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ORIGIN OF THE LITHIUM-RICH BRINE, CLAYTON VALLEY, NEVADA

Chapter L

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Abstract

The lithium-rich brines pumped from beneath Clayton Valley, Nevada, provide about one-third of the present United States requirements for lithium. Although the pre-Tertiary rocks in the vicinity do not contain anomalous amounts of lithium, the Tertiary volcanics that abound in the area could have been the origin of the lithium. Extensive diagenetic alteration of vitric material has taken place, and high lithium concentrations are associated with smectite in the Miocene Esmeralda Formation exposed east of the playa. The brines contain about 20 percent sodium chloride and as much as about 320 parts per million of lithium. The deuterium contents of two samples of the brine are –97 and –113 per mil Vienna Standard Mean Ocean Water. The deuterium content of the brine is close to that of the recharge to the aquifers beneath the playa. Springs in the recharge area range in δD from –106 to –114. The brine results from solution by ground water of halite beds that are high in lithium. These salt beds probably were formed during the desiccation of a small saline lake that occupied the position of the present playa.

INTRODUCTION

In the first part of this century, demand for sodium and chloride, sodium carbonate, borates, and potash salts led to an extensive reconnaissance of playa lakes throughout the western United States. The playa in Clayton Valley near Silverpeak, Nev., was first studied by Dole (1912), who found high concentrations of sodium chloride in near-surface brines but made no mention of lithium. The lithium deposit at Silverpeak remained undiscovered until the late 1950's, when the Leprechaun Mining Company[2] of Las Vegas, Nev., while searching for potassium brines, discovered high concentrations of lithium in the subsurface brines of the playa. In 1964, Foote Mineral Company acquired the property to develop the brine as a primary source of lithium.

Foote Mineral Company pumps brine from depths of about 100–250 m (meters) into a series of evaporating ponds (Barrett and O'Neil, 1970). Solar evaporation results in the precipitation of sodium chloride and the concentration of lithium. Brines that initially contain about 300 ppm (parts per million) lithium thus are concentrated to as much as 5,000 ppm lithium. After precipitation of the sodium chloride, lithium carbonate is precipitated in a processing plant. Production of Li_2CO_3 from the Clayton Valley brine field began in 1967 and has continued to the present. The reported annual capacity of about 6,500 metric tons of Li_2CO_3 represents about one-

third of the present United States requirements and is about 90 percent of all nonpegmatite lithium production in the United States.

GEOGRAPHIC SETTING

Clayton Valley is one of a group of intermediate-size valleys in west-central Nevada. It has a playa floor of about 100 km^2 (square kilometers) that receives surface drainage from an area of about 1300 km^2. Figure L1 shows the location of the important physiographic features in the vicinity. The playa floor is surrounded by alluvial fan slopes and these, in turn, by mountain ranges, including the Silver Peak Range on the west and the Palmetto Mountains and Montezuma Range on the south and southeast. The Weepah Hills and Paymaster Ridge form mountain barriers on the north and the east, respectively. Altitudes range from 1,300 m on the playa floor to 2,880 m at Piper Peak in the Silver Peak Range.

There is no evidence of anomalous amounts of lithium in pre-Tertiary rocks. The Tertiary volcanic rocks, however, are considered likely to be involved in the origin of the lithium deposit because volcanism could have provided the heat energy and hydrothermal activity required to mobilize lithium from volcanic glass and other relatively unstable minerals. About 100 km^3 (cubic kilometers) of lava erupted from the Silver Peak volcanic center in the western part of Clayton Valley about 6 million years ago (Robinson, 1972).

East of Clayton Valley, more than 100 km^3 of Tertiary ash-flow and air-fall tuff is exposed at Clayton Ridge and as far east as Montezuma Peak. These predominantly flat-lying, pumiceous rocks are interbedded with tuffaceous sediments between Clayton Ridge and Montezuma Peak; but at Montezuma Peak these rocks are altered considerably and dip at angles of as much as 30°. In the Montezuma Range, they are unconformably overlain by rhyolitic agglomerates. The source of these tuff sheets may have been a volcanic center to the east near Montezuma Peak, or to the south in the Montezuma Range, or the Palmetto Mountains, or Mount Jackson, or perhaps even the Silver Peak center to the west.

Tertiary sedimentary rocks are exposed in the Silver Peak Range, in the Weepah Hills, and in the low hills east of the Clayton Valley playa. These rocks all are included in the Esmeralda Formation (Turner, 1900). The Esmeralda Formation consists of sandstone, shale, marl, breccia, and conglomerate, and is intercalated with volcanic rocks, although Turner (1900) excluded the major ash-flow units and other volcanic rocks in defining the formation. The rocks of the Esmeralda Formation in and around Clayton Valley apparently represent sedimentation in several discrete Miocene basins. The age of the lower part of the Esmeralda Formation in Clayton Valley is not

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[2]Use of company names is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.
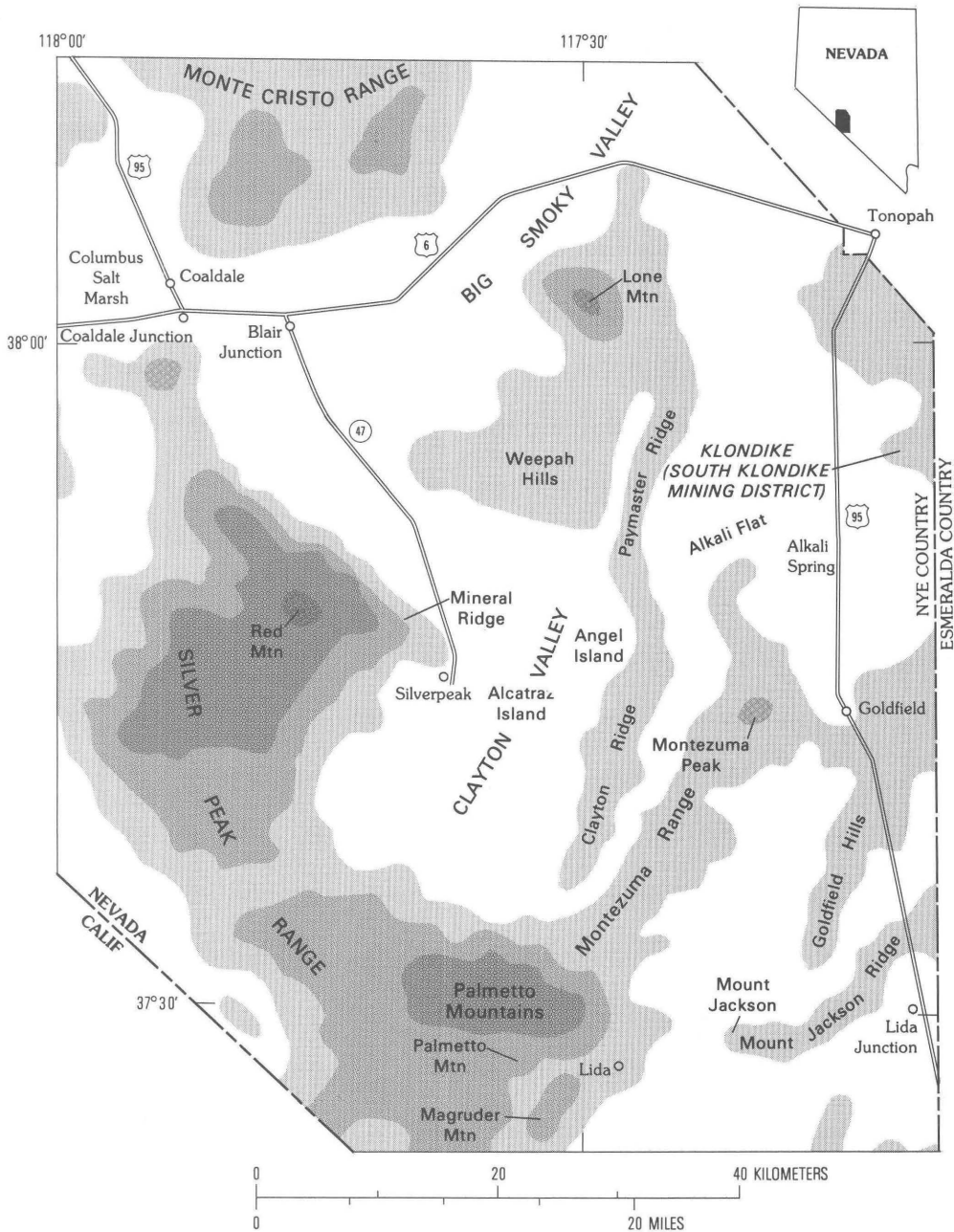
Figure L1. Major physiographic features in area of Clayton Valley, Nev. Modified from Albers and Stewart (1972).

known, but an air-fall tuff in the uppermost unit of the Esmeralda Formation has a K-Ar (potassium-argon) age of 6.9 ± 0.3 Ma (million years) (Robinson and others, 1968).

Extensive diagenetic alteration of vitric material to zeolites and clay minerals has taken place in the tuffaceous sandstone and shale of the Esmeralda Formation, and anomalously high lithium concentrations (as much as 120 ppm lithium) accompany the alteration. However, lithium concentrations in these rocks generally are less than 200 ppm except where smectite is present, and the high lithium concentration associated with smectite is confined to the Esmeralda Formation exposed east of the playa. High lithium concentrations in these rocks is in hectorite, a lithium clay mineral thought to have been precipitated from alkaline lake waters (J. R. Davis, unpub. data).

GEOLOGY OF THE BASIN FILL

In mapping the Quaternary deposits of Clayton Valley, the playa surface, the surrounding alluvial fans and slopes, and the sand dunes are easily distinguished. A

large part of the playa surface has been changed by the construction of roads and evaporating ponds, but prior to this construction the northeastern part of the playa was characterized by a central zone of soft, moist silt and salt, an intermediate zone of silt and sand, and a marginal zone of either travertine or vegetated mounds of soft, puffy silt (Motts and Matz, 1970). The southwestern part of the playa is higher and dryer than the central zone of the northeastern part, and is similar to the marginal vegetated zone there. Alluvial fans are highly dissected and deeply entrenched in the southeastern part of the valley and less dissected elsewhere. Fan surfaces of at least two different ages can be distinguished in many parts of the valley. Sand dunes are in the southern part of the valley and are partially stabilized by vegetation.

The subsurface stratigraphy of the basin fill is known from numerous wells drilled in the playa and adjacent alluvial slopes drilled by Foote Mineral Company between 1964 and 1978, and by the U.S. Geological Survey in 1912 and 1977. Poor sample recovery, contamination of cuttings, and the highly faulted nature of the playa sediments inhibited a clear understanding of the stratigraphy until Foote Mineral Company initiated an exploratory drilling program in 1976 using rotary drilling with reverse circulation and careful logging of the cuttings by well-site geologists. Much of the data collected since that time is still proprietary, but data from several wells are available (Davis and Vine, 1979), making the following summary possible.

Essential to understanding the subsurface data is the concept of fluctuating pluvial and interpluvial climates throughout the Pleistocene. During pluvial periods, which were cooler or wetter than today, shallow-water lacustrine conditions favored deposition of mud in the central part of the valley, merging laterally with fluvial and deltaic sands and muds and with well-sorted beach sands and gravels. During interpluvial periods, like the present, ephemeral lacustrine conditions favored deposition of muds, silt, sand, and evaporite minerals in the central part, grading laterally to alluvial deposits. The gravity data (Wilson, 1975) and subsurface stratigraphic correlations (fig. L2) suggest that the center of deposition and subsidence in Clayton Valley was in the northeastern arm of the playa throughout late Quaternary time. This center of deposition is bounded on the south and east by steeply dipping normal faults that parallel the two fault-scarp trends in alluvial gravels of late Quaternary age. The thickest clastic and chemical sedimentation was confined to the downdropped area north and west of these faults.

The lacustrine sediment that was deposited near the center of pluvial lakes in Clayton Valley is generally green to black calcareous mud. About half of the mud, by weight, is smectite and illite, which are present in nearly equal amounts. Calcium carbonate generally makes up 10–20 percent of the mud, and koalinite, chlorite, sand- and silt-size volcaniclastic detritus, traces of woody organic material, and diatoms compose the rest. In the northeastern arm of the playa, thick layers of evaporite minerals are interbedded with lacustrine muds. These evaporite minerals probably were precipitated as the lake dried up during interpluvial periods. The correlation between the only radiometric date from the subsurface of

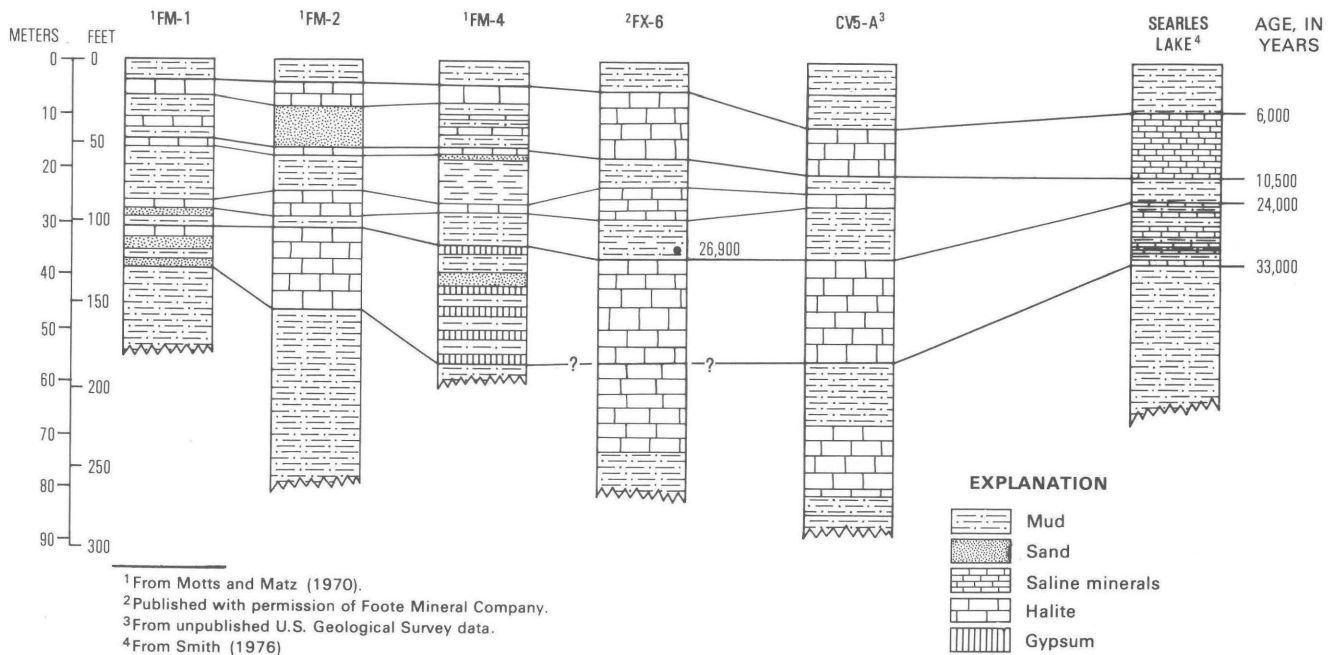Figure L2. Well logs from Clayton Valley, Nev., and correlation with Searles Lake, Calif.

[1] From Motts and Matz (1970).
[2] Published with permission of Foote Mineral Company.
[3] From unpublished U.S. Geological Survey data.
[4] From Smith (1976)

Clayton Valley (fig. L2) to nearby wells suggests that the pluvial stratigraphy in Clayton Valley possibly can be correlated with that in Searles Lake, Calif. (Smith, 1979) and Lake Lahontan, Nev. (Benson, 1978). If the correlation of these salt and mud cycles is correct, the upper salt bed in well CV5–A was deposited since the last pluvial period ended about 10,500 years B.P. The underlying mud and salt sequence was deposited during the last pluvial period from 24,000 to 10,500 years B.P. (fig. L2).

Subsurface Hydrology

The structural and stratigraphic setting of Clayton Valley has contributed to a complex hydrologic system. The Paleozoic rocks in Clayton Valley contain much thinner sequences of carbonate rocks and probably do not form the effective fractured aquifers that they do 150 km to the southeast at the Nevada Test Site (Winograd and Thordarson, 1975). However, the upper Cenozoic rocks include alluvial sediments, bedded tuffs, and welded tuffs that act as aquifers. The chemical character of the ground water varies considerably within the basin, and three basic types can be identified: (1) cold, dilute ground water in the bedrock highlands; (2) thermal, saline ground water near the playa margin; and (3) cold, saline brines of the playa zone.

The cold, dilute ground-water reservoir of the bedrock highlands is recharged by infiltration through the soil zones, alluvial channel bottoms, and bedrock fractures, but the thin alluvial cover and the low porosity and permeability of the clastic Paleozoic bedrock impedes deep circulation and large reservoir size.

The thermal ground-water system obtains its heat from deep circulation or from contact with a shallow magma chamber. Circulation to at least 1-km-depth would be necessary to acquire this heat from contact with rocks heated due to the geothermal gradient, and the basin structure would require at least 500 m of this circulation into bedrock that is relatively impermeable except where fractured. However, the Quaternary cinder cone and Pliocene volcanics north of the playa suggest the presence of a magma chamber that could create a heat flux in excess of the normal geothermal gradient.

The aquifers of the central playa zone contain cold, saline ground water. The recharge of these economically important aquifers is central to the topic of brine evolution and will be discussed.

Groundwater Geochemistry

The subsurface brines used for lithium production in Clayton Valley are sodium chloride brines of about 20 percent salinity when they are first pumped from the playa (table L1). More dilute ground waters from the playa zone have similar proportions of major constituents, with salinities as low as 1 percent. Lithium seems to correlate well with concentration of these waters and shows no correlation to temperature; the thermal ground water has major-ion composition nearly identical to cold ground waters of similar concentration.

All the ground waters from the vicinity of the playa are supersaturated with respect to calcite, the clay mineral hectorite, and the zeolite phillipsite. The brines also are supersaturated with respect to cristobalite and analcime, whereas some of the more dilute waters are saturated with respect to sepiolite. No natural brines analyzed from Clayton Valley are saturated with respect to gypsum or halite.

The solute chemistry of the ground waters in Clayton Valley and the adjacent basins does not support the concept of subsurface drainage into Clayton Valley from the adjacent basins (Rush, 1968; Motts and Matz, 1970). There certainly appears to be no lithium-enriched source waters in any of the other basins, which makes the possibility of inflow unimportant in considering the chemical evolution of the brines.
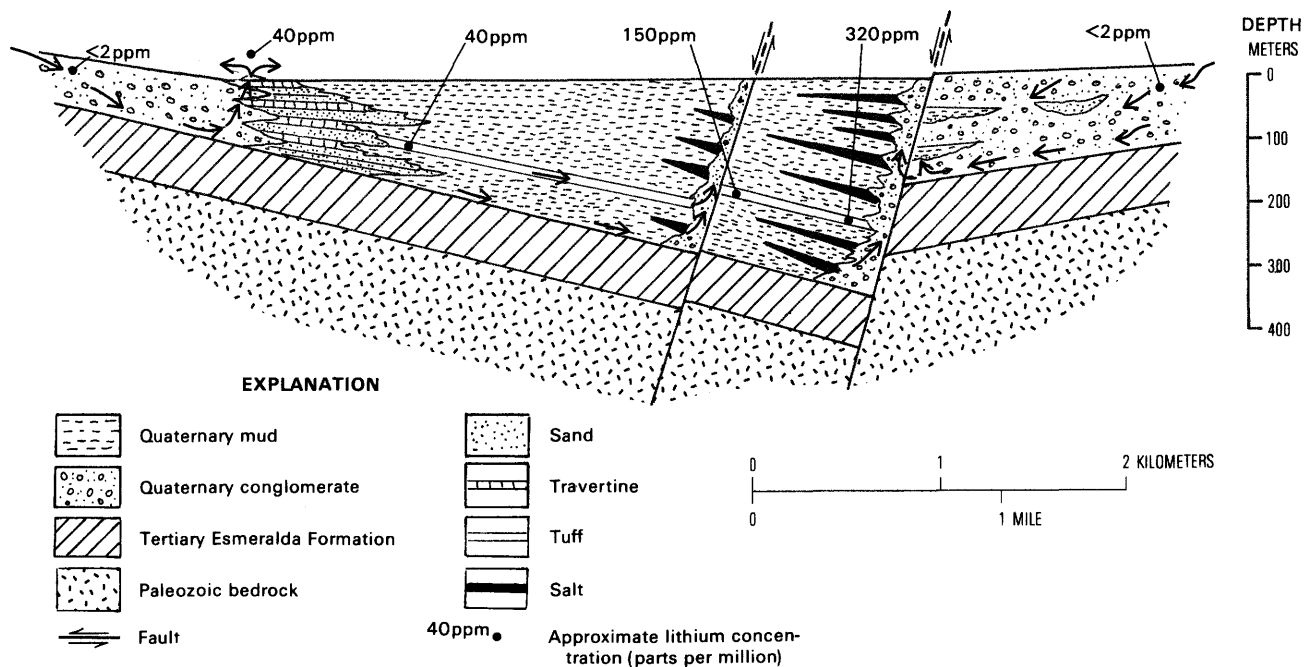
Brine Evolution

The most lithium-enriched brines are in the downfaulted northeastern arm of the playa. Brine is produced primarily from the southeast-dipping air-fall tuff bed or "ash aquifer." Although some brine previously was produced from the permeable salt beds overlying the ash aquifer, the practice was abandoned due to dissolution of the salt and collapse around the wells. The highest lithium concentrations are found in brines produced from the tuff where it abuts the faults and forms a structural trap for the dense brines (fig. L3).

The lithium-enriched, sodium-chloride brines in Clayton Valley are typical of the sodium-sulfate-chloride brines that evolve during evaporation of inflow waters having approximately equal bicarbonate and calcium plus magnesium contents (Eugster and Jones, 1979). The halite and gypsum beds in the surface give direct evidence of high salinity levels during the interpluvial periods, but the isotopic composition of the brine suggests that it was not formed by evaporative concentration, and therefore the brine cannot be a residual pore water.

Deuterium composition in a brine increases during evaporation due to differential fractionation of the lighter hydrogen isotope in the vapor phase. A careful study of this process has been made at Owens Lake, Calif., which is about 100 km to the southwest of Clayton Valley. At Owens Lake, the fractionation mechanism was shown to increase the deuterium values from about $\delta D = -115$ per mil on the inflow to $\delta D = +3$ per mil in evaporated brines of similar composition to those in Clayton Valley (Fried-

Table L1. Partial solute chemistry of selected ground waters from Clayton Valley

[Leaders (---) indicate no data; temp. (°C), temperature in degrees Celsius; SMOW, Standard Mean Ocean Water]

Sample source	Depth (meters)	Temp. (°C)	Concentration (parts per million) Na	Cl	Li	Molar Na/Cl	Molar Li/Cl	δD (per mil SMOW)
			Wells					
CV1-----------	96	22.0	7,073	11,788	27	0.923	0.012	---
CV2-----------	53	21.0	7,094	10,837	29	1.0097	0.014	---
CV3-----------	127	33	9,775	15,640	42	0.952	0.014	---
CV4-----------	242	36	12,700	20,500	58	0.954	0.014	---
CV5-----------	72	22	5,900	9,850	26	0.9255	0.013	---
CV5A----------	218	19.5	82,375	132,860	283	0.9435	0.011	---
FM116---------	---	19.5	63,750	100,000	230	0.9083	0.013	-97
FM133---------	---	19.5	46,930	69,400	180	0.9826	0.012	-113
			Springs					
Minneosta-----	---	---	60	100	.05	0.8966	---	-109
Coyote--------	---	---	57	75	.05	1.1905	---	-109
Tarantula-----	---	---	105	120	.05	1.3529	---	-111
Big-----------	---	---	52	55	.05	1.4375	---	-114
McNamara------	---	---	31	65	.05	0.6842	---	-106
Waterworks----	---	---	350	740	0.69	0.7204	---	---

EXPLANATION

Quaternary mud
Quaternary conglomerate
Tertiary Esmeralda Formation
Paleozoic bedrock
Fault
Sand
Travertine
Tuff
Salt
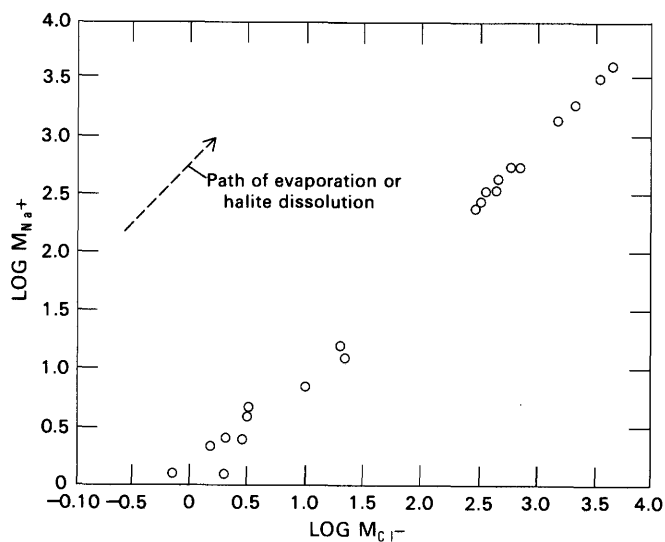40ppm● Approximate lithium concentration (parts per million)

Figure L3. Generalized cross section of Clayton Valley playa, showing structural position of the major tuff-bed aquifer and inferred directions of ground-water movement.
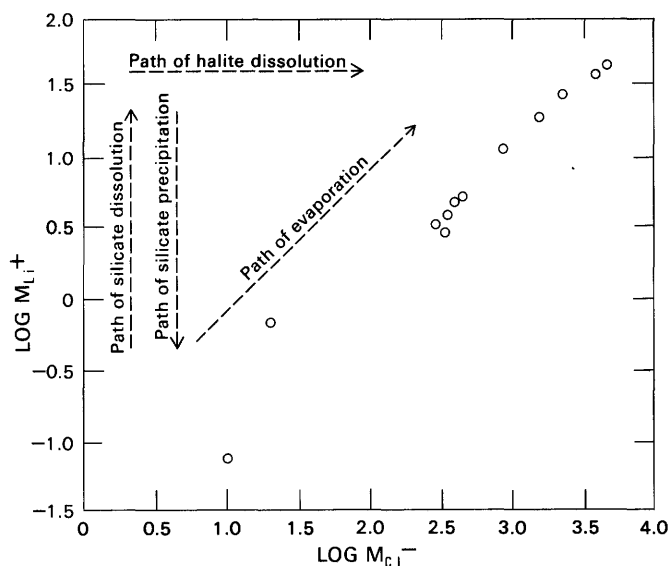
man and others, 1976). However, in Clayton Valley, the brines have deuterium compositions approximately equal to the inflow (table L1), indicating that the brine was not produced by evaporative concentration of the inflow waters. Furthermore, the isotopic compositions of the two brine samples from Clayton Valley show considerable variation ($\delta D = -97$ per mil and $\delta D = -113$ per mil). This variation probably is due to seepage of small amounts of the isotopically heavy waters in the evaporating ponds into the aquifer near well FM 116. Well FM 113 is located away from the ponds, and the deuterium concentration from that well ($\delta D = -115$ per mil) is similar to that of potential ground-water recharge emanating in the Silver Peak Range to the west or in the Palmetto Mountains to the south.

Further study of the geochemistry of the hydrologic system also suggests that the brine is produced primarily from dissolution of halite. Dilute inflow in the basin varies in sodium and chloride concentrations, having molar Na:Cl that range from 0.6 to 1.4 (table L1), whereas ground waters and brine from the playa have molar Na:Cl near unity regardless of concentration. Given the large amount of variation in the Na:Cl of the inflow waters, it is difficult to conceive of any process other than dissolution of halite that always would produce an Na:Cl so near unity.
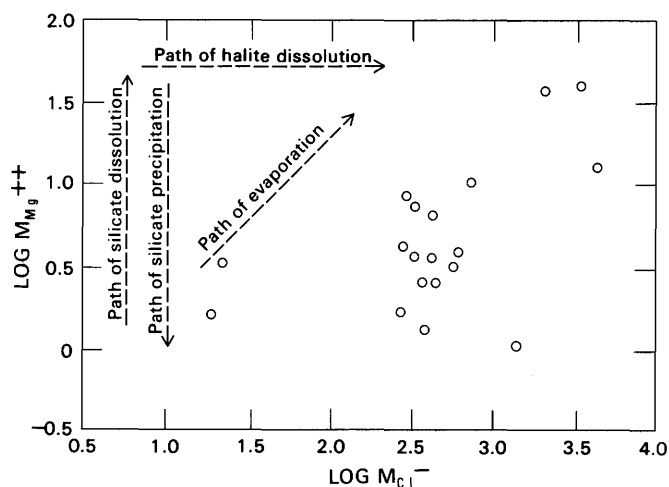
Plots of molar chloride concentrations against various cation concentrations (figs. L4–L6) give added insight to the problem of brine evolution. Figure L4 demonstrates how the Clayton Valley brines and more dilute ground waters from the playa plot on a trend of equal molar proportions of sodium and chloride. Figures L5 and L6 show

Figure L5. Plot of molar (M) chloride (Cl) and lithium (Li) concentrations in water samples from Clayton Valley.

Figure L6. Plot of molar (M) chloride (Cl) and magnesium (Mg) concentrations in water samples from Clayton Valley.

that the lithium and magnesium increase in proportion to chloride concentration, although magnesium shows much more variation than lithium. These trends indicate that the lithium, and to a lesser extent magnesium, were concentrated with chloride by the same evaporative processes that led to halite precipitation.

Microscopic examination of halite and gypsum crystals reveals fluid inclusions as well as fine-grained detrital material incorporated in many crystals. Roedder and Bassett (1981) reported that bedded halite may contain several

Figure L4. Plot of molar (M) chloride (Cl) and sodium (Na) concentration in water samples from Clayton Valley.

weight percent water or brine in the form of fluid inclusions, intergranular fluids, and hydrous minerals. Fluid in the inclusions or intergranular pores would be a lithium-enriched bittern, and release of this fluid during halite dissolution could be modeled as a closed system. The linear trend of the lithium-chloride plot (fig. L5) supports the closed-system model, whereas the deviation from the linear trend in the magnesium-chloride plot (fig. L6) suggests that the magnesium concentration in the brine has been altered, probably by interaction with hydrous minerals or by cation-exchange with clays.

CONCLUSIONS

The playa sediments in Clayton Valley were deposited in a lithium-enriched environment. The lack of evidence for large pluvial lakes in Clayton Valley and the general character of the subsurface sediments suggests that the depositional environment probably was a playa or shallow lake that evaporated to total or near dryness in some seasons or years. This process concentrated dilute inflow with low lithium concentrations many times. The mechanism that we propose for the formation of the present lithium brine is that dilute, lithium-containing, sodium-chloride waters were concentrated by evaporation on a playa during interpluvial periods. Halite was deposited with a bittern fluid enriched in lithium. During the last 10,000 years, meteoric water has penetrated the playa sediments, dissolving halite, and producing a brine similar in concentration and chemistry to an evaporative brine.

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