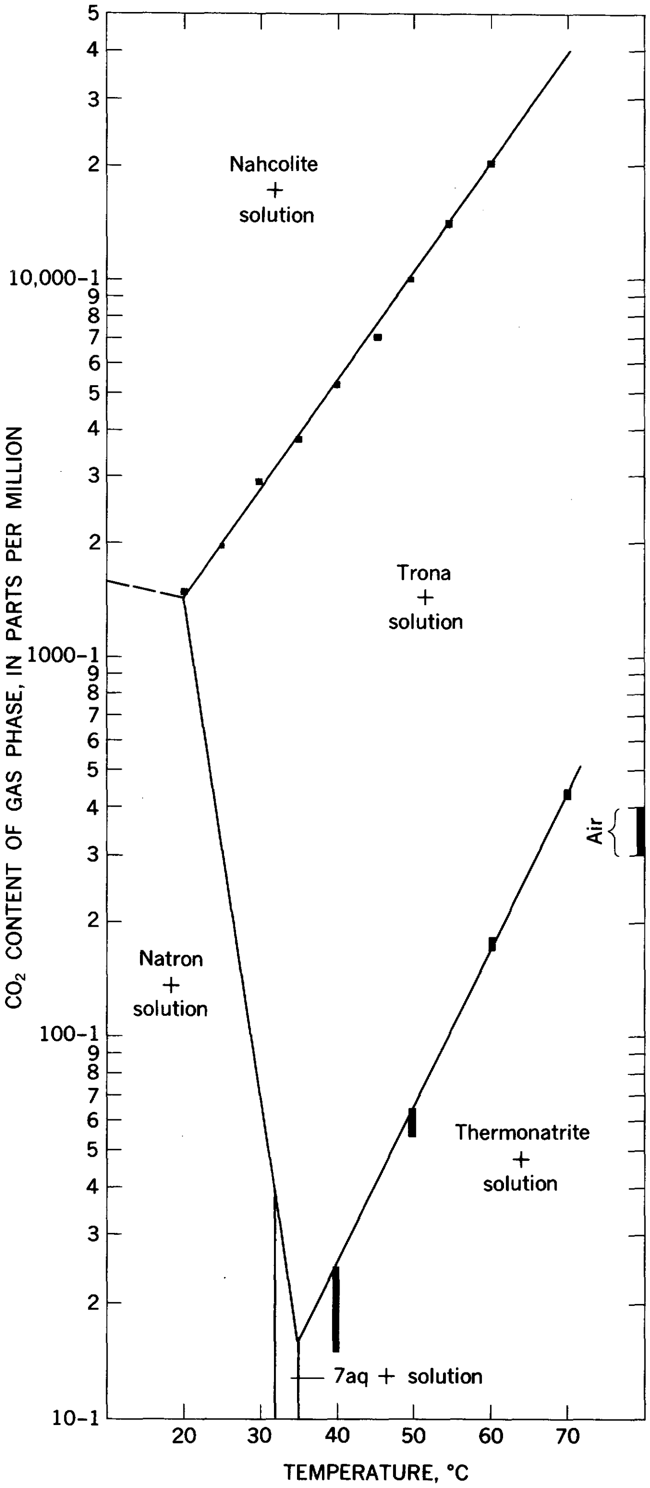

FIGURE 22.—CO_2 content of a gas phase in equilibrium with saturated sodium carbonate-sodium bicarbonate brines as determined by Eugster (1966, fig. 3). The CO_2 content of present-day air is shown on the right.

1962; Bolin and Keeling, 1963). This range of values is shown in figure 22; between 30° and 60°C, it lies well within the range of trona+solution+gas. In fact, nahcolite could only precipitate if P_{CO_2} of the atmosphere were increased tenfold, whereas thermonatrite would require a substantial decrease. This explains well why trona is usually the sodium carbonate-bicarbonate mineral precipitating from brines at the earth's surface. Significant departure from equilibrium (or, more probably, separation from the atmosphere as CO_2 reservoir) is necessary to form nahcolite or thermonatrite. On the other hand, natron will be the stable phase in equilibrium with the atmosphere at temperatures below about 25°C. These data cannot, of course, be applied to efflorescent crusts where brine is not present at all times.

The relations between temperature, the bicarbonate quotient of the solution, and the CO_2 content of the gas phase for the assemblage nahcolite + trona + solution + gas are given in figures 23 and 24 and have been derived from the data shown in figures 19, 20, and 22. The bicarbonate quotient for this solution increases roughly linearly with temperature (fig. 23), whereas the CO_2 content increases logarithmically (fig. 24). The curve of figure 24 can be used to arrive at a rough estimate of the bicarbonate quotient a brine must have, if equilibrated with present-day air. The value is about 0.15±0.03. This extrapolation assumes that P_{CO_2} of the gas phase depends primarily on the bicarbonate:carbonate ratio of the solution and not on the nature of the solids present (trona + nahcolite or trona alone). This is only approximate, as Henry's law constants depend on the concentration of the solution (see Harned and Owen, 1958). A solution in equilibrium with trona + nahcolite contains 8.8 percent Na at

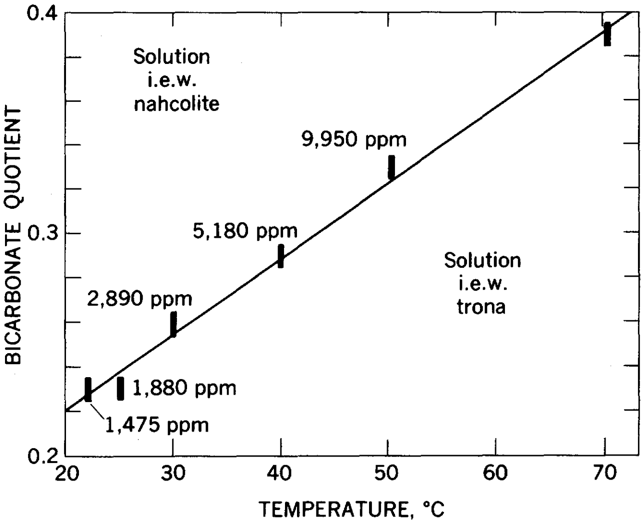

FIGURE 23.—Relations between temperature, the bicarbonate quotient of the solution, and the CO_2 content, in parts per million, of the gas phase for the assemblage nahcolite + trona + solution + gas. Data from Wegscheider and Mehl (1928) and Eugster (1966). i.e.w.: in equilibrium with.

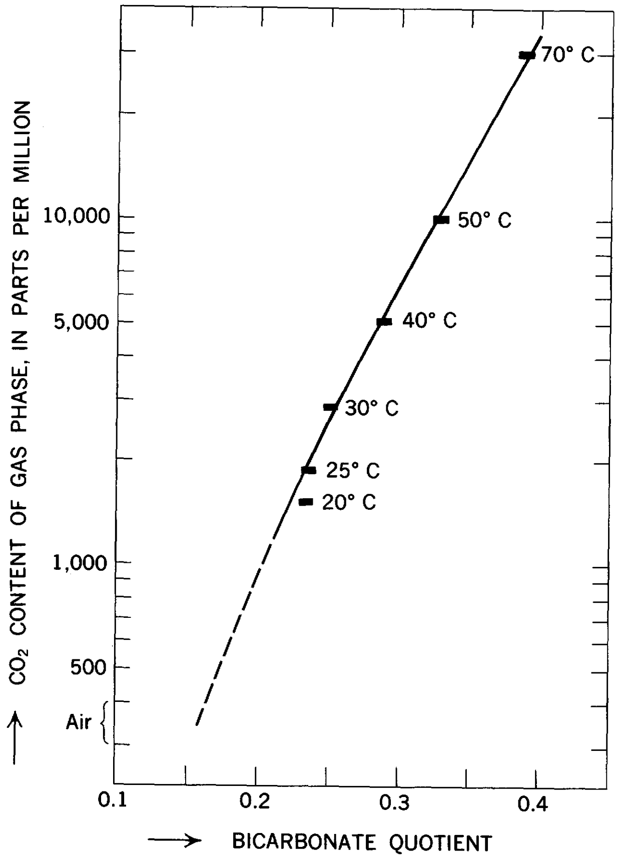

FIGURE 24.—Relation between CO_2 content of a gas and the bicarbonate quotient of a solution in equilibrium with it, saturated with respect to trona + nahcolite at temperatures ranging from 20° to 70°C. Data from Wegscheider and Mehl (1928) and Eugster (1966). A crude extrapolation to the CO_2 content of present-day air yields a bicarbonate quotient of 0.15 ± 0.03.

40°C, whereas a solution with a bicarbonate quotient of 0.15 at 40°C is in equilibrium with trona alone and contains 10.4 percent Na. Nevertheless, the discrepancy is small if no other salts, such as NaCl, are present. Therefore, if trona precipitates from a shallow, well-stirred lake today, the bicarbonate quotient of the brine can be expected to lie close to 0.15. This is the value indicated in figure 20. Supporting evidence for the value of 0.15 comes from the analysis of Lake Magadi brine given in table 15. This brine, which comes from a shallow lagoon of Lake Magadi (Baker, 1958), is nearly saturated with respect to trona and has a bicarbonate quotient of 0.14. In contrast, the Deep Springs Lake brines (Jones, 1965) given in table 17 show generally higher values, but these are mainly interstitial in muds and therefore not equilibrated with the atmosphere. For further comparison with natural brines, see page B54.

In summary then, figures 19–24 define the conditions for the deposition of trona from sodium carbonate-bicarbonate brines within the geologically significant range of 20°–70°C. Sodium concentrations in the brine must be at least 8.75 g Na/100-g solution and not more than 14.2 g Na/100-g solution. Bicarbonate quotients can range from 0.02 to 0.35, and the CO_2 content of the gas phase in equilibrium with trona + solution can vary from very low values (20 ppm) to a maximum of 20,000 ppm, depending upon temperature.

Several mechanisms are possible by which monomineralic trona can precipitate from sodium carbonate-sodium bicarbonate brines. These mechanisms involve loss of H_2O, loss or addition of CO_2, or decrease in temperature. Of the many possible paths, two are of special interest: evaporation at constant P_{CO_2}, such as in a shallow, well-stirred lake in equilibrium with the atmosphere, and precipitation of trona by addition of CO_2 without loss of H_2O, such as in a hypolimnion or in pore fluids. For thick trona beds of the Wilkins Peak Member, evaporation in a shallow, well-aerated brine lake seems to be the only feasible mechanism for the accumulation of a monomineralic bed of trona. Thick beds of trona, however, would almost certainly be very porous because of the occluded brine. Such pores and cavities can be filled with solid trona only by the precipitation of additional trona, which gradually replaces the brine. This precipitation is brought about by the addition of CO_2, derived either from the atmosphere or from biogenic processes within or immediately adjacent to the trona bed. (See also discussion on p. B54–B56).

At an accumulation rate of 145 years per foot, the brine must have been at the salting stage for at least 1,200 years to deposit 8.5 feet of trona. Even if we use the maximum apparent rate of accumulation for Lake Magadi (12 yr per ft, see p. B35), the salting stage for a single bed would have lasted at least 92 years. During this time, the brine must have contained at least 8.8 g Na/100 g brine (25°–40°C) and probably more. If the CO_2 content of Eocene air was similar to present-day air and if the lake was well stirred, the brine would have had a bicarbonate quotient of about 0.15 and would have contained 9.7, 10.0, 10.2, or 10.5 percent sodium at 25°, 30°, 35°, or 40°C, respectively.

Perhaps the most serious objections to these deductions come from the fact that the Gosiute Lake brines from which trona precipitated cannot possibly have been simple sodium carbonate-bicarbonate brines. It is therefore necessary to find models for the composition of the natural brines and to evaluate the effect of the presence of other ions in the brine on the trona precipitation.

SALINITY AND COMPOSITION OF GOSIUTE LAKE AT SALTING LEVEL

We have just seen (p. B44) that for the deposition of trona a carbonate-bicarbonate brine in equilibrium with air must have a bicarbonate quotient of about 0.15. Arbitrarily assuming a temperature of 30° C, we can read from figure 19 the sodium content necessary for a brine to be saturated with respect to trona. This value is about 104,000 ppm Na^+. It should be made clear however, that the brines represented in figure 19 are hypothetical and contain no chloride. As noted above, this is most improbable for a natural saline lake.

No model of Gosiute Lake brine at salting level is likely to be as realistic as the chemical compositions of present-day sodium carbonate-rich lakes that are precipitating trona. Accordingly, the compositions of the brine in two such lakes, one sample from Abert Lake brine pool, Oregon, and three from Lake Magadi, Kenya, are given in table 15. It is noteworthy that these brines contain rather large quantities of choride but neither Ca nor Mg. Because they may be instructive, we have added the compositions of a second group of four more brines of lesser concentration. Two of these brines contain small quantities of Ca and Mg, and, as would be expected, all four have conspicuously larger amounts of HCO_3. We shall use the first analysis in table 15 as a model for the Gosuite Lake brine because it represents the open water in the lake, which is clearly in equilibrium with the atmosphere. This brine, unlike the others in this first group, is slightly undersaturated with respect to trona. From the second group of less concentrated brines in table 15, we have selected the last analysis to serve as another model of Gosiute Lake brine. This model is actually an analysis of one of the hot springs typical of those that supply the salts to Lake Magadi.

The inferred salinity of the Gosiute Lake brine at trona salting stage is rather close to the salinity of Great Salt Lake (284,000 ppm) in 1963 at the lowest stage in its recorded history.

From the point of view of mineral equilibria, one of the most important constituents not yet considered is chlorine. Halite has been found in considerable volume in some trona beds in the Green River Basin. Certainly, the presence of much Cl^{-1} in a brine will affect the conditions under which trona will precipitate. Phase equilibria in the system $NaHCO_3$–Na_2CO_3–NaCl–H_2O will therefore be discussed next. Consideration of these equilibria will also make it possible to calculate the maximum amount of trona that can be precipitated from a Lake Gosiute brine before saturation in halite occurs.

MINERAL EQUILIBRIA IN THE SYSTEM $NaHCO_3$–Na_2CO_3–NaCl–H_2O AND THE EFFECT OF NaCl ON THE DEPOSITION OF TRONA

Freeth (1923) gives data on this system for 0°, 15°, 25°, 30°, 35°, 45°, and 60°C. Wegscheider and Mehl

TABLE 15.—*Chemical analyses (in parts per million) of brines from existing sodium carbonate-rich lakes, springs, or pools, that either are at or may arrive at, trona-salting stage*

[The first and last analyses of this table have been selected to serve as models of Gosiute Lake brines. nd, not determined]

	Date sampled	pH (field)	Ca	Mg	Na	K	HCO_3	CO_3	SO_4	Cl	SiO_2	Bicarbonate quotient	Dissolved solids (calculated)
					Concentrated brines								
Lake Magadi, Kenya.[1] Model of Gosiute Lake brine near salting stage	1962	9. 90	------------		91, 600	1, 550	12, 200	72, 200	984	48, 000	456	0. 14	227, 000
Abert Lake brine pool, Oregon [2]	8/63	9. 8	------------		119, 000	3, 890	0	60, 300	9, 230	115, 000	nd	0	309, 000
Lake Magadi, Kenya [3]	6/66	11. 06	------------		132, 000	2, 280	Trace	106, 000	219	84, 400	1, 055	0	324, 000
Do.[3]	6/66	10. 11	------------		110, 000	1, 530	Trace	95, 000	97	50, 700	583	0	247, 000
					Less concentrated brines								
Abert Lake, Oreg.[3]	7/64	9. 75	------------		15, 200	604	3, 840	6, 920	792	12, 700	128	0. 36	39, 300
Do.[4]	1/62	9. 6	1. 4	0. 6	22, 000	752	5, 930	9, 460	990	19, 300	nd	. 38	55, 900
Mono Lake, Calif.[5]	3/59	9. 6	4. 5	34. 0	21, 500	1, 170	5, 410	10, 300	7, 380	13, 500	nd	. 34	56, 600
Hot spring, Little Magadi Lake, Kenya.[3] Model of Gosiute Lake brine at dilute stage	6/66	9. 05	------------		12, 600	239	15, 600	3, 540	147	5, 950	90	. 81	30, 200

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[1] Hay, R. L. (1966, p. 33); analyst, S. L. Rettig, U.S. Geol. Survey.

[2] Jones (1966, p. 184–185); analyst, S. L. Rettig, U.S. Geol. Survey.

[3] Jones, Rettig, and Eugster (1967); analyst, S. L. Rettig, U.S. Geol. Survey.

[4] Jones (1966, p. 184–185); analyst, A. S. Van Denburgh, U.S. Geol. Survey.

[5] Jones (1966, p. 184–185); analysts, J. Barnhart and R. K. Reaves, U.S. Geol. Survey.

(1928) determined some solution compositions at 30°, 49.7°, and 89.5°C.

A complete anlysis of the data in this four-component system is rather complex. Simplifications are possible, as we are primarily interested in temperature, bicarbonate quotient (or P_{CO_2}), accumulation of sodium necessary for trona precipitation, and maximum permissible chloride concentration without precipitation of halite. Isothermal sections showing percent sodium versus percent chlorine (g sodium and chlorine, respectively, per 100-g solution) of the saturated solutions are given in figure 25. Even a cursory examination of these sections reveals the pronounced effect the addition of NaCl has on the crystallization of trona. Trona is now a stable phase at temperatures as low as 0°C, where it can crystallize from chloride-rich brines. With rising temperature the trona field expands towards solutions poorer in chloride until at 20°C it appears as a stable phase in the chloride-free system. This effect is still visible in the 25° and 30°C sections, where an addition of chloride broadens the trona field at the expense of the nahcolite field.

The compositions of brines saturated only with respect to halite are given in table 16 in terms of g NaCl/100-g water, g NaCl/100-g solution, g sodium/100-g solution, and g chlorine/100-g solution. These data appear as points H (highest chlorine concentration) in the isothermal sections of figure 25. From each of these points (H) a straight line drawn to the origin of the diagram represents electrically neutral undersaturated solutions which contain Na^{+1} and Cl^{-1} ions only. Points below this line ("chloride line") are solutions in which the excess Cl^{-1} ions are balanced by some other cation in addition to Na^{+1}. Such solutions are not of interest for Green River brines. Above this line are the bicarbonate-carbonate-chloride brines (or brines with other additional anions) with which we are concerned. Distance from the "Chloride line" is a measure of the total carbonate to chloride ratio.

TABLE 16.—*Compositions of sodium chloride brines saturated in halite*

Temperature in ° C	0°	10°	20°	30°	40°	50°	60°
g NaCl/100-g water	35.7	35.8	36.0	36.3	36.6	37.0	37.3
g NaCl/100-g solution	26.3	26.4	26.5	26.6	26.8	27.0	27.2
g sodium/100-g solution	10.3	10.4	10.4	10.5	10.5	10.6	10.7
g chlorine/100-g solution	16.0	16.0	16.1	16.1	16.3	16.4	16.5

Solutions in equilibrium with nahcolite and with trona still occupy by far the largest part of the diagram. The addition of NaCl increases the Na contents of the saturated brines considerably. The size of the nahcolite + solution field is reduced, whereas that for trona + solution is not changed much with respect to ranges of Na contents, except that it extends towards much lower temperatures (p. B46). The intersections of the field boundaries with the ordinate are defined by the data of figure 19. Again, there is a small area of ambiguity with respect to carbonate solutions, because the Na contents of solutions saturated with respect to natron and $Na_2CO_3{\cdot}7H_2O$ increase slightly with an addition of HCO_3^- to the bicarbonate-free system. New assemblages appearing in figure 25 are solution + trona + halite, solution + nahcolite + halite, and solution + halite.

Figure 25 becomes more useful if the bicarbonate quotients are contoured on the nahcolite+solution and trona+solution fields. This was done in figure 26 for the 30°C isotherm, using the data of Freeth (1923), because the data of Wegscheider and Mehl (1928) are incomplete. Unfortunately, there are discrepancies of as much as 10 percent for the Na contents of NaCl-rich brines in equilibrium with trona and with thermonatrite for the two sets of data. However, the bicarbonate quotients for solutions of trona+nahcolite+solution assemblages agree well with each other. Bicarbonate quotients of such solutions increase slightly with increasing chloride content from 0.26 in the chloride-free system to 0.28 in the presence of 4.6 percent chloride to 0.30 in the presence of 9.1 percent chloride (Freeth's data; Wegscheider and Mehl give 0.29 for a chloride content of 11.1 percent) and to about 0.46 at saturation with halite. In other words, addition of NaCl extends the field of stability of trona+solution towards higher bicarbonate ratios.

Bicarbonate contours in the solution+trona and solution+nahcolite fields have been interpolated, and they are much less reliable than those along the solution+trona+nahcolite boundary (fig. 19).

POSSIBLE CRYSTALLIZATION CONDITIONS

We may now discuss the mechanisms for trona precipitation from Na_2CO_3–$NaHCO_3$–NaCl brines in a manner similar to that for chlorine-free brines (p. B36–B46). Different paths are summarized in the isothermal section for 30° C, figure 27, which is an exact copy of the section shown in figure 26.

The three paths considered are again:

1. Isothermal evaporation with or without change in CO_2.
2. Addition of CO_2, no loss of H_2O.
3. Change in temperature.

Path 1 is again subdivided as follows:

1*a*. No loss of CO_2.
1*b*. Some loss of CO_2.
1*c*. Exchange with a reservoir of fixed CO_2 content.

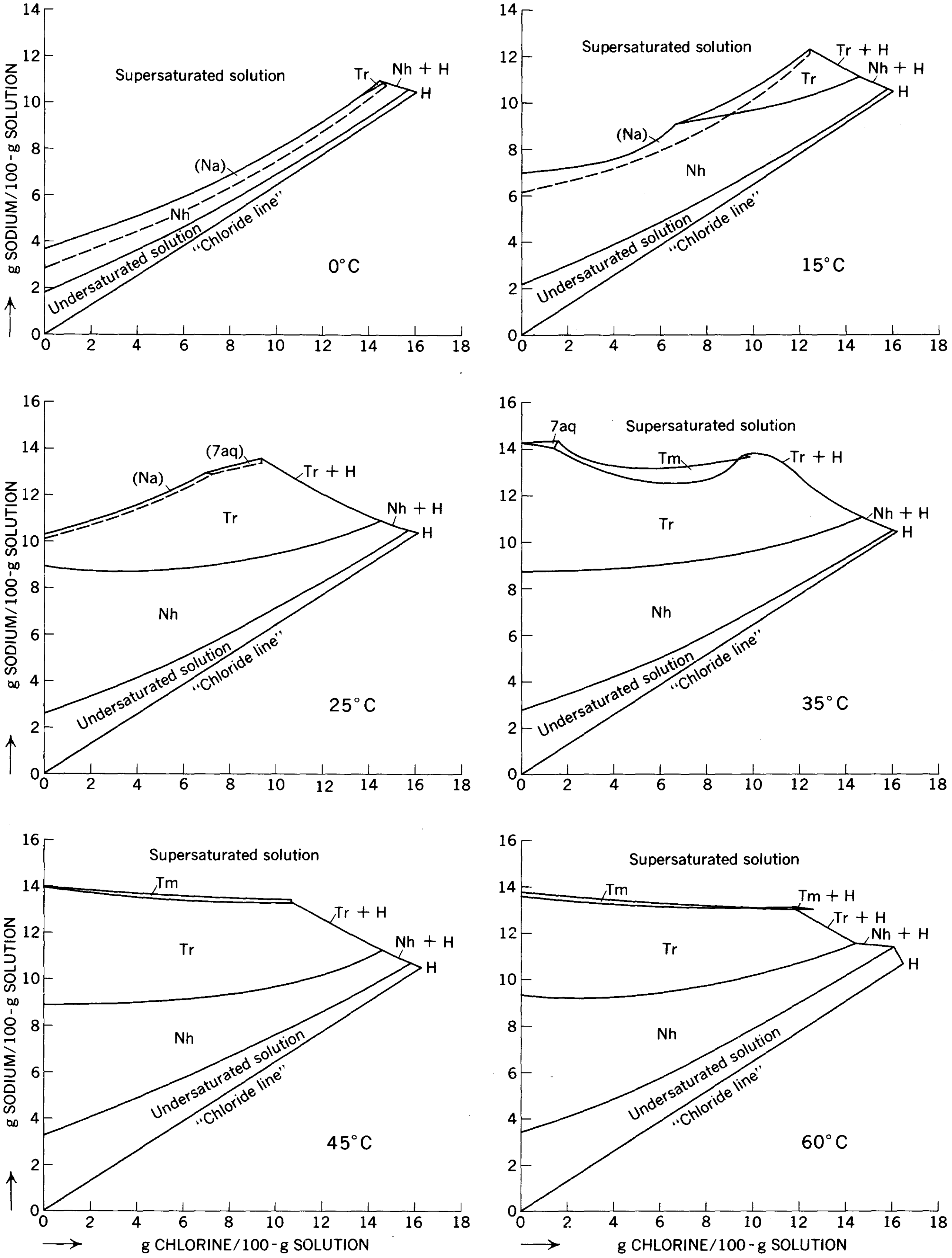

FIGURE 25.—Isothermal sections showing percent sodium versus percent chlorine (g sodium and g chlorine, each per 100 g solution) of the saturated solutions for six different temperatures, 0°, 15°, 25°, 35°, 45°, and 60°C. Tr, trona; Na, natron; Nh, nahcolite; H, halite; Tm, thermonatrite; 7 aq, $Na_2CO_3 \cdot 7H_2O$. For a more detailed discussion of a particular section, see figure 26.

CRYSTALLIZATION BY ISOTHERMAL EVAPORATION WITH OR WITHOUT GAIN OR LOSS OF CO_2

1. No change in CO_2 *content.*

Consider an undersaturated solution with a sodium and chlorine content indicated by point *A* (fig. 27), and a bicarbonate quotient of 0.15. This solution is undersaturated because its bicarbonate quotient is smaller than that of the bicarbonate-quotient contour of point *A* for the assemblage nahcolite + solution. Upon evaporation, the Na:Cl ratio remains constant, the plotted composition of the solution moves away from the origin from *A* towards *B*, and the bicarbonate quotient remains constant. At point *B*, the solution becomes saturated with respect to trona. Upon further evaporation, trona precipitates, and the composition of the solution moves away from the intersection of the 0.505 contour with the ordinate, that is, from *B* to *C*. At *C*, thermonatrite begins to precipitate, and the solution moves to *D* while both thermonatrite and trona precipitate. At *D*, halite begins to crystallize. The solution remains at *D* and crystallizes to a mixture of trona + thermonatrite + halite. The amount of each solid present can be calculated from the composition of the original solution at point *A;* the chlorine content determining the amount of sodium that will enter halite (60.66 percent chlorine + 39.34 percent sodium, as represented by the "chloride line" from the origin to the point halite + solution). The remaining sodium is distributed between trona and thermonatrite (bicarbonate quotients of 0.505 and 0, respectively) according to the bicarbonate quotient of the original solution. (For detailed calculations, see p. B54 and table 20.)

Consider now an undersaturated solution at *E*, with a bicarbonate quotient of 0.50. The changing composition of this solution, upon evaporation, moves to *F*, at which time it becomes saturated with respect to nahcolite. As nahcolite precipitates, the composition of the solution moves away from the intersection of the 1.0 bicarbonate contour (the value for nahcolite) with the ordinate, that is, it moves from *F* to *G*. At *G*, trona joins, and the solution has a bicarbonate ratio less than 0.50. As bicarbonate ratios increase along the nahcolite + trona boundary with increasing concentration, some nahcolite must redissolve as trona precipitates, while the composition of the solution moves from *G* to *H*, at which point halite begins to crystallize. The composition of the solution will remain as at *H*, if the original bicarbonate ratio was greater than 0.50. If the original bicarbonate ratio was smaller than 0.50, all nahcolite will have to be converted before the composition of the solution leaves *G* and moves to *D* with trona + thermonatrite + halite as the final product.

2. Loss of CO_2

If CO_2 is lost during evaporation, the solution at *A* is not saturated until it reaches point *B′*. At *B′*, trona crystallizes, and the solution moves to *C′*, at which thermonatrite joins. The path $B' \rightarrow C'$ is curved upwards, as the bicarbonate quotient of the solution is decreased both because of the crystallization of trona and the continued loss of CO_2. As thermonatrite and trona crystallize, the composition of the solution moves from *C′* to *D*, at which time halite begins to precipitate. The final trona to thermonatrite ratio depends on the original bicarbonate quotient of the solution and the amount of CO_2 lost during evaporation, whereas the final amount of halite, of course, is unaffected by the CO_2 loss.

3. Equilibrium with a CO_2 *reservoir*

Consider the undersaturated solution of point *A* and assume that the CO_2 reservoir has a CO_2 content corresponding to that of the solution saturated with trona at point *B* (300–400 ppm). During evaporation, as the plotted composition of the solution moves from *A* towards *B*, its CO_2 content will adjust to that of the reservoir. At *B*, trona begins to precipitate, the solution becomes enriched in chlorine, and its composition moves along a P_{CO_2} isobar (or approximately a bicarbonate-quotient contour) from *B* to *I*, where halite joins trona. The composition of the solution stays as at *I* until dryness, while CO_2 is being added from the reservoir to replenish the amount removed by trona precipitation. Again, evaporation in equilibrium with a CO_2 reservoir can lead to thick trona accumulations, without nahcolite or thermonatrite being involved. Now trona is associated with halite, however, if the solution reaches point *I*.

In the discussion so far, we have assumed a bicarbonate quotient of 0.15, derived for the chlorine-free system (p. B44). We shall now investigate the effect of chlorine on the bicarbonate quotient of saturated solutions.

Bicarbonate quotients of solution in equilibrium with nahcolite + trona have been calculated from Freeth's data (1923) and are plotted in figure 28 as a function of chloride content and temperature. Addition of sodium chloride seems to cause less than 10 percent increase in the bicarbonate quotient of the solution up to about two-thirds saturation with halite. At saturation with halite, however, the bicarbonate quotients are much higher. Although values at those high chloride concentrations are probably much less accurate, the increase seems to be real, as it exists for every temperature investigated. In other words, at very high NaCl

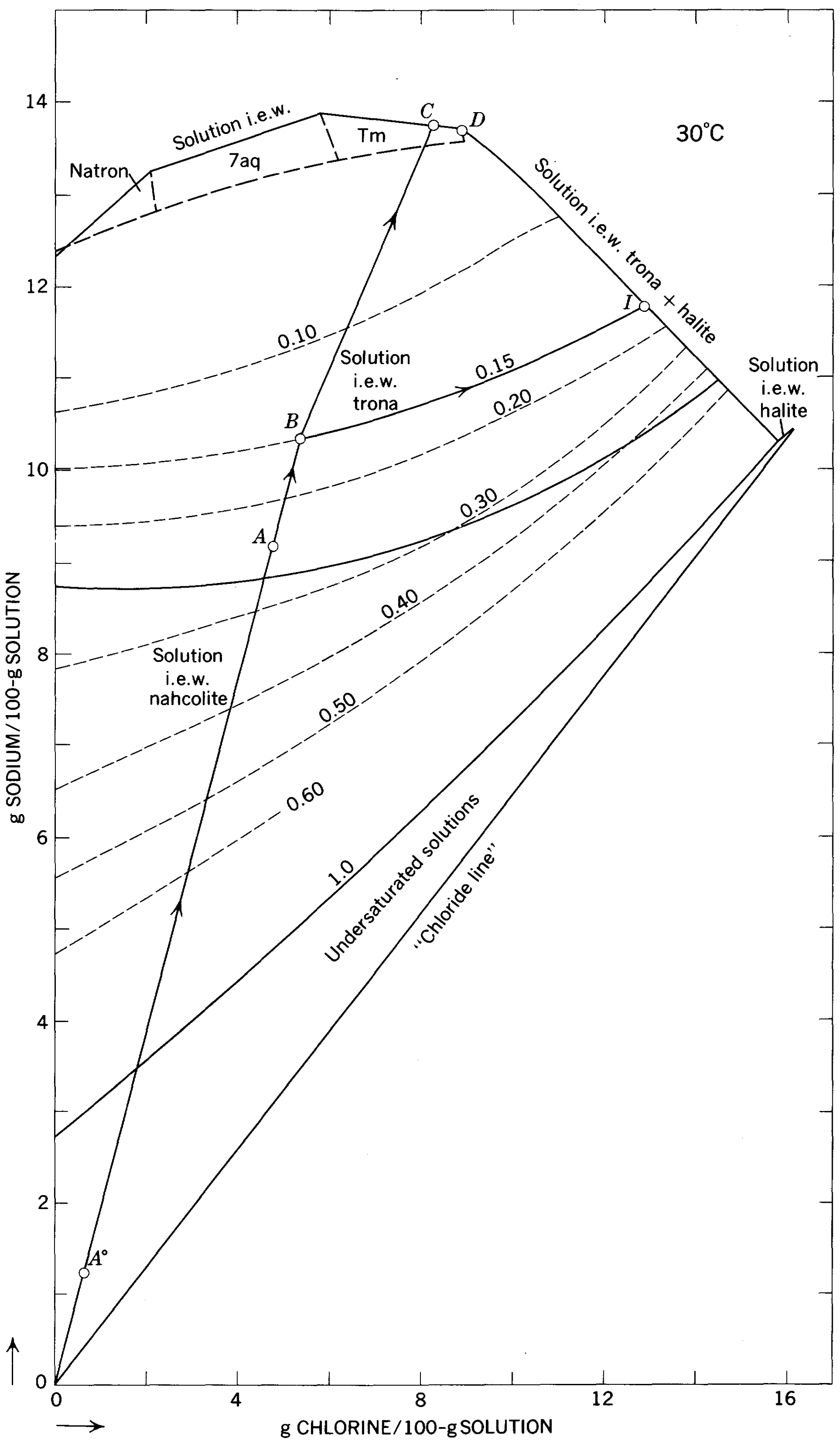

FIGURE 26.—Isothermal section for 30°C (see also fig. 25) for the saturated solutions in the system Na_2CO_3-$NaHCO_3$-$NaCl$-H_2O, constructed from the data of Freeth (1923) and Wegscheider and Mehl (1928) and presented in terms of the sodium and chlorine contents of the solutions.

contents, trona becomes stable in solutions having bicarbonate quotients as high as 0.46. This quotient is almost high enough to make trona congruently soluble.

From this increase in the bicarbonate quotient at high chloride content, one might conclude that the CO_2 content of a gas phase equilibrated with trona + nahcolite + halite + solution must be considerably higher than that equilibrated with trona + nahcolite + solution (fig. 24). This is not true.

The CO_2 content of a gas phase equilibrated with trona + nahcolite + halite + solution has been determined by Eugster (1966) and is shown in figure 29. The values found were little different from those of the chloride-free assemblage; hence, the influence of the atmosphere as a CO_2 reservoir will not be strongly affected by the addition of NaCl. P_{CO_2} contours near the trona-nahcolite boundary will therefore remain essentially parallel to that boundary, even close to saturation with halite (or cross obliquely from the trona to the nahcolite field), while bicarbonate-quotient contours at high chloride concentrations cross from the nahcolite field into the trona field at fairly steep angles. Evaporation proceeding in equilibrium with the atmosphere, of course, forces the compositions of the solutions to follow the P_{CO_2} isobars, and not bicarbonate quotient contours. This must, at high chloride concentrations, lead to considerable increases in the bicarbonate quotient before saturation in halite is reached.

From the data available it is not possible to deduce the bicarbonate quotient of a solution saturated with trona + halite and in equilibrium with present-day air. The ratio is probably still near 0.15 (the value for trona + solution in the absence of NaCl, see p. B44), and possibly as high as 0.20.

A corroboration of the high bicarbonate quotients possible for chloride-rich solutions in equilibrium with trona is shown by analysis of natural brines of Deep Springs Lake given by Jones (1965) and reproduced in table 17. The bicarbonate quotients of brines saturated with trona (alone or with other solids) range from 0.16 to 0.47. This is in excellent agreement with the experimental data. The highest value recorded for Deep Springs brines is for an assemblage trona + nahcolite + halite + burkeite + solution. Assuming a temperature near 30°C, the assemblage nahcolite + trona + halite + solution gives an experimentally determined bicarbonate quotient of 0.46 (figs. 26, 28; the presence of burkeite apparently does not alter the bicarbonate quotient significantly). On the other hand, in table 15 we have given analyses of saturated brines from Lake Magadi and Albert Lake brine pool, which have extremely low bicarbonate quotients. Small quantities of bicarbonate present analytical difficulties, and although bicarbonate is commonly reported as 0 or as a trace, some bicarbonate may nevertheless be present. But the bicarbonate quotients can be as low as 0.02, trona still remaining as the stable phase (fig. 19). Precipitation of trona probably accounts for the extreme depletion of bicarbonate from these concentrated brines.

TABLE 17.—*Compositions of brines from Deep Springs Lake, Calif.*

[Compositions from Jones (1965); temperatures and identification of solids from B. F. Jones, oral commun., 1966]

Sample No. (Jones, 1965, table 6)	Temperature (°C)	HCO_3 (ppm)	CO_3 (ppm)	$\frac{HCO_3}{HCO_3+CO_3}$ (b.q.)	Molal ratio	Solids in equilibrium with the brine
DL 1	<20	12,600	20,900	0.38	0.23	Trona + halite.
2	<20	12,400	19,500	.39	.24	Do.
2B	19	5,330	6,640	.45	.28	Undersaturated.
2C	19	3,770	5,570	.40	.25	Do.
2J	27	1,690	23,400	.07	.03	Burkeite.
2P	25	1,210	22,700	.05	.03	Do.
3A	<20	15,300	18,400	.45	.29	Trona + halite.
3B	<20	11,100	18,900	.37	.22	Do.
13	(?)	8,720	20,500	.30	.17	Trona.
21	(?)	5,320	14,700	.27	.15	Burkeite.
22	(?)	16,000	18,200	.47	.30	Trona + nahcolite + burkeite+halite.
24	(?)	8,730	17,400	.33	.20	Burkeite.
29C	(?)	8,640	15,900	.35	.21	Burkeite + halite.
39C	25	18,700	23,800	.44	.28	Undersaturated.
39D	29	12,500	63,300	.16	.09	Trona + burkeite.
51	27	9,360	22,100	.30	.17	Trona + burkeite + halite.
68	31	12,800	20,400	.39	.24	Burkeite + halite.

CRYSTALLIZATION BY ADDITION OF CO_2, NO EVAPORATION

Let us now return to figure 27. A solution whose composition is represented by *K* is undersaturated with respect to trona when its bicarbonate quotient is less than that of the contour of the saturation surface for point *K* (say 0.12). If CO_2 is added, the composition of the solution moves from *K* to *L* while the absolute amounts of sodium and chloride remain unchanged. The percent of Na and Cl decreases very slightly because of the CO_2 added to the solution (the length

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EXPLANATION FOR FIGURE 26

Bicarbonate quotients (short-dashed lines) have been contoured. The dashed field boundaries at high sodium contents refer to the ambiguities with respect to natron, 7 aq, ($Na_2CO_3 \cdot 7H_2O$) and thermonatrite. (See text and fig. 19.) The "chloride line" refers to solutions containing sodium and chlorine only. Carbonate-bicarbonate-chloride solutions lie above this line, if sodium is the only cation present. (See text also.) Point *A* represents the simplified composition of a model of Gosiute Lake brine near the salting stage. It is based on a Lake Magadi brine (see table 15). Point *A* represents the simplified composition of a much more dilute Gosiute Lake brine. This is based on the composition of a Magadi hot spring (see table 15). Points *B, C, D,* and *I* represent compositions of brines after evaporation of brine *A* along the paths $A \rightarrow B \rightarrow C \rightarrow D$ and $A \rightarrow B \rightarrow I$. i.e.w.: in equilibrium with.

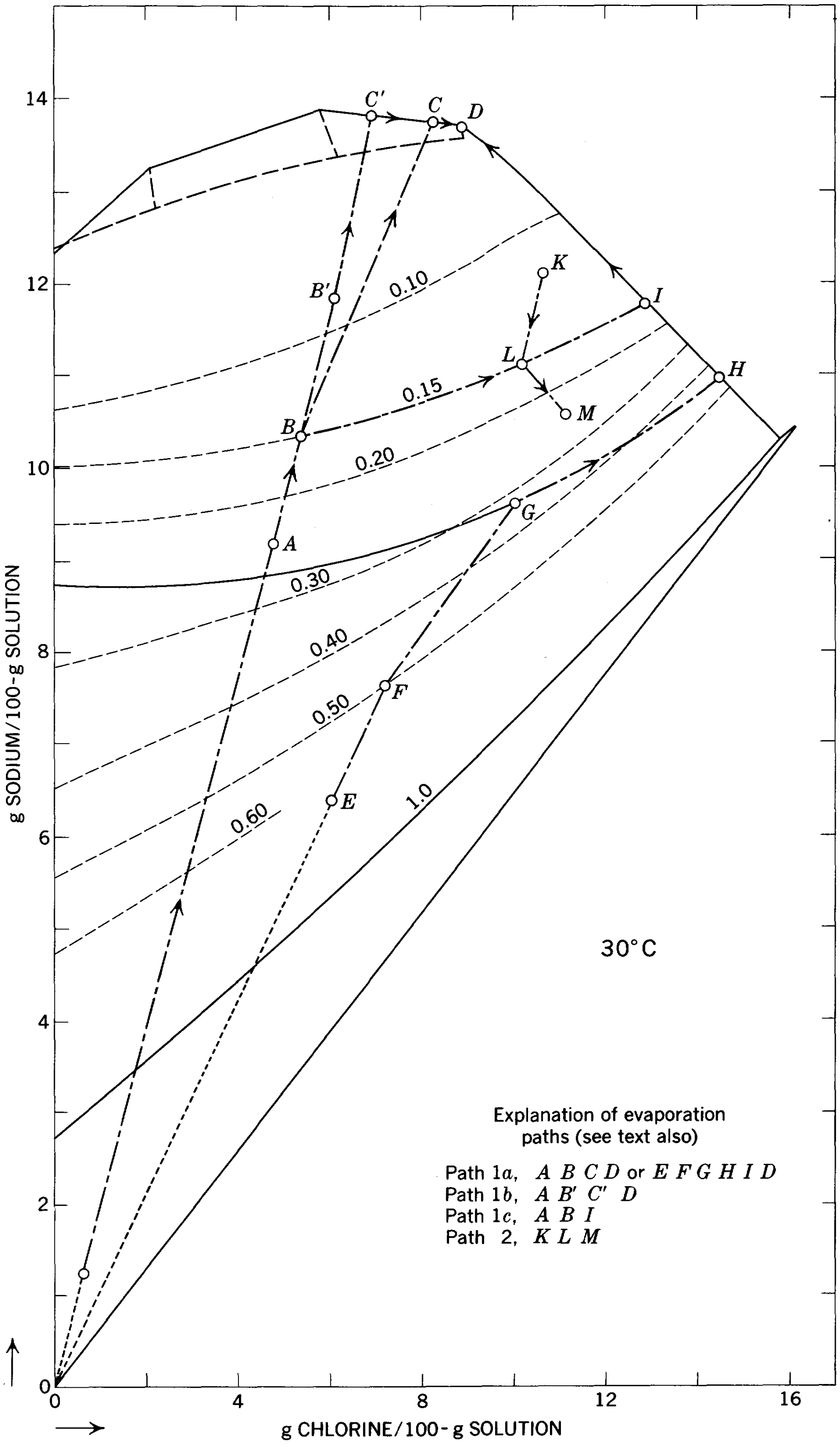

FIGURE 27.—Isothermal trona precipitation paths plotted on the 30°C isotherm of figure 26. Labels of fields and values for the bicarbonate-quotient contours have been omitted for simplicity.

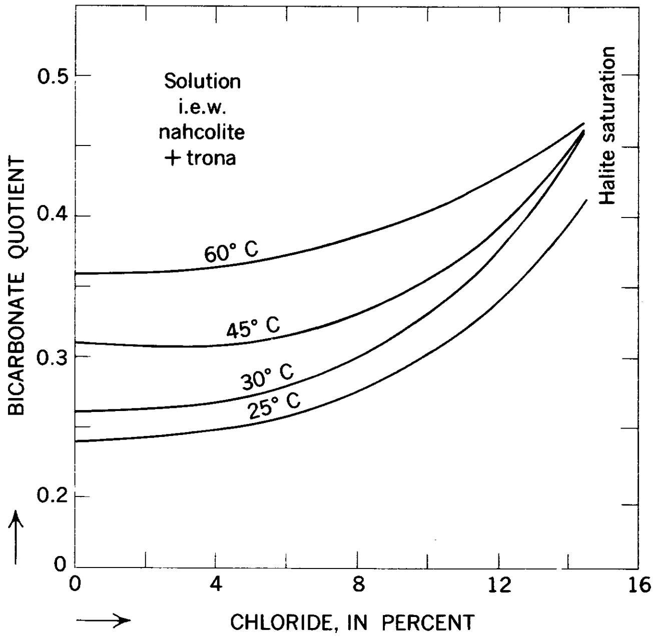

FIGURE 28.—Bicarbonate quotients of solution in equilibrium with nahcolite + trona plotted as a function of chloride content and temperature. Calculated from Freeth's (1923) data. The data for 0 percent chloride are those of figure 23. i.e.w.: in equilibrium with.

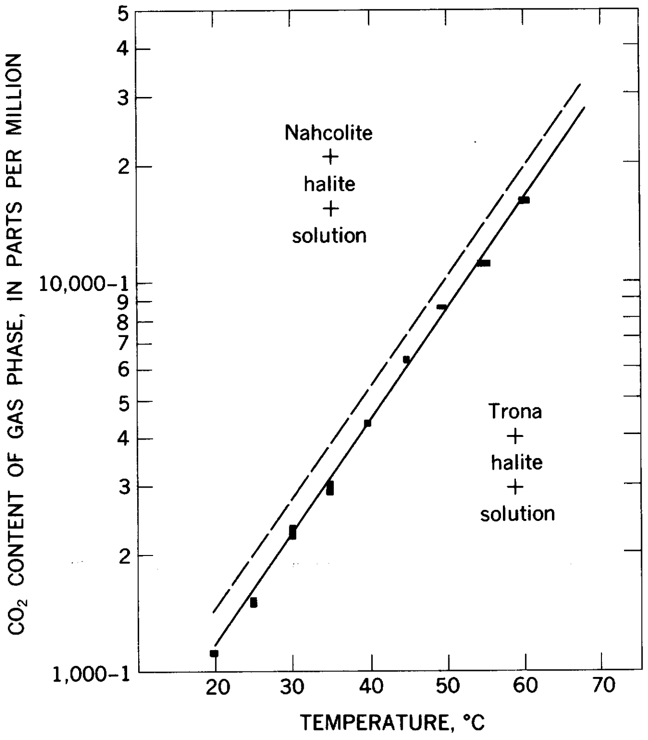

FIGURE 29.—CO_2 content of a gas phase equilibrated with trona + nahcolite + halite + solution. (From Eugster 1966, fig. 4.) The dashed curve is for a gas phase equilibrated with trona + nahcolite + solution and is taken from figure 22.

of the path $K \rightarrow L$ has been exaggerated for the sake of clarity). At *L* the solution has become saturated with trona, because it has reached the bicarbonate quotient of *L* (say 0.15). Trona precipitates upon further addition of CO_2 and the composition of the solution moves to *M*, while its Na content decreases because of the precipitation of trona, and its chloride content increases. Figure 30 shows the effect of chloride on this type of precipitation at 30°C. It was constructed from figure 26 by making sections at constant chloride contents of 5 and 10 percent. The 0 percent chloride section is identical with the 30° isotherm of figure 19. Figure 30 shows that the presence of NaCl does not significantly alter the amount of trona that can be precipitated by addition of CO_2. For instance, at a chloride content of 5 percent, a solution with a bicarbonate ratio of 0.03 contains 13.7 g Na/100-g solution, and one with a bicarbonate quotient of 0.28 contains only 8.8 g Na/100-g solution. Thus, if the bicarbonate quotient is raised to 0.28, approximately 4.9 g Na will precipitate and form 16.1 g of trona (the precise values are slightly lower, because, during the precipitation, the chloride content rose above the 5 percent value, which, at a bicarbonate ratio of 0.28, requires a slightly higher Na content of the solution).

If sufficient CO_2 is being added, the path of the changes in composition of the solution may go from *M* to the trona-nahcolite boundary in figure 27, at which time nahcolite precipitates. It is unlikely, however, that saturation in halite can ever be reached simply by an addition of CO_2, unless the original solution was already close to saturation with respect to halite. Therefore, this path again (p. B49) represents an ideal mechanism for precipitating trona from interstitial solutions or from brine bodies overlain by fresher water. Figure 27

EXPLANATION FOR FIGURE 27

Paths 1 and 2 represent the following conditions:
1*a*. Isothermal evaporation at constant CO_2.
1*b*. Isothermal evaporation coupled with some loss of CO_2.
1*c*. Isothermal evaporation in equilibrium with a CO_2 reservoir, fixing the bicarbonate quotient of the solution at a value of 0.15 (p. B44).
2. No loss of H_2O, but addition of CO_2.

For a detailed discussion of the individual paths, see text. *A* is the starting brine for path 1 and has been chosen so as to approximate Gosiute Lake waters (see fig. 26 and text).

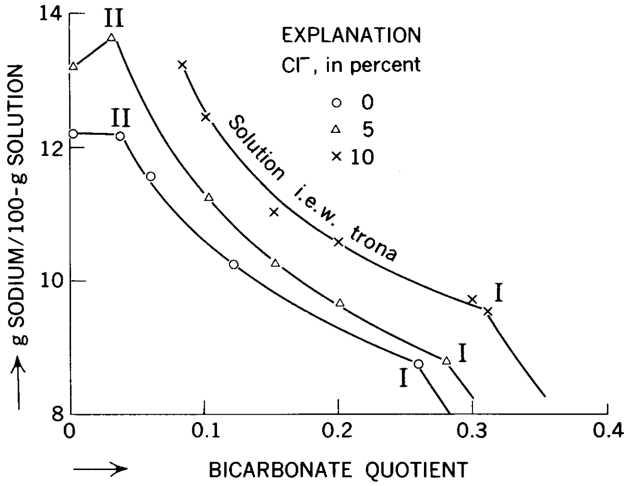

FIGURE 30.—Sodium content of saturated solutions at 30°C plotted against bicarbonate quotients. The chloride contents are contoured at 0, 5, and 10 percent. The 0 percent chloride contour is that of figure 19. Points I and II have the same meaning as in figure 21. i.e.w.: in equilibrium with.

shows that trona alone will precipitate from brines of complex composition, even those rich in chlorine.

Change in temperature

In the chloride-free system, temperature within specific limits has little effect on the solubility of trona (fig. 19), and a decrease in temperature causes the precipitation of only a small amount of trona. A close examination of figure 25 reveals that this is also true in the presence of NaCl.

Calculation of deposition paths

Figures 26 and 27 provide all the information necessary to evaluate quantitatively the deposition of trona from NaCl-bearing brines at 30°C. As an example, we present the calculations for the path that represents the most likely fate of the Gosiute Lake waters during the formation of the bedded trona.

The composition of a brine with a given bicarbonate quotient (b.q.) can be calculated for any point of figure 26 in the following manner: g Na/100-g solution, g Cl/100-g solution, and b.q. are given. We assign corresponding amounts of Na to the three anions Cl, HCO_3, and CO_3, where

g Na :g Na in solution
g Na′ :g Na assigned to NaCl
g Na″ :g Na assigned to $NaHCO_3$
g Na‴:g Na assigned to Na_2CO_3

$$\text{g Na}' = \text{g Cl} \times 0.649$$

$$\text{g Na}'' + \text{g Na}''' = \text{g Na} - \text{g Na}'$$

$$\text{g HCO}_3 \times 0.377 + \text{g CO}_3 \times 0.768 = \text{g Na}'' + \text{g Na}'''$$

$$\text{g CO}_3 = \left(\frac{1-\text{b.q.}}{\text{b.q.}}\right) \text{g HCO}_3$$

$$\text{g HCO}_3 = \frac{\text{g Na}'' + \text{g Na}'''}{0.377 + 0.768 \left(\frac{1-\text{b.q.}}{\text{b.q.}}\right)}$$

$$\text{g H}_2\text{O} = 100\ \text{g} - (\text{g Na} + \text{g Cl} + \text{g HCO}_3 + \text{g CO}_3).$$

From these relations the composition of the solution can be calculated for every point of figure 26, whether the brine is saturated or not, provided the bicarbonate quotient is known.

A model of the simplified composition of Lake Gosiute brine near the salting stage is given in table 15. It is based on the Na, Cl, HCO_3^{-1}, and CO_3^{-2} contents of a Lake Magadi brine, collected at the surface. We have plotted this brine as point *A* in figures 26 and 27 and have given its composition, in terms of g/100 g brine, in table 18. This brine has a bicarbonate quotient of 0.14 and is slightly undersaturated with respect to trona, as the saturated brine would have a bicarbonate quotient of about 0.24 (fig. 26).

A more dilute model of simplified Lake Gosiute brine can be arrived at as follows: The Lake Magadi brine used to obtain point *A* derives its constituents primarily through evaporation of water from a series of hot springs. A hot-spring analysis from Magadi is given in table 15. It is very similar in composition to the brine, except that it is, of course, much more dilute and has a much higher bicarbonate quotient. We have used its Na content and the Na:Cl ratio of point *A*, to locate *A*° (fig. 26), the dilute model of Lake Gosiute. The composition of point *A*° is also given in table 18.

TABLE 18.—*Compositions in weight percent, of solutions at points A°, A, B, I, and C in figure 26.*

[Solutions *A*° and *A* are undersaturated, those at *B*, *I*, and *C* are saturated with respect to trona, trona + halite, and trona + thermonatrite, respectively. A bicarbonate quotient of 0.15 was asssumed for solutions at *B* and *I* and of 0.0 for solution at *C*. The location of point *A* is based on the sodium and chlorine content and the bicarbonate quotient of the surface brine of Lake Magadi (table 15). Point *A*° corresponds to the more dilute model of Lake Gosiute. It is based on the sodium content of the Magadi hot spring (table 15) and the Na:Cl ratio of point *A*]

	.A°	*A*	*B*	*I*	*C*
Na	1. 26	9. 16	10. 30	11. 70	13. 71
CO_3	1. 01	7. 30	8. 17	4. 93	10. 73
HCO_3	. 16	1. 16	1. 44	. 87	--------
Cl	. 66	4. 80	5. 40	13. 09	8. 43
H_2O	96. 91	77. 58	74. 69	69. 41	67. 13
b.q	. 14	. 14	. 15	. 15	0

We now consider quantitatively the fate of 100 g of hypothetical Gosiute Lake water, using the dilute model represented by point *A*° (fig. 26, table 18). Evaporation leads from point *A*° through point *A* to point *B*, all three points lying on a line through the origin, indicating a constant Na:Cl ratio. We assume saturation to occur at a bicarbonate quotient of 0.15. This is based on equilibration with the atmosphere (p. B44). Hence, point *B* lies on the intersection of the line *A*°–*A* with the bicarbonate contour of 0.15 (fig. 26). The Na and Cl contents of *B* are read from figure 26, and the CO_3^{-2}, HCO_3^{-1}, and H_2O contents are then calculated from the equations on page B54. The composition of point *B* is given in table 18.

Once the brine has arrived at point *B*, a number of paths are possible, depending upon whether CO_2 is added during evaporation or not. We consider two extremes: (1) evaporation in equilibrium with the atmosphere (path *B*→*I*) at constant bicarbonate quotient (summarized in table 19) and (2) evaporation without replenishment of CO_2 (summarized in table 20).

Point *I* is located at the intersection of the 0.15-bicarbonate-quotient contour with the trona+halite boundary (fig. 26). Its composition is given in table 18

In table 19 (equilibrium with atmosphere) we start with 100 g of hypothetical Lake Gosiute brine of composition *A*°. During evaporation, the composition of the brine changes along the line from *A*° to *B*, no precipitation occurs, and the Na and Cl contents remain unchanged. Much water must evaportate and CO_2 may be exchanged with the atmosphere to adjust to a bicarbonate quotient of 0.15. The proportions of the values in column 2, table 19, must conform to the composition of *B* given in table 18, the conversion factor being based on Na or Cl. Thus, we find that at *B*, the salting stage, only 12.24 g of the original 100 g sample are left—that is, the model lake-water sample has shrunk to less than one-eighth of its original mass. To establish a bicarbonate quotient of 0.15, 0.01 g CO_2 was added from the atmosphere. So far, there is no difference between the values in tables 19 and 20.

TABLE 19.—*The fate of 100 grams of hypothetical Gosiute Lake brine (dilute model) of composition A° (Magadi hot spring, see tables 15 and 18) evaporated in equilibrium with the atmosphere, at a constant bicarbonate quotient of 0.15 (path* A°→B→I)

[All values in grams]

	1	2	3	4	5	6
Point Phase	*A*° Solution	*B* Solution	I^{initial} Solution	I^{initial} Trona	I^{final} Trona	I^{final} Halite
g Na	1.26	1.26	0.59	0.67	0.16	0.43
g CO_3	1.01	1.00	.25	.58	.15	--------
g HCO_3	1.16	.18	.04	.59	.14	--------
g Cl	.66	.66	.66	--------	--------	.66
g H_2O	95.91	9.14	3.50	.35	.08	--------
Σ	100.0	12.24	5.04	2.19	.53	1.09
H_2O evaporated	--------	87.77	5.21		3.42	
CO_2 added	--------	.01	.20		--------	
H_2O used in CO_3^{-2} conversion	--------	--------	.08		--------	

	Grams
Total trona	2.72
Total halite	1.09
Trona before halite saturation	2.19 (80.5 percent)
Total H_2O evaporated	96.40
H_2O in trona	.43
CO_2 added	.21

TABLE 20.—*The fate of 100 grams of hypothetical Gosiute Lake brine of composition* A° *evaporated without addition of* CO_2 *from an external source (path* A°→B→C)

[All values in grams]

	1	2	3	4	5	6
Point Phase	*A*° Solution	*B* Solution	C^{initial} Solution	C^{initial} Trona	C^{final} Thermonatrite	C^{final} Halite
g Na	1.26	1.26	1.06	0.20	0.63	0.43
g CO_3	1.01	1.00	.82	.18	.82	--------
g HCO_3	1.16	.18	--------	.18	--------	--------
g Cl	.66	.66	.66	--------	--------	.66
g H_2O	95.91	9.14	5.19	.11	.24	--------
Σ	100.00	12.24	7.73	.67	1.69	1.09
H_2O evaporated	--------	87.77	3.84		4.95	
CO_2 added	--------	.01	--------		--------	

	Grams
Total trona	0.67
Total thermonatrite	1.69
Total halite	1.09
H_2O evaporated	96.56
	100.01
CO_2 added	−.01
	100.00

If evaporation continues, in equilibrium with the atmosphere, trona will precipitate and the brine composition moves to *I*. In column 3, table 19, we have calculated the composition of the remaining brine. The proportions of the constituents are those of column *I*, table 18. As no halite precipitates, we enter the value of Cl of column 2 in column 3 and adjust the other constituents accordingly. This indicates a loss of 0.67 g Na, obviously the amount contained in trona precipitated from *B*→*I*. Using the trona formula, we calculate all other constituents and enter them in column 4, table 19. During passage from *B*→*I* 5.21 g water evaporated and 2.19 g trona precipitated. Comparing column 4 with column 2, we notice that much more HCO_3^{-1} was incorporated into trona than was originally available. This must have been accomplished through CO_2 addition from the atmosphere. CO_3^{-2} can be converted to HCO_3^{-1} according to the reaction

$$CO_3^{-2}+H_2O+CO_2\rightleftharpoons 2HCO_3^{-1}$$

or HCO_3^{-1} can be formed directly through

$$CO_2+H_2O\rightleftharpoons H^{+1}+HCO_3^{-1}.$$

As 0.17 g CO_3^{-2} (1.00−0.25−0. 58) are available, they can be combined with 0.05 g H_2O and 0.12 g CO_2 to obtain .304 g HCO_3^{-1}. This leaves an HCO_3^{-1}

shortage of 0.11 g (0.59+0.04−0.18−0.34), indicating the takeup of an additional 0.08 g CO_2 from the atmosphere, and 0.03 g H_2O from the brine. Thus, a total of 0.20 g CO_2 is taken up from the atmosphere, and 0.08 g H_2O was consumed in the conversions to bicarbonate ions. The sum of the constituents in columns 3+4 plus the loss of H_2O minus the gain of CO_2 must add up to the constituents in column 2.

During further evaporation, halite coprecipitates with trona, while the composition of the saturated solution stays the same as at *I* (table 18) .This path, if evaporation continues to dryness, is described by the passage from I^{initial} to I^{final}. During this passage, all Cl is incorporated into halite (table 19, col. 6), and the remaining amount of Na determines the additional amount of trona being precipitated (table 19, col. 5). Again, more bicarbonate is consumed than is available, indicating conversion of CO_3^{-2} to HCO_3^{-1} by CO_2 uptake. In the end, however, an excess of CO_3^{-2} is available, and the net exchange of CO_2 with the atmosphere is cancelled out. From the fact that the values in columns 5+6 must equal the sum of the constituents in column 3, we find that an additional 3.42 g water have evaporated.

In summary, when left to desiccate completely at a bicarbonate quotient of 0.15, the 100 g of hypothetical Gosiute Lake water of point *A*° composition have yielded 2.72 g trona, 80 percent of which appears before halite saturation, and 1.09 g halite. Of the water lost, 96.40 g have evaporated, and 0.43 g are trapped in the trona. The atmosphere had supplied 0.21 g CO_2.

The fact that four-fifths of the potential trona can be precipitated before saturation with halite occurs, seems quite adequate to account for the monomineralic beds of trona in the Wyoming Green River Formation. If influx of fresher water occurred before the brine reached point *I*, no halite was deposited; or, if some had been deposited, it would probably have been dissolved.

There is another reason why saturation with respect to halite does not occur readily. In our model we have assumed perfect equilibration with the atmosphere. It is obvious that only the top few inches of the brine body have a chance to achieve this. Kinetic problems of CO_2 uptake and migration, as well as the formation of surface crusts of trona, will prevent equilibration of the deeper brines with the atmosphere. As such brines often occupy as much as half of the volume of trona-brine bodies, their fate with respect to the final bed of solid trona is rather important.

To illustrate another extreme possibility, we have calculated the fate of 100 g of hypothetical Gosiute Lake brine of composition *A*°, assuming that no CO_2 is added. This corresponds to the path $A°\rightarrow A\rightarrow B\rightarrow C\rightarrow D$. The results are given in table 20. To obtain the values of column 4, we simply incorporate all the HCO_3^{-1} available into trona (0.67 g). The remaining constituents are placed in the solution (col. 3). To obtain the water content of the solution, we must locate point *C*. Its location is defined by the two parameters: Na/Cl=1.61 and bicarbonate quotient=0. Actually, it is placed on the trona + thermonatrite boundary, which has a finite, if very small bicarbonate quotient (0.03). The composition of *C* is also given in table 18. Upon further evaporation, the solution composition actually moves from *C* to *D*. As no HCO_3^{-1} is available, we have omitted that short stretch and simply calculated the total amount of halite precipitated (col. 6). The remaining Na and CO_3^{-2} are incorporated into thermonatrite, $Na_2CO_3 \cdot H_2O$.

In summary, the 100 g of hypothetical Gosiute Lake brine have yielded 2.36 g sodium carbonate salts, only one-third of which is trona. Again, 1.09 g halite form and 96.56 g water evaporate. The mineralogic observations indicate that neither Gosiute Lake nor Lake Magadi follows this path to the end. This is one extreme model, however, just as table 19 represents the other extreme possibility.

The actual path taken in a specific instance, lying between those two extremes, depends upon the relative rates at which water is lost and at which CO_2 is supplied. Near the surface, CO_2 is probably supplied fast enough to retain a bicarbonate quotient of 0.10 to 0.15 (path $B\rightarrow I$). A few feet down, however, H_2O is probably lost faster through diffusion than CO_2 is added. The composition of the brine will move from *B* towards *C*, remaining saturated with trona, and reach an intermediate point, whose location is dictated by its concentration and bicarbonate quotient. Further loss of H_2O or addition of CO_2 leads to precipitation of trona and to a movement of the composition of the brine towards a position intermediate between *I* and *C*. A stable equilibrium will be reached very soon for brine-trona assemblages in all layers, except those near the surface. The greater the depth, the less likely it is that halite saturation will ever occur. In fact, some tens of feet below the surface, H_2O loss is very small, and trona precipitation is probably entirely dependent on CO_2 addition. Decay of organic matter is the most likely source of the CO_2 necessary to transform a trona + solution assemblage into a solid trona bed. In the process, a considerable amount of NaCl-bearing brine must have been squeezed out.

We clearly do not yet fully understand the mechanisms of trona precipitation in a natural setting. Studies now under way at Lake Magadi hopefully will clarify some of these points. In the meantime, the only data available are those of Baker (1958) on Lake Magadi. In table 21 we give bicarbonate quotients calculated from Baker's data for brines near the surface (I–III) and for brines at depth from drill cores A–D. Brines at the surface are reasonably equilibrated with the surface, whereas most of the deep brines are greatly impoverished in HCO_3^{-1}. Deposition of trona from deep brines depends entirely on an addition of CO_2 from outside the system. This is analogous to the deposition of trona from brines in the interstices of muds.

TABLE 21.—*Bicarbonate quotients calculated from Baker's (1958) data on brines of Lake Magadi, Kenya*

	Bicarbonate quotient		*Bicarbonate quotient*
I	0.10	B170	0.086
II	.12	C20	.008
III	.06	52	.008
A41	.04	62	.015
65	.21	75	.016
120	.15	121	.016
B20	.008	D21	.009
50	.013	87	.020
72	.081	91	.028
112	.012	104	.040
125	.008	128	.024

I. Brine at surface of lake.
II. Brine 4 ft below surface.
III. Brine 8 ft below surface.
A–D. Brines from boreholes A–D; figure is depth in feet.

In figure 31 we have plotted the Lake Magadi brine data given by Baker (1958) and by Jones, Rettig, and Eugster (1967). Points *A*, *B*, *C*, and *D* are those of figure 26. Most of the data points are from deep brines of the boreholes. The data seem to indicate that the original Na:Cl ratios of these brines were higher. This agrees with the opinion of Stevens (see Baker, 1958), that the chlorine content of Lake Magadi is increasing rather rapidly, perhaps through recirculation. The path for these chlorine-poorer brines might be $B' \rightarrow C'$. The brines of boreholes A and C seem to follow the path calculated in table 20 (no CO_2 addition), whereas those of boreholes D and B (in part) are moved towards the line *I–C*, probably because of CO_2 addition.

Our model of trona precipitation seems to work reasonably well, though many details remain to be clarified in specific instances.

Desposition from interstitial brines

A substantial amount of trona present in the Green River does not occur in trona beds but as disseminated crystals in the carbonate mud (Fahey, 1962, pl. 2). This trona must have precipitated from brines interstitial in mud after burial, as the trona, much like the shortite described on page B11, cuts the lamination of the oil shale. The brine was probably incorporated near saturation and at a bicarbonate quotient of 0.15, say with a composition of point *B*. Upon burial, P_{CO_2} rose, mainly through biologic activity, and the brine became supersaturated with respect to trona by the mechanism discussed on page B49, B53–B54. Quantitative calculations are not possible, because we are probably dealing with a partially open system. The precipitation of trona in a place of high P_{CO_2} leads to a decrease of the sodium concentration and sodium activity in the immediate environment. Thus, an activity gradient is established, both with respect to CO_2 and Na, which causes sodium diffusion from the neighboring areas. This diffusion continues as long as the CO_2 production is sufficient to maintain the P_{CO_2} gradient. Significantly, saturation with respect to halite cannot be reached in this way, as the chlorine concentration is not raised by the trona precipitation. This fact explains why halite does not occur in the carbonate muds. (See also p. B65.)

The eventual fate of the residual interstitial brine remains open to speculation. Probably only a small amount of the originally occluded sodium is finally contained in the disseminated trona. Some probably reacts with the carbonate mud to form pirssonite and eventually shortite (see p. B60; fig. 32); the remainder, together with most of the chlorine as well as the other constituents, must have been either converted into authigenic minerals or squeezed out during compaction. Some filtration through osmotic membranes is possible, but not demonstrated. Carbonate muds are usually considered to be poor membranes and would not retain much salt, unless the presence of organic matter drastically alters their properties. (See also p. B65.) Hence, the disseminated saline and other authigenic minerals in the Green River Formation are believed to have precipitated either through addition of CO_2 (trona) or through chemical reaction of the brines with the carbonate and tuffaceous muds (shortite, analcite, northupite, loughlinite, and others).

If complete dessication of a brine starting at point *A* takes place, the final salt mixture would consist of two-thirds trona and one-third halite. Culbertson (1966) gives details on the distribution of halite in the Wilkins Peak Member. He states (p. 162) that "At most places halite constitutes only a few percent of the bed, but locally it exceeds 80 percent." Halite is concentrated in the lower parts of the deposit (holes 3–5 of Culbertson, 1966) and has possibly been accumulated there through re-solution of halite precipitated nearer the margins. Thus, the beginning of a zonation exists similar to that described by Hunt (1966), Jones (1965), Hardie (1965), and G. I. Smith (1962).

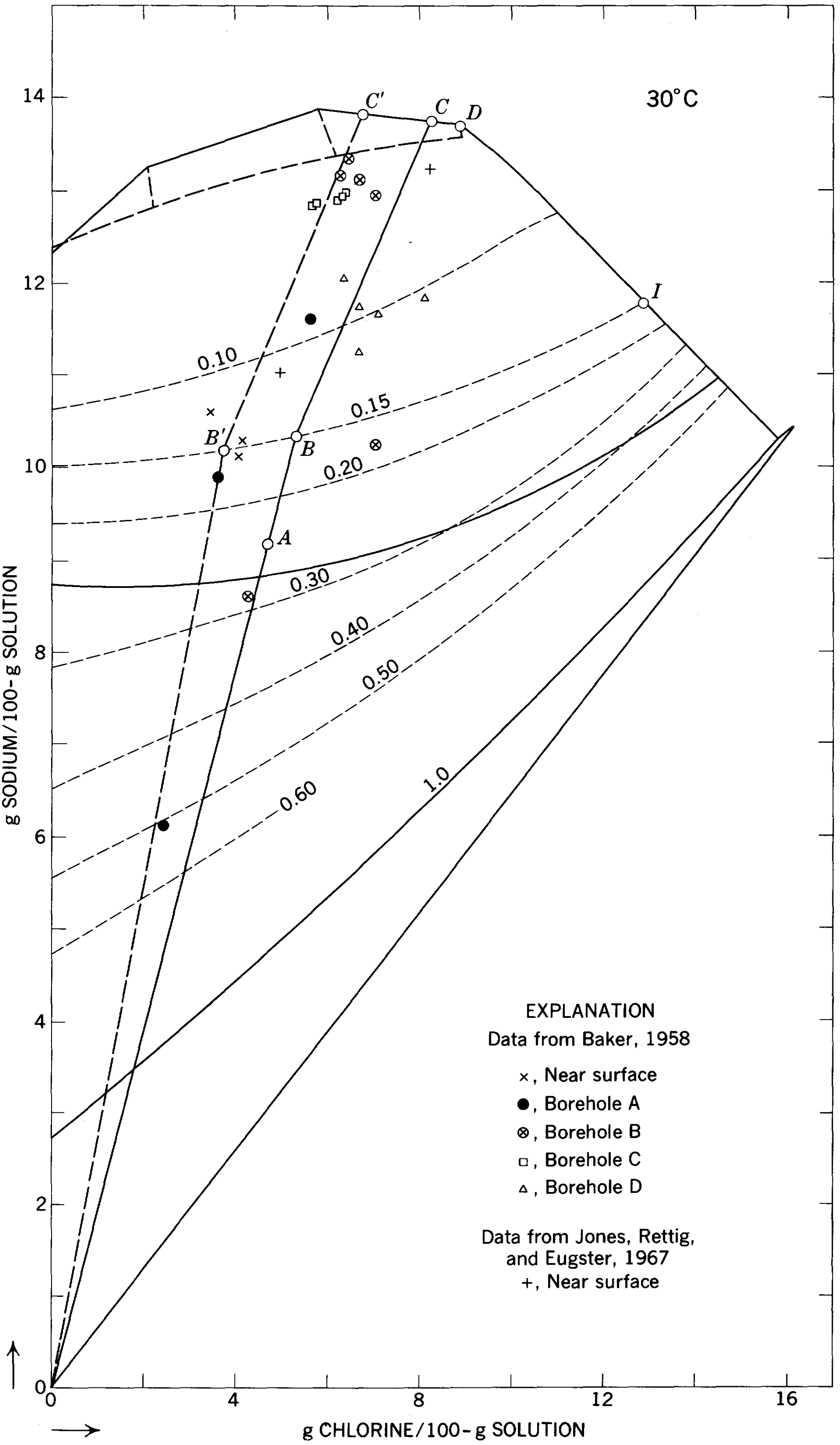

FIGURE 31.—Data from Baker (1958) and Jones, Rettig, and Eugster (1967) on brines of Lake Magadi, Kenya, plotted on the graph of figure 26. Path *B*→*C* is the same as path *B*→*C* of figure 26. Path *B′*→*C′* is based on the assumption that the model brine is poorer in chloride than the present brines of Lake Magadi.

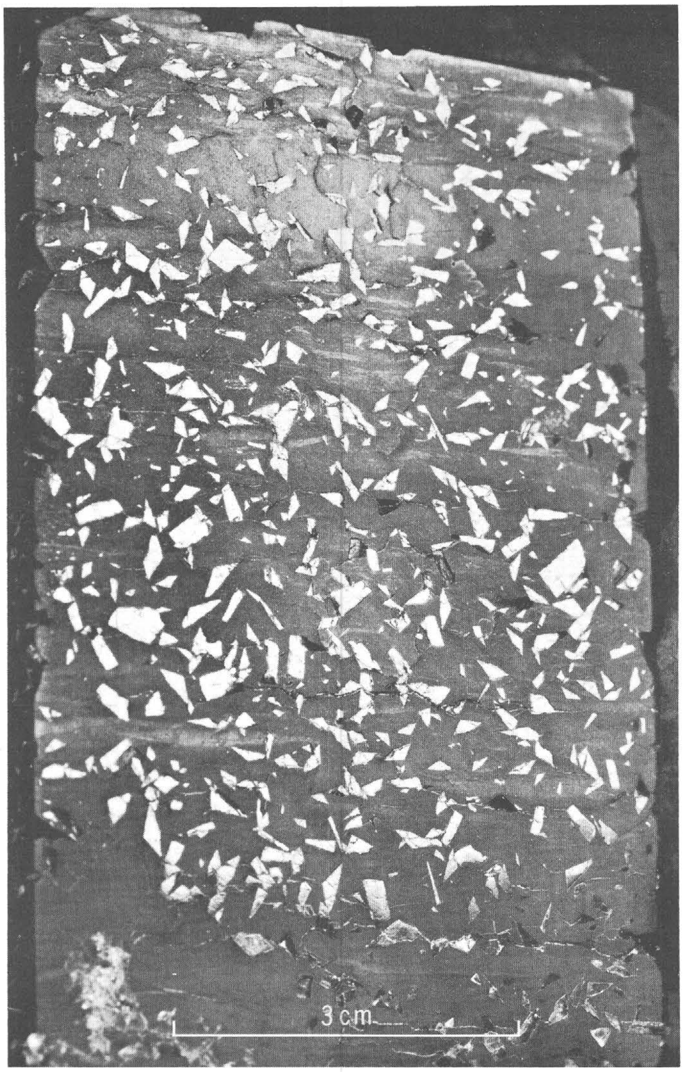

FIGURE 32.—Polished surface of a core billet from the John Hay, Jr., well 1 (sec. 2, T. 18 N., R. 110 W.) showing shortite crystals rather uniformly dispersed through an essentially homogeneous low-grade oil shale.

GEOCHEMISTRY OF AUTHIGENIC MINERALS

AUTHIGENIC MINERALS

SHORTITE

To learn more about the conditions under which shortite might have formed, its theraml stability was investigated experimentally.

Shortite was synthesized by standard hydrothermal techniques in sealed gold tubes from mixtures of trona + calcite and Na_2CO_3 + calcite and from pirssonite at temperatures between 125° and 300°C and a water pressure of 2,000 bars. Table 22 contains details of the experiments. An excess of water was present in all experiments. Reactions are extremely sluggish, and equilibrium is not established in less than 1 month.

TABLE 22.—*Results of hydrothermal experiments at 2,000 bars, resulting in the synthesis of shortite*

Run No.	Starting material	Temperature (°C)	Time (hours)	Products
226	Sh 1	75	2,800	Trona + calcite.
131	1	120	330	Do.
216	1	125	2,800	Shortite + calcite.
220	1	150	2,800	Do.
222	1	175	2,800	Shortite + calcite + trona (trace).
45	1	190	472	Shortite + calcite + nahcolite (trace).
12	1	200	476	Shortite.
10	1	304	476	Do.
24	1	428	120	Calcite + thermonatrite + nahcolite (trace).
17	1	500	40	Calcite + nahcolite + ??.
154	2	200	680	Shortite + calcite.
160	2	300	680	Shortite + calcite (trace).
360	3	50	440	Pirssonite + calcite.
348	3	75	960	Do.
225	3	75	2,800	Do.
161	3	100	680	Do.
217	3	125	2,800	Shortite + calcite.
219	3	150	2,800	Shortite.
223	3	175	2,800	Do.
153	3	200	680	Do.
350	Nat. Sh	75	960	Pirssonite + shortite + nahcolite.
218	do	125	2,800	Shortite + calcite.
221	do	150	2,800	Do.
224	do	175	2,800	Do.
349	Nat. P	75	960	Pirssonite.
132	do	120	330	Pirssonite + calcite.
134	do	250	330	Shortite + nahcolite.
130	Nat. G	120	315	Calcite + thermonatrite.
135	do	250	315	Shortite + calcite.

Code for starting materials:
Sh 1, trona + calcite, bulk composition = shortite.
Sh 2, Na_2CO_3 [anh.] + calcite, bulk composition = shortite.
Sh 3, Na_2CO_3 [anh.] + calcite, bulk composition = $Na_2CO_3 \cdot CaCO_3$.
Nat. Sh, natural shortite.
Nat. P, natural pirssonite.
Nat. G, natural gaylussite.

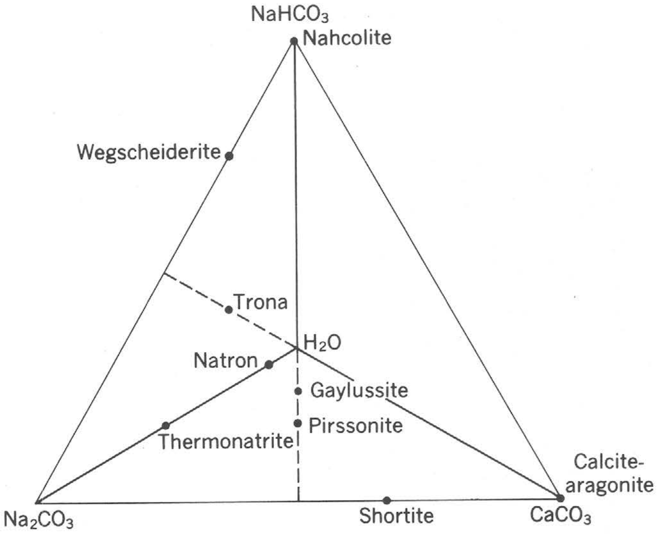

FIGURE 33.—Compositions of the solid phases in the system $NaHCO_3$–Na_2CO_3–$CaCO_3$–H_2O. From Eugster and Smith (1965, fig. 2).

Figure 33 is a plot of the system $NaHCO_3$–Na_2CO_3–$CaCO_3$–H_2O and shows the compositions of the phases encountered. Of particular interest is the dehydration reaction:

$$\underset{\text{pirssonite}}{Na_2CO_3{\cdot}CaCO_3{\cdot}2H_2O} + \underset{\text{calcite}}{CaCO_3} = \underset{\text{shortite}}{Na_2CO_3{\cdot}2CaCO_3} + 2H_2O.$$

The position of this equilibrium is, of course, a function of temperature, pressure, and the activity of H_2O, a_{H_2O}. Shortite forms from pirssonite + calcite by an increase in temperature, a decrease in a_{H_2O}, or a decrease of pressure, or any combination of these parameters. At a water pressure of 2,000 bars, the equilibrium temperature is above 75°C (run 350) and below 125°C (run 217), or at 100° ±25°C. The pressure dependency of the transition temperature must be small, because only condensed phases are involved and the volume changes are small. Addition of NaCl, however, has a marked effect on the activity of H_2O and therefore on the pirssonite-shortite transition temperature. For the mirabilite-thenardite transition, for instance, D'Ans (1933) found that the equilibrium temperature changed from 32°C (no NaCl in brine) to 16°C (saturated in NaCl). By extrapolation to the carbonate-chloride brines of the Green River Formation, the temperature would have had to be about 90° ±25°C for shortite to precipitate directly, the exact temperature depending primarily on the NaCl content of the brines involved. Assuming an average geothermal gradient, 90°C would be equivalent to about 5,000 feet in depth. This would then be the minimum cover necessary for shortite to form in the presence of solutions. In the absence of solutions, shortite could form from pirssonite at the much lower values of a_{H_2O} provided by vapor phase only and at lower temperatures (see, for instance, Eugster and Smith, 1965). It is very unlikely, however, that no solutions were present while shortite grew, because of the textural observations mentioned above.

If these deductions are correct, shortite formed as soon as the temperature of the oil shale reached about 90°C. If the sodium-rich brines were introduced at that time, shortite formed directly by reaction of the brine with dolomite and calcite. It is more likely, however, that interstitial brines were always present. In this case pirssonite would already have been present, as it forms readily in such an environment. It has been found extensively in the carbonaceous muds of Searles Lake, Calif., and was present at the bottom of the deepest hole at 875 feet (Smith and Pratt, 1957; Eugster and Smith, 1965).

In the Green River Formation, upon reaching a depth of burial of roughly 5,000 feet, pirssonite would have reacted with $CaCO_3$ to form shortite. Individual shortite crystals, of course, would not have to replace pirssonite crystals in a pseudomorphic sense but would grow wherever local conditions were most favorable.

NORTHUPITE

Northupite, $Na_2CO_3{\cdot}MgCO_3{\cdot}NaCl$, occurs abundantly in the Wilkins Peak Member (p. B9). Fahey (1962) has discussed the mode of occurrence in the John Hay, Jr., well 1 and has noted several interesting textural relationships. In the saline zone of the well, which is 555 feet thick, northupite constitutes about 2.2 weight percent of the oil shale and marlstone. Northupite is also common at Searles Lake (Eugster and Smith, 1965).

The chemical reactions by which northupite may form have been discussed in detail by Eugster and Smith (1965); their figure 14, in which the stability of northupite is expressed in a schematic isothermal-isobaric a_{H_2O}–a_{CO_2} diagram, is shown here as figure 34. Northupite appears in all fields of the lower left-hand (shaded) part of the diagram through reaction of dolomite and halite with sodium carbonates. In general, northupite is formed as a result of a decrease in either a_{H_2O} or a_{CO_2}, or both, except when gaylussite is involved. It seems to form readily near room temperature, whenever the compositional requirements are met. Figure 34 is drawn for excess halite, but northupite can, of course, form equally well in the absence of halite, if the necessary NaCl is supplied by the brine. Halite is frequently absent from northupite assemblages even at Searles Lake.

Unfortunately, few data on the stability of northupite are available. The mineral was synthesized by Schulten (1896); Wilson and Ch'iu (1934) obtained it at 50°C and $P_{CO_2}=0.25$ atm.

Northupite is the only authigenic chlorine-bearing mineral of the Green River Formation. The amount of chlorine contained in northupite is a very small fraction of the chlorine that originally must have been present in the occluded brines. Most of the chlorine was apparently lost through squeezing out of undersaturated brines because of compaction.

LOUGHLINITE

Loughlinite $(Na_2,Mg)_2Si_3O_6(OH)_4$, occurs in the saline zone of the Green River Formation in small amounts, and it is about as abundant as analcite. It was discovered by Fahey (1948), who noted its presence in the core from the John Hay, Jr., well 1 (Fahey, 1962). It was also found by Regis and Sand (1957). Fahey (1962) found it below the main trona bed (at 1,600 ft) in veinlets and lenses at 1,620, 1,633–1,639, 1,665, and 1,672 feet. Regis and Sand (1957) observed it to form at the expense of dolomite+quartz.

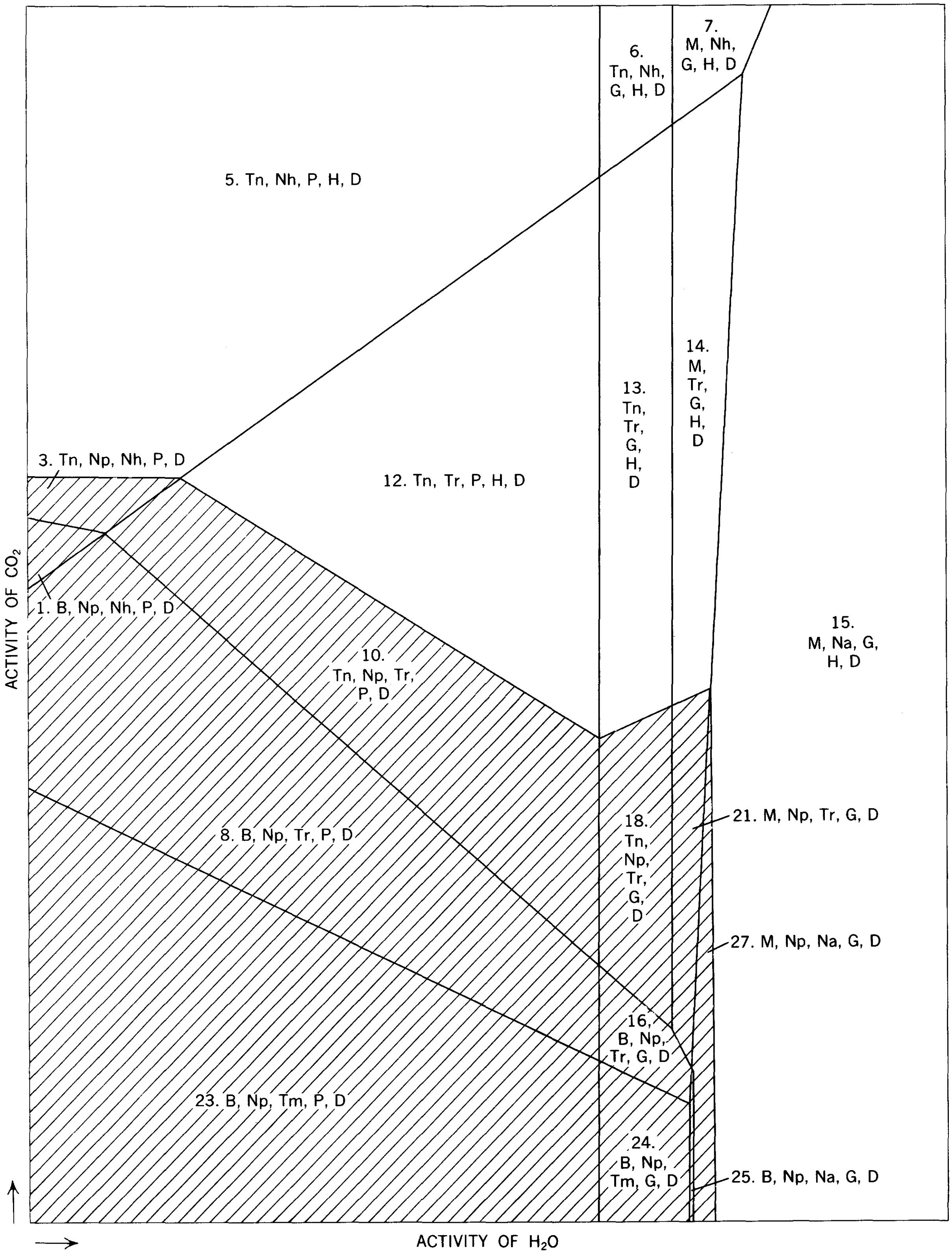

FIGURE 34.—A schematic isothermal-isobaric a_{H_2O}–a_{CO_2} diagram expressing the stability of northupite with respect to the solid phases; Tn, thermonatrite; Nh, nahcolite; Na, natron; P, pirssonite; H, halite; D, dolomite; G, gaylussite; Tr, trona; Np, northupite; B, burkeite; M, mirabilite. Northupite is stable in the shaded part of the diagram. From Eugster and Smith (1965, fig. 14).

The following two idealized reactions can be formulated:

$$\underset{\text{troan}}{2(Na_2CO_3\cdot NaHCO_3\cdot 2H_2O)}+\underset{\text{dolomite}}{3CaMg(CO_3)_2}+\underset{\text{quartz}}{9SiO_2}+H_2O \rightleftarrows \underset{\text{loughlinite}}{3(Na_2MgSi_3O_6(OH)_4)}+\underset{\text{calcite}}{3CaCO_3}+7CO_2$$

and

$$\underset{\text{northupite}}{Na_2CO_3\cdot MgCO_3\cdot NaCl}+\underset{\text{quartz}}{3SiO_2}+2H_2O \rightleftarrows \underset{\text{loughlinite}}{Na_2MgSi_3O_6(OH)_4}+\underset{\text{halite}}{NaCl}+2CO_2.$$

Trona and dolomite are present in the immediate vicinity (Fahey, 1962), and silica, in the form of quartz, chert, or volcanic ash, is present elsewhere in the section. No experimental data are available on the condition of loughlinite formation, but it seems clear that it can form whenever silica-bearing solutions come in contact with trona and dolomite. As silica is very soluble in sodium carbonate brines (Jones, 1965, p. A29–A30), this does not happen infrequently. In fact, it is somewhat surprising that loughlinite is not a common constituent above the main trona bed (17), where trona+dolomite assemblages are as abundant as they are below that bed. Perhaps the minimum temperature for loughlinite formation is such that a certain depth of burial is required.

ANALCITE

Analcite occurrences somewhat similar to those of the Green River Formation (Bradley, 1929a) have been described by Van Houten (1965) and by Wilkinson and Whetten (1964). The stability of analcite has been discussed by Coombs, Ellis, Fyfe, and Taylor (1959), Saha (1961), and Campbell and Fyfe (1965). Of particular interest is the temperature significance of the reaction

$$\underset{\text{analcite}}{NaAlSi_2O\cdot H_2O}+\underset{\text{quartz}}{SiO_2}\rightleftarrows \underset{\text{albite}}{NaAlSi_3O_8}+H_2O.$$

Campbell and Fyfe (1965) show that analcite may be replaced by albite at temperatures as low as 190±10°C. In the presence of brine this temperature will be lowered further, but it still must be above any temperatures reached by the Wilkins Peak Member.

Thus, the analcite-albite reaction defines an upper temperature limit, just as the pirssonite-shortite reaction defines a lower limit for the Wilkins Peak Member. Rough estimates would put the temperature range between about 80°C and perhaps 170°C, with little dependence upon total pressure and somewhat greater sensitivity to the activity of H_2O of the brine present. Authigenic albite is present in other parts of the Green River Formation (Moore, 1950; Milton, 1957) and is presumably due to a slight rise in temperature.

PYRITE

Pyrite is a conspicuous example of a mineral that clearly formed in the very early stages of compaction. Many finely crystalline aggregates of pyrite, and locally also pyrrhotite, are very much flattened in the plane of the bedding. Also, some oil-shale beds contain a great abundance of minute spherules of pyrite. These probably formed a little below the mud-water interface at the bottom of Gosiute Lake. This probability is based on analogy with the closely similar, or identical, minute spherules of pyrite that form today just below the surface of hydrogen sulfide-saturated, richly organic muds in many lakes. On the other hand, both the pyrite cubes and the pyrrhotite crystals undoubtedly formed later after much, or all, of the compaction had taken place. This is shown by wholly undistorted euhedral crystals of pyrite and delicate feathery crystals of pyrrhotite (fig. 8).

SOURCES OF CONSTITUENTS FOR AUTHIGENIC MINERALS

As has been mentioned repeatedly, the most plausible source of the authigenic minerals, such as disseminated trona, shortite, northupite, analcite, loughlinite, and others, is brine occluded in the sediments during deposition. Fortunately, the plausibility of this hypothesis can be tested rather simply. The test below shows that occluded brines could easily have provided all the sodium necessary to account for the observed sodium-bearing minerals in a unit column of sediments of the saline facies of the Wilkins Peak Member. An extension of the same reasoning permits us to infer that the principal amounts of all the other authigenic minerals can also be safely ascribed to the occluded brines.

Let us take a column of rock 1 cm^2 in area and as tall as the thickness of the saline zone in the John Hay, Jr., well 1; that is, 555 feet, or 16,070 cm; volume 16,070 cm^3. As this rock has an average bulk density of about 2.1 (porosity about 15 percent) the whole column weighs 16,070 cm^3×2.1=34,000 g. Imagine next that this rock is transformed back into its original wet uncemented condition, and, that all this soft material is piled into one column (1 cm^2 in cross section) and is not compacted. Assume further, that it all retains the original porosity that it had just after being deposited, that is, say 70 percent. With this porosity, the 34,000 g of material would make a column 70 percent ÷ 15 percent = 4 ⅔ times as high, about 75,000 cm, and having a volume of 75,000 cm^3. Of this volume, 70 percent, 52,500 cm^3, of course, is pore space. Now imagine this pore space filled with brine having a Na^+ concentration, say 8.0 g Na/100 g solution, or, for each g Na, 10.875 cm^3 fluid. We can assume, then, that this unit column of sediment contained 52,500 cm^3 $\div$ 10.875 cm^3/ g Na = about 4,800 g Na.

Now compare this potentially available amount of Na^+ with that actually found in sodium-bearing minerals in the unit column of rock in the saline facies that we started with. From table 23, we see that this is estimated to total 451 g Na, or less than one-tenth that available.

TABLE 23.—*Estimated amounts of sodium-bearing authigenic minerals and the corresponding weights of sodium in a unit column (1 cm^2) of the saline zone of the John Hay, Jr., well 1 core*

Minerals	Percent in rock	Grams mineral in unit column	Percent Na in mineral	Grams Na in unit column
Shortite	10.0	3,374.7	7.50	253.0
Northupite	2.2	742.5	9.25	68.7
Nonbedded trona	1.2	404.9	30.50	123.5
Loughlinite	.2	67.5	3.35	2.3
Analcite	.2	67.5	5.21	3.5
				451.0

The occluded brines, of course, contained considerable quantities of other constituents; therefore, it is not difficult, even without further analysis, to believe that they also provided most of the materials for the other authigenic minerals. The brines, however, almost certainly reacted with constituents already in the muds, such as dolomite, from which probably came most of the magnesium for the northupite, loughlinite, stevensite, bradleyite, magnesioriebeckite, talc, chlorite, and neighborite. Dolomite might also have supplied the additional calcium necessary for the formation of shortite from pirssonite. Shards of glassy volcanic ash undoubtedly provided much of the silica and alumina for the analcite and authigenic feldspar. The ash probably also supplied the boron for the searlesite, labuntsovite, and leucosphenite. Silica, however, must have been supplied in considerable quantities by the streams (table 7), and the brine at salting level might have contained more than 2,500 ppm SiO_2. (See Jones and others, 1967.)

Even in the mixolimnion of Gosiute Lake, the silica regimen must have been different from that in most existing lakes (see also Jones and others, 1967) because there was no diatom flora and no sponge fauna. This assertion is based on repeated careful searches for diatoms and sponge spicules over an interval of some 40 years by Bradley. These searches ranged throughout the whole stratigraphic thickness of the Green River Formation in Wyoming and concentrated on beds far below and far above any salines. Shore facies many miles geographically from the site of any salines were examined with especial care. Many of the rock samples were examined independently by K. E. Lohman, of the U.S. Geological Survey. Lohman reports (oral commun., 1961) that no nonmarine diatoms as old as middle Eocene have yet been found anywhere in the world. In Gosiute Lake the silica brought in by streams and springs or leached from volcanic ash that fell directly into the lake must have precipitated either from the lake water, perhaps as magadiite (see Eugster, 1967), or reacted with other constituents to form some of the authigenic silicates. Chalcedony and quartz are fairly common in parts of the Wilkins Peak Member.

In a lake containing as much sodium carbonate as Gosiute Lake must have had during the Wilkins Peak stage, the iron must have been distributed through the lake water, or brine, in the form of some stable complex—perhaps a yellowish organic complex such as Shapiro (1957, 1958) has identified in lake waters. That organic iron complex maintains its integrity in an alkaline environment. Whether such an iron chelate was occluded, as such, in the bottom muds is unknown. The iron in the Wilkins Peak sediments, however, was fixed, sooner or later, as pyrite, pyrrhotite, siderite, or in the silicates magnesioriebeckite or acmite (Milton, Chao, Fahey, and Mrose, 1960).

One might guess that other metallic elements, such as titanium, zirconium, niobium, zinc, and manganese, even though never present in more than very minor amounts, were also mobile in the pore solutions because they all occur in one or another of the authigenic minerals of the Green River Formation. It is conceivable that some of these inferred complexes (for example, manganese and zinc) were so stable that they persisted with the other most soluble salts and were eventually flushed out of the basin during the Laney stage along with much of the potassium and chlorine that must have eventually left the lake basin by that means. Extremely stable manganese and zinc organic complexes in sea water have been described (Rona and others, 1962).

MECHANISM FOR DISPERSION OF AUTHIGENIC MINERAL GRAINS

In many of the more massive, homogeneous layers of dolomitic marlstone containing differing amounts of organic matter in the saline facies of the Wilkins Peak Member, the isolated, euhedral crystals of shortite have a surprisingly uniform distribution (fig. 32). Moreover, this uniformity of dispersal seems to be independent of the size of the individual crystals. In the sample illustrated in figure 32, the uniformity of dispersion was analyzed as follows:

The photograph was enlarged to about 38×51 cm, and on a transparent overlay a point was plotted for each crystal, regardless of its size. Each dot was placed approximately at the center of gravity of the exposed section of the crystal. Then a reticle of 5-cm squares was placed over the plotted points, oriented first one way, then at 45°, and the number of points in each square was recorded. The sample represents the distribution of about 1,700 points in 154 squares. The frequency histogram plotted from these data is shown in figure 35.

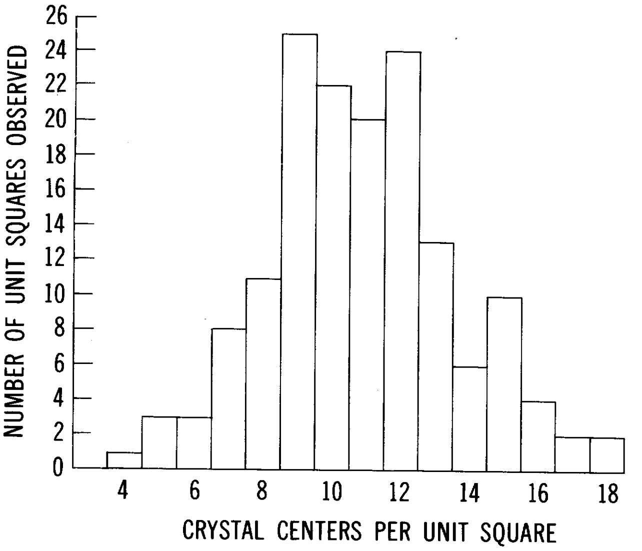

FIGURE 35.—Histogram showing the distribution of the centers of the crystals shown in figure 32. The histogram approximates a normal distribution curve (standard deviation = 2.5) and is a measure of the uniformity of dispersion of the crystals.

It is evident that the dispersion is not uniform, though the histogram roughly approximates a normal distribution curve. Departures from uniform dispersion may be accounted for by real irregularities in the spacing of the crystals and by apparent irregularities introduced by the fact that the plane of the polished rock cuts crystals that have a random orientation and, of course, cuts different crystals at different distances from their centers of gravity. Consequently, an unknown number of the "centers" selected are probably appreciably displaced from the true centers of gravity of each crystal.

The calculated standard deviation of the histogram in figure 35 is 2.5.

This and other similar dispersion patterns in virtually homogeneous rocks suggest that the crystals (originally pirssonite) started to grow at the sites of favorable nuclei. The fact that some beds have large crystals and others small suggests further that the crystals, once started, grew until the supply of constituents in the occluded brine was exhausted. Intuitively, it seems likely that more crystals started to grow, but that certain ones gained an early advantage and grew at the expense of many others. If these shortite crystals formed after compaction had ceased, as we believe, the constituents in the pore solutions must have moved to the centers of active growth by diffusion because the upward flow resulting from compaction must have ceased.

DIAGENESIS OF THE LAKE BEDS

OCCLUDED BRINES

According to our interpretation of the paleolimnology of the Wilkins Peak Member of the Green River Formation, a body of brine facies was being deposited there. While the beds of trona and mixed trona and halite were being deposited, the brine surface must have been exposed to the air most of the time, though at times it may have sunk below the salt surface itself. As we interpret the paleolimnology, while all the marlstone, dolomitic mudstone, and oil shale, even including the partings in the salt beds, were being deposited, the brine must also have been overlain by mixolimnion. When thin, this mixolimnion may have been more or less ephemeral, but most of the time it must have been rather thick and bicarbonate rich. The existence of a well-developed mixolimnion seems essential to us to permit the uniform distribution of such enormous quantities of $CaCO_3$ over hundreds and thousands of square kilometers of lake area. (See p. B23.)

From this picture of the paleolimnology, it follows that most of the water occluded in the sediments of the saline facies must have been a brine. About all we can say of the salinity of this brine is that it ranged from that out of which trona and, at times halite, precipitated to something less concentrated. If only brine was occluded in these sediments, we might expect that saline minerals would be rather uniformly distributed vertically through the rocks of the saline facies. We have already seen, however, that is not so. They are distributed through the sediments generally in zones of greater or lesser abundance. In some zones, the saline minerals are so abundant that they make up layers of interlocking crystals; in others, the crystals are widely and rather uniformly spaced. Moreover, at irregular intervals through the saline facies, beds, or groups of beds, ranging in thickness from about 1 cm to as much as 2 m, contain no saline minerals.

Some mechanism other than varying composition of the original occluded brines seems called for. This fact is discussed briefly below, after first considering the role of compaction and the consequent movement of pore solutions.

ROLE OF COMPACTION

The upward movement of pore water through compacting sediments plays a more important role in diagenesis than may be generally realized.

At, and just below, the mud-water interface, pore water must have made up 70 percent or more of the volume of the mud. As additional sediment came down, the added weight compressed the mud and expressed some of the pore water. Emery and Rittenberg (1952, p. 747–757), working with cores of fine-grained marine mud (of almost ideally uniform grain size), found that the water content decreased at a decreasing rate with depth. Indeed, the curve is an exponential curve. From their data they calculated that, if the rate of sedimentation were uniform, the present thickness of any annual layer of sediment could be determined from the expression

$$L=L_0\,\frac{100-W_0}{100-W_n}$$

where L is the present thickness of a buried annual layer, L_0 is the original thickness of an annual layer of sediment, and $100\text{-}W_0$ and 100-*Wn* are the percent pore volume in the respective layers.

Such a relationship, determined for muds containing a large percentage of clay minerals, might only approximate the compaction rates for muds with a high content of virtually incompressible, nonhydrophilic, equigranular carbonate particles, such as characterize much of the sediment in the Wilkins Peak Member.

Emery and Rittenberg (1952, p. 758–763) computed the numerical values for the one of their cores that they studied most intensively. Among other things, they found the significant and startling fact that through each cm^2 of the sediment at the bottom of this core (only 526 cm below the mud-water interface) 398 ml of pore water had passed since it was deposited some 3,500 years ago. For a shale that had been buried to a depth of 5,000 feet and that has a porosity of about 5 percent, they calculated that 32,000 ml of pore water had passed through each cm^2 since it was originally deposited (Emery and Rittenberg, 1952, p. 760).

In view of the magnitude of the upward flow of pore solutions during compaction, it is particularly pertinent to consider next what may happen to the salts in the system.

SALT FILTERING EFFECT OF SEDIMENT PORES

The pore water in any sediment is expressed upward as the mud compacts under the increasing load of successive increments of new sediment. The soluble salts occluded in any particular layer, therefore, probably moved upward into successively younger layers, particularly during the early stages of compaction, that is, within the first few hundred years. Thereafter, as the pores decreased to a critical size they probably served as a filter that permitted water to pass but not the salts. Organic matter trapped in the pores undoubtedly decreased their effective size and augmented the filtering effect. Such a mechanism may account, in part at least, for the observed concentrations of saline minerals in zones.

This restraining effect of the small pores on the salts is supported by unpublished laboratory experiments by Eugster and by the much more extensive studies of Bredehoeft, Blyth, White, and Maxey (1963), Von Engelhardt and Gaida (1963), and Milne, McKelvey, and Trump (1964).

Because much of the mud that originally made up the sediments of the saline facies contained organic matter, the occluded water and brines probably contained H_2S and therefore had a low Eh. Even though the anaerobic bacterial activity that produced the H_2S ceased after some unknown depth of burial, the pore solutions probably retained their reducing characteristic to great depths. This inference is borne out by the presence of unoxidized pyrite, or pyrrhotite, throughout the whole thickness of the saline facies.

Several of the most abundant authigenic minerals (shortite, northupite, and authigenic feldspars) are anhydrous. If these formed from earlier hydrous minerals (such as pirssonite, $Na_2Ca(CO_3)_2{\cdot}2H_2O$; gaylussite, $Na_2Ca(CO_3)_2{\cdot}5H_2O$, and others) water would have been added to the pore solution system. Many other authigenic minerals contain some water of crystallization. Notable among these minerals for their high water content are loughlinite $(Na_2,Mg)_2Si_3O_6(OH)_4$ and stevensite ($Mg_3Si_4O_{11}{\cdot}2H_2O$. Notable also is trona ($Na_2CO_3{\cdot}HNaCO_3{\cdot}H_2O$) with its two molecules of H_2O, because authigenic trona crystals are extremely abundant in many beds of the saline facies. All these, and other hydrous authigenic minerals, must have abstracted water from the pore solutions. No attempt has been made to calculate the amounts of water added to, or subtracted from, the pore-water system through the formation of anhydrous or hydrous minerals. It may be that such anhydrous minerals as shortite formed late in the diagenesis partly because of a deficiency of water.

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