

Lithium Occurrence in the Brines of Clayton Valley, Esmeralda County, Nevada

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ABSTRACT

Lithium-bearing brines occur in Clayton Valley, an undrained structural depression filled with Quaternary unconsolidated sediments consisting chiefly of clays and saline minerals. The lithium occurs in a sodium chloride brine which contains subordinate amounts of potassium and minor amounts of magnesium and calcium.

Although lithium-bearing hot springs are present at the periphery of the playa, the evolution of Clayton Valley strongly suggests that the lithium has been derived from the leaching and weathering of Tertiary lacustrine and volcanic sediments exposed east of the valley. Concentration of the lithium-bearing solutions into brines was accomplished by solar evaporation.

INTRODUCTION

Prior to the late 1930's the prime sources of lithium were pegmatite bodies containing high-grade but relatively small concentrations of lithium minerals. In these bodies only spodumene, lepidolite, amblygonite, petalite, and eucryptite have been commercial sources of lithium.

The best known and most productive of the pegmatites were mined in the Black Hills of South Dakota. Several other pegmatites in southern California, northern New Mexico, and Colorado also had noteworthy records of production in those early years. Presently, the largest producing district is located in the tin-spodumene belt of North Carolina.

Prior to World War II, lithium was also discovered in a new form. The brine of Searles Lake, California, was found to contain 0.015 percent Li_2O . Although the concentration was low, this type of occurrence suggested that additional sources might be located in other playa basins.

In the early 1960's an especially promising brine was discovered near Silver Peak in Clayton Valley, Nevada by

Leprechaun Mining and Chemical Company of Las Vegas.

In 1964, the Foote Mineral Company acquired Leprechaun's leases and continued exploration and development. Presently, the brine is pumped from the playa sediments by a series of gravel-packed wells and stored in large artificial ponds. There it is concentrated by solar evaporation, thence carried to a plant where it is chemically converted into lithium carbonate. The extracted brine contains an average of 0.065 percent Li_2O .

GENERAL FEATURES OF CLAYTON VALLEY

Clayton Valley is located in Esmeralda County, south-central Nevada. It lies approximately 25 miles (40 km) east of the Nevada-California border, 35 miles (56 km) southwest of Tonopah, Nevada. Silver Peak, population about 200, is the only community in the valley. The area is accessible via State Highway 47.

As Clayton Valley lies in the eastern rain shadow zone of the Sierra Nevada, it is very arid. The evaporation rate is about 54 inches (1.37 m) per year, while precipitation amounts to about 5 inches (13 cm) per year.

The valley is an undrained structural depression surrounded by mountains. Although part of the Great Basin of the Basin and Range physiographic province, the mountains lack the parallelism shown by most ranges of the Great Basin. Instead, they show an arcuate trend defined by the Silver Peak Range on the West, the Palmetto mountains to the south and the Montezuma mountains to the east (Fig. 1). The mountains rise to elevations of 9450 feet (2870 m), 9250 feet (2810 m) and 8400 feet (2550 m) respectively. The crest of the Weepah Hills which bound Clayton Valley on the north varies in elevation from about 5000 feet (1520 m) at the western margin to 7700 feet

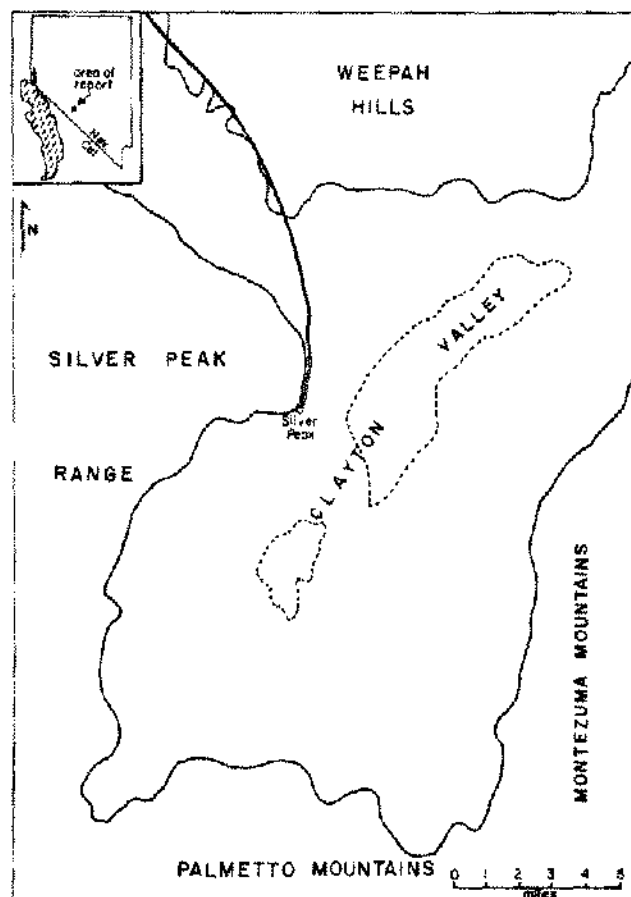


Figure 1. Location map.

(2340 m) at the eastern margin. They form the foothills of Lone Mountain.

The playa which lies at an elevation of about 4600 feet (1400 m) occupies an area of about 20 square miles (50 km²). The playa surface consists principally of a mixture of clay minerals, halite, and gypsum. Calcium carbonate forms an abundant cement. Smectite, present in clay-rich layers, causes these to expand when wet and to exfoliate when dry. Where the water table is near the surface, clay expansion produces fairly pronounced mounds.

PREVIOUS STUDIES

The geology of the Silver Peak region was first described by Turner (1900, 1909) and by Spurr (1906). The Silver Peak playa was investigated by Dole (1913). More detailed investigations of the Silver Peak Range area, the Palmetto Mountain area, and the Weepah Hills area have been described in several theses (Robinson, 1962; McKee, 1961; Moiola, 1962). A preliminary geologic map of Esmeralda County incorporating data from several investigators was prepared by Albers and Stewart in 1965.

The alteration to zeolite of sediments and volcanics in

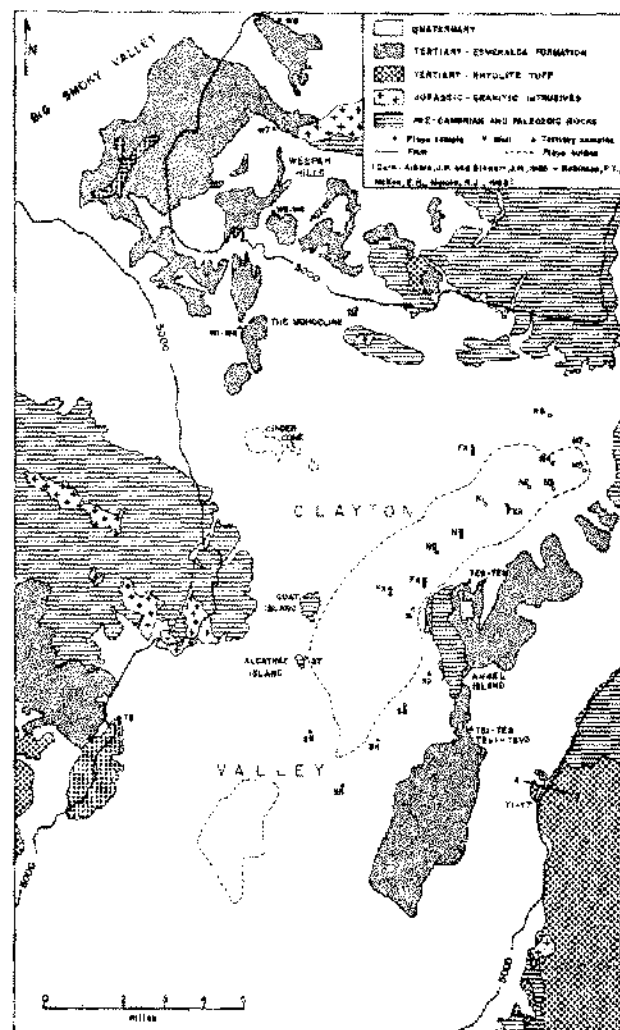


Figure 2. Generalized Geology of the Clayton Valley Region, Esmeralda County, Nevada.

the Silver Peak Range was studied by Robinson and in the Weepah Hills by Moiola (1964).

Tertiary volcanism and sedimentation in the Silver Peak Region have been comprehensively studied by Robinson, McKee, and Moiola (1968).

GENERALIZED GEOLOGIC HISTORY OF THE REGION

The rocks that compose the nearby mountain ranges consist of an exceptionally wide variety of age and types (Fig. 2).

Extensive outcrops of pre-Cambrian and Paleozoic rocks are found on the western, eastern, and northern borders of Clayton Valley (Fig. 2). Pre-Cambrian rocks are almost exclusively made up of carbonates, but comprise some crystalline rocks that contain one lepidolite-bearing pegmatite. The Paleozoic rocks, mainly Lower

Cambrian in age, are miogeosynclinal in character and consist of quartzites, carbonates and shales.

Intrusive rocks of Jurassic age are associated with the Sierra Nevada batholith, the main mass of which lies about 40 miles (64 km) west of the area. In the Clayton Valley area, the Jurassic intrusives form an arcuate zone around the southern margin of the valley in the Palmetto Mountains. A few outcrops are found in the Weepah Hills and in a few scattered places in the Silver Peak Range and in the Montezuma Mountains.

The most important sequence of rocks, in which the geologic evolution of the Basin and Range Province is recorded is the Upper Miocene to Pliocene sequence of tuffaceous sediments of the Esmeralda formation.

As defined by Turner, the sequence consists of some 15,000 feet (4,500 m) of lacustrine sediments which include poorly sorted conglomerates and sandstones, limestone, mudstones, and tuffaceous units (Robinson, McKee, and Moiola, 1968). Fossil gastropods and fish suggest a relatively fresh environment of deposition (Turner, 1900).

Two major volcanic and structural events are recorded in the Tertiary sediments. An early Miocene volcanic period, widespread in other parts of Nevada is represented only by a single welded tuff unit, with an age of 22 million years, exposed at the northern end of the Silver Peak Range. This tuff was ejected prior to the block faulting episode which disrupted the external drainage of the region and created several partially closed basins into which the lower part of the Esmeralda formation was deposited.

Stratigraphic studies of Robinson, et al. (1968), showed that although the rock sequences assigned to the Esmeralda formation are generally similar in individual valleys, they differ greatly in detail. Lateral and vertical changes are abrupt and angular unconformities are numerous. These observations strongly suggest that the sediments were deposited in separate basins.

A second major period of faulting, accompanied by volcanic eruptions, culminated in middle Pliocene time and resulted in the deformation of the lower Esmeralda beds creating an angular unconformity. The oldest sediments above the unconformity, assigned to the upper Esmeralda unit, have been dated at 6.9 million years (Robinson, McKee, and Moiola, 1968).

A widespread ash fall tuff crops out around Clayton Valley. Its age suggests that its deposition was contemporaneous with upper Esmeralda sediments, while in some areas it appears to have preceded them. The only major structural event to follow the deposition of upper Esmeralda sediments was the 3000-foot (1510 m) uplift of the Silver Peak Range.

Although the present topography was largely established by late Pliocene time, faulting has been active through the Pleistocene up to the present time as evi-

denced by the presence of fault scarps near Angel Island in Clayton Valley.

GENERAL NATURE OF THE PLAYA AND CORE SEDIMENTS

The playa material consists mainly of a mixture of saline minerals and detritus eroded from the surrounding hills. The detritus is mostly fine, being principally composed of clay-size material (minus two microns, e.s.d.). The clay-size fraction ranges from 7 percent to 60 percent in the playa samples, and reaches 70 percent in some core samples.

X-ray diffraction studies of the less-than-two micron fraction of playa and core samples indicate that four clay types are present:

1. smectite
2. illite
3. chlorite
4. kaolinite

The proportions of these clays vary considerably. In general, smectite and illite are the most abundant of the four, and chlorite and kaolinite are subordinate. The x-ray patterns also reveal the presence of a zeolite.

LITHIUM IN THE PLAYA AND CORE SEDIMENTS

Chemical analyses of bulk samples show that the sediments in the basin have an unusually high lithium content. Lithium concentrations in surface playa samples vary from 350 ppm to 1171 ppm, (Fig. 2, Table I), while values ranging from 260 ppm to 1713 ppm were recorded in core samples (Fig. 2, Tables II, III).

Evaluation of the lithium content of various size fractions revealed that the lithium is concentrated in the clay mineral fraction (Table IV). Although this suggested a relationship between lithium and smectite, the samples

TABLE I
Chemical and Mineralogic Variation
in Playa Samples ($<2\mu$ fraction)^a

Southern Sector		Northern Sector	
Sample No.	Li+ (ppm)	Sample No.	Li+ (ppm)
S1	1022	N1	920
S2	1058	N2	350
S3	1171	N3	920
S4	498	N4	530
S5	410	N5	500
S6	449	N6	620
S7	499	N7	510
		N8	800
		N9	600

^aValues corrected for carbonate and saline cements

TABLE II
Chemical, Mineralogic and Textural
Variation in Bulk Samples from Well FX-4^a

FX-4	
Sample Depth (feet)	Li+ (ppm)
17	1670
45-52	420
67	410
78-80	1610
110-115	420
115-118	1310
142-149	320
160-162	1100
175-176	680
181-185	950
188-189	1073
191	410
228-236	500
248	1050
264	370
273	1470
275	1132
327	380
357	950
387	260
417	600
442	827
456	1550
507	840
512	1520
530	1713
535	840
553	710
555	400
583	490

^aValues corrected for carbonate and saline cements

TABLE III
Chemical, Mineralogic and Textural
Variation in Bulk Samples from Well FX-6^a

FX-6	
Sample Depth (feet)	Li+ (ppm)
76	1158
113	466
118	1643
147	505
164	854
197	1276
213	837
243	507
283	1022

^aValues corrected for carbonate and saline cements

were nevertheless subjected to further examination in order to determine whether the lithium was present as an exchangeable cation or held a structural cation in the clay structure. The first alternative was tested by subjecting a lithium-rich sample to exchange reactions with calcium and barium. The results of the experiment indicated that

TABLE IV
Lithium Concentration (ppm) as a Function of Size

Well No.	Sample Depth (feet)	Bulk Sample	-1 μ	-0.3 μ
FX-4	78	1110	1538	2860
FX-4	115	1210	—	2770
FX-4	191	410	—	870
FX-2	35	750	—	1920

TABLE V
Relationship Between Spring Water and Brine Compositions

Ion Species	Spring (ppm)	Spring x10 (ppm)	Brine (ppm)
Li+	38	380	380
K+	934	9,340	7,700
Na+	9,220	92,200	66,200
Mg++	64	640	600
Ca++	443	4,430	580
Cl ⁻	13,700	137,000	95,200
SO ₄ ⁻	500	5,000	11,100

¹ Foote Mineral Company analyses, 1966 data.



Figure 3. Hectorite laths—Quaternary marl—core sample collected 273 feet (83 m) below the playa surface—replica of -2 μ fraction e.s.d.—14,000X.

the lithium is nonexchangeable. Further evaluations using x-ray diffraction and electron microscopy techniques confirmed that the clay mineral hectorite is present (Fig. 3), and that, consequently, the lithium is held in the octahedral layer of the clay structure.

BRINE CHEMISTRY

Chemically, the brine which saturates the sediments of the Clayton Valley basin is relatively simple. It is a sodium chloride solution containing minor amounts of potassium and sulfate and subordinate quantities of calcium and magnesium (Table V). This unusual chemical system permits the recovery of lithium as a primary product.

Although the presence of gypsum and halite in the basin suggests an obvious mechanism for the concentration of weak solutions into brine, the source of the cations in the brine is less obvious. Many playas in the Basin and Range Province contain sodium chloride as the main saline mineral, but some of them also contain unusually large concentrations of borates, sodium carbonate, and potash salts. The presence of such minerals suggests a wide range of chemical compositions for the parent solutions.

Several hypotheses have been proposed to explain the chemical character of playa brines. Among these, the most important are:

1. leaching of older Tertiary saline beds.
2. hot springs.
3. leaching of bedrock.

That the chemistry of many playas has been controlled by the leaching of older saline beds has been well substantiated (Spurr, 1906; Gale, 1912). In a survey of the distribution of borate deposits, Spurr noted that a broad belt of Tertiary sediments extends east of the Sierra Nevada from northern Nevada to the Mojave desert in California. As some of the Tertiary beds contain colemanite, a genetic relationship between the Tertiary source material and the Quaternary saline accumulation was suggested.

A simple solution mechanism satisfactorily explains the chemistry of several but not all of the playas. Many playas which have similar peripheral country rock have nonetheless different chemistries (Spurr, 1906; Muessig, 1966). This is also true of the Clayton Valley region. Clayton Valley, Fish Lake Valley, and Big Smoky Valley have similar rocks exposed at their margins. Nevertheless, Clayton Valley contains lithium, Fish Lake Valley contains boron, while Big Smoky Valley contains only some sodium chloride. This strongly suggests local control, especially local springs which commonly occur at the margins of the playas. Such springs apparently have contributed abundantly to several playas of the Great Basin and to some thirty-five South American playas investigated by Muessig (1966).

In Clayton Valley, most of the lithium in the brine may have been brought to the basin from nearby hot springs that appear to be genetically related to volcanic rocks of Tertiary and Quaternary age that flank Clayton Valley. This possibility is suggested by the observation that, if the water now issuing from the springs were to be concentrated to one-tenth of its present volume, its composition would approximate that of the brine (Table V). Moreover, the presence of halite and gypsum and the lake beds suggests a high rate of evaporation during sedimentation.

It must be remembered, however, that the chemistry of the springs may reflect to a large extent contamination by the brine. White (1957) points out that probably only ten percent of the composition of hot springs can be attributed

to juvenile water and that ninety percent is derived by reaction with country rock or mixing with meteoric water during ascension to the surface. This may well be the case for the hot springs in Clayton Valley.

The occurrence of lithium in the playa sediments as well as in the brine suggests therefore an alternate hypothesis, namely that the lithium may have been contributed to the playa through the weathering and leaching of country rock exposed around Clayton Valley. If so, one could expect to find there units of relatively high lithium content. This hypothesis was tested by sampling the extensive outcrops of faulted and tilted lacustrine and volcanic sediments of the Esmeralda Formation (Fig. 2).

ROCKS PERIPHERAL TO CLAYTON VALLEY

Esmeralda formation

The distribution of lithium in the Tertiary sediments suggests a natural areal subdivision into a lithium-rich and a lithium-poor province. These have been designated as follows:

- a) Province A—consisting of the Esmeralda formation and the volcanic ash-fall tuff exposed east of Clayton Valley.
- b) Province B—comprising the Esmeralda formation exposed north and west of Clayton Valley (Fig. 2).

Bulk sample analyses indicate that sediments in Province A contain an average of 650 ppm Li, while only 40 ppm Li was recorded in Province B (Table VI). Similarly, analytical data on the water soluble portion of the samples indicate that the sediments of the Esmeralda formation exposed east of the valley are significantly higher in li-

TABLE VI

Lithium concentration in bulk samples^a from the Esmeralda formation exposed north and east of the playa

NORTH		EAST	
Sample No.	Li ⁺ (ppm)	Sample No.	Li ⁺ (ppm)
W1	40	TE1	710
W2	60	TE2	910
W3	20	TE3	860
W4	20	TE4	910
W5	20	TE5	780
W6	60	TE6	400
W7	70	TE7	390
W8	30	TE8	710
		TE9	160

^aSamples washed once with distilled water

TABLE VII

Concentration of soluble lithium, sodium, and potassium in samples from the Esmeralda formation exposed east of the playa

Sample No.	Li ⁺ (ppm)	Na ⁺ (%)	K ⁺ (ppm)
TE 1	32	1.28	540
TE 2	14	0.80	210
TE 3	115	1.39	300
TE 4	60	1.56	390
TE 5	60	1.39	240
TE 6	20	1.47	300
TE 8	80	1.52	2660
TE 9	60	0.89	330
TE10	30	0.22	260
TE11	140	1.08	380

thium, sodium, and potassium than samples collected north of the valley (Tables VII, VIII).

The Esmeralda sediments exposed east of Clayton Valley consist principally of marls very similar to the playa sediments. Numerous thin ash beds occur throughout the 350-foot section studied. These occur both in unaltered form and in layers altered to phillipsite. Subaerial erosion creates a typical badland topography (Fig. 4).

X-ray studies of the -2μ fraction of each of several samples of the marls reveal a mineralogy similar to that of the playa deposit. Four clay minerals are present:

1. smectite
2. illite
3. kaolinite and chlorite

The smectite in the sediments of this section was identified as hectorite on the basis of morphology and chemistry. Electron micrographs (Fig. 5) showed the presence of abundant lath-shaped hectorite particles similar to those found in the playa.

The direct influence as a source area of the Esmeralda formation exposed east of the valley on the geochemical character of the playa sediments is clearly shown on Figure 6. Lithium data on the clay fraction of playa samples indicate that samples with the highest lithium concentration lie on the eastern side of the playa in a zone immediately adjacent to the lacustrine marls of the Esmeralda formation. The lithium concentrations decrease westward and northward as the distance from the lithium-rich Tertiary outcrops increases.

Although the variations in lithium content shown in the playa sediments and brine correspond to variations in the lithium content of the Tertiary rocks that flank the playa, the ultimate source of the lithium is obscure. As the Tertiary sediments appear to have formed in an environ-

TABLE VIII

Concentrations of soluble lithium, sodium, and potassium in samples from the Esmeralda formation north of the playa

Sample No.	Li ⁺ (ppm)	Na ⁺ (%)	K ⁺ (ppm)
W1	10	0.91	170
W2	10	0.76	270
W3	8	0.44	60
W5	9	0.46	50
W6	8	0.12	40
W7	16	2.60	220
W8	6	0.11	100



Figure 4. Tertiary Esmeralda formation exposed east of the Clayton Valley playa and south of Angel Island; the view is northeast. Subaerial erosion creates a typical badland topography.

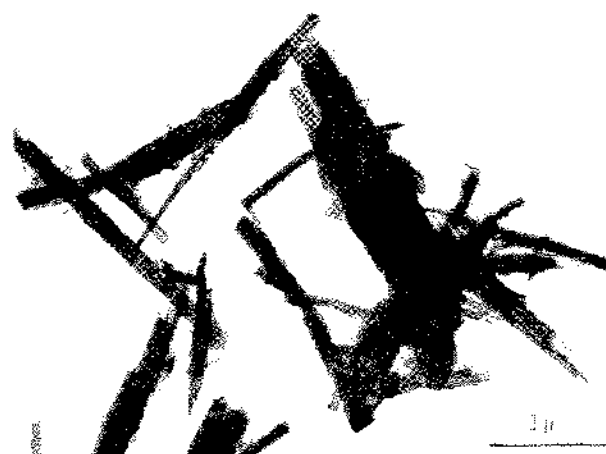


Figure 5. Hectorite laths—Tertiary Esmeralda formation exposed east of Clayton Valley—dispersion of -1μ fraction e.s.d.—23,000.

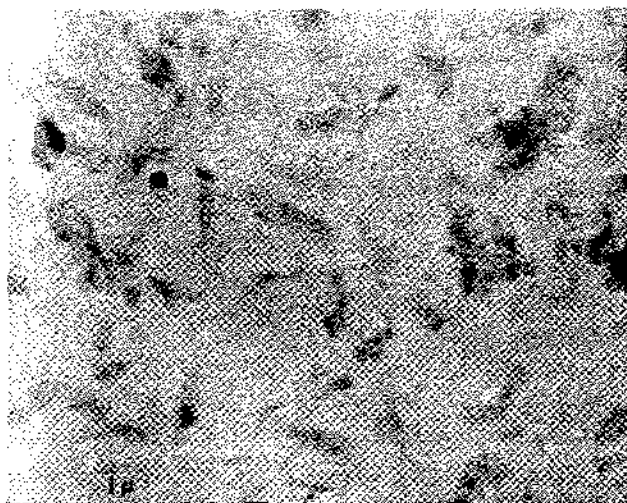


Figure 8. Halite laths—Tertiary volcanic tuff exposed east of Clayton Valley—Dispersion of -2μ fraction e.s.d.—42,000X.

a fresh-water environment. This is also evidenced by the presence of five ash beds which are composed of unaltered glass. The presence of gypsum from 230 feet to 130 feet (70–40 m) reflects an increasingly saline environment while maximum salinity developed during the deposition of the upper 130 feet (40 m) of sediments which contain abundant halite as well as gypsum. Interbedded halite, gypsum, and clay beds indicate that salinities fluctuated considerably during that interval.

The variations in salinities were no doubt controlled by variations in precipitation and run-off during Pleistocene time when the mountainous areas to the west were the sites of intermittent glaciation. This influence was well documented by a study of the sediments of Searles Lake, California (Smith, 1966). The pluvial periods, equivalent to glacial periods in the highlands, provided an increased amount of precipitation and runoff which resulted in the formation of temporary lakes in structural depressions of the Basin and Range Province. During these periods, the basins received principally clays and coarse detritus. During the drier interpluvial stages, excessive evaporation led to an increase in salinity and resulted in the precipitation of various evaporite minerals. The nature of the saline suite in Clayton Valley indicates that the salinity trend, while irregular, developed progressively.

Evidence of pluvial and interpluvial stages similar to those obtained in Searles Lake is not obvious in Clayton Valley. Portions of the upper section of cores are missing, and halite is not concentrated in two obvious layers as in Searles Lake but occurs throughout the upper 130 feet (40 m) of sediments. A sample of clay collected at 122 feet (37 m) in well FX-6 (Fig. 2) was dated at 26,900 years b.p., indicating a Middle Wisconsin age. On the other hand, two well-defined salt layers exist in well FX-2 (Fig. 9) and

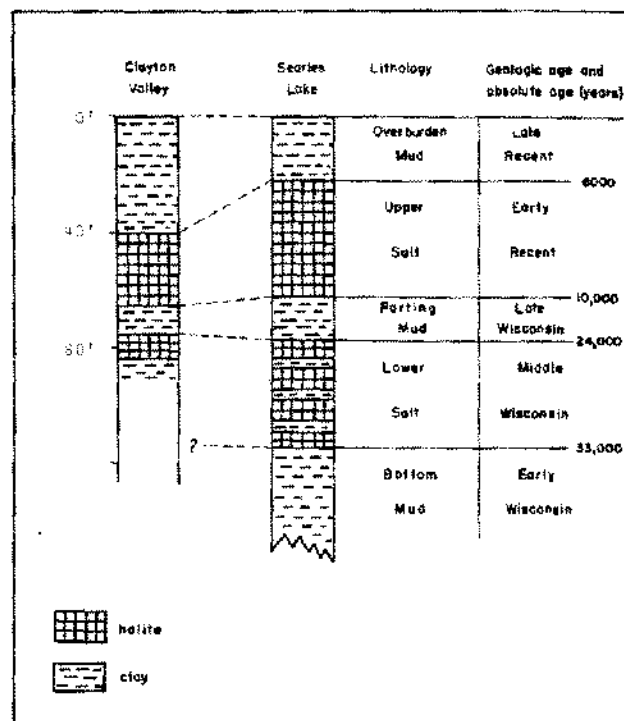


Figure 9. Correlation (?) of Clayton Valley with Searles Lake (Searles Lake section modified after Smith, G.I., 1966). One inch (2.5 cm) equals 40 ft (12 m).

suggest that the section may possibly be equivalent to that of Searles Lake. If the core section in well FX-2 is stratigraphically equivalent to that in well FX-6, then the clay that separates the two salt layers in well FX-2 (68–76 feet, 20.6–23.1 m, Fig. 9) is probably equivalent to the parting mud of Late Wisconsin age as recognized at Searles Lake (Smith, 1966).

Although the sedimentation in Clayton Valley is undoubtedly related to the glacial events in the western United States, additional cores and age determinations will be necessary to establish a more detailed and precise correlation with these events.

EVOLUTIONARY MODEL OF CLAYTON VALLEY

The presence of lithium-rich sediments and salts in the rocks surrounding Clayton Valley indicates that the basin has been the sedimentological and chemical end-product of a series of events which began in Late Tertiary time and resulted in the formation of the present deposit.

The nature and distribution of the Tertiary sediments around Clayton Valley indicate that the Tertiary environment became enriched in lithium after the deposition of the thick ash fall tuff now extensively exposed in the region. If equivalent to a similar ash-fall tuff present in the

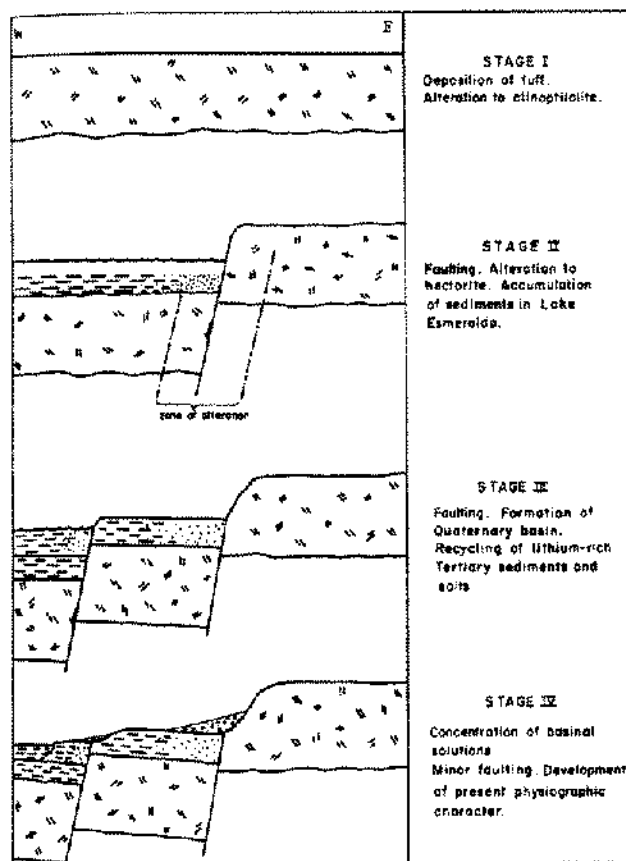


Figure 10. Idealized evolutionary model of Clayton Valley. The diagram represents an east-west cross-section across the eastern side of the valley.

Silver Peak Range, located west of the valley, it is lower to middle Pliocene in age.

Following the deposition of the ash-fall tuff (Fig. 10, stage I), faulting disrupted the area and created a structural depression into which the Esmeralda sediments exposed east of the playa accumulated (Fig. 10, stage II). The eastern and southern limits of the basin probably coincided with the arcuate fault proposed by Albers and Stewart (1965). The northern boundary is not known and the relationship of these sediments to those exposed to the north in the Weepah Hills is not altogether clear.

The detritus deposited in the Tertiary Esmeralda basin consisted mainly of hectorite and clinoptilolite derived from the alteration of the volcanic tuff and of sediments supplied by the pre-Tertiary country rocks. The occurrence of hectorite along a fault zone suggests that the alteration of the tuff to clay was restricted to the zone and that the fault acted as a conduit for lithium-bearing solutions. The chemical nature of the basinal waters was probably influenced by the character of the solutions which rose along the fault zone and by the nature of the alteration and weathering by-products.

Renewed faulting in the Quaternary period followed the deposition of the Esmeralda beds and resulted in a smaller structural basin into which (Fig. 10, stage III) the lithium-bearing sediments and interstitial salts of the Esmeralda formation were recycled. Gravity profiles (Robinson, McKee, and Moiola, 1968) indicate that bedrock occurs 1350 feet (410 m) below the present surface of the playa.

Minor faulting and erosion have controlled and determined the present physiographic character of the valley (Figure 10, stage IV).

CONCLUSIONS

Clayton Valley is a Quaternary structural depression which contains a lithium-rich brine of economic importance. The occurrence of lithium was favored by a peculiar combination of chemical, structural and climatic conditions.

The accumulation of lithium in the basin appears to be the result of a series of events which began in late Tertiary time. The alteration of a Tertiary volcanic ash-fall tuff to hectorite along a narrow fault zone indicates that lithium-rich solutions were already available in the Tertiary environment. The altering solutions fed along the faults and the by-products of the alteration and weathering reactions probably controlled the chemistry of the depositional environment of the Tertiary Esmeralda basin.

Renewed faulting activity in the Quaternary created a new structural depression into which the Tertiary sediments and salts were recycled.

Concentration of basinal solutions to brine strength was progressive and has continued to the present time. The climatic conditions which led to the conditions favorable for concentration were also controlled by the glacial events in the Sierra Nevada.

The presence of hot springs at the periphery of the playa suggests a possible origin for the present brine. Whether the springs represent true juvenile water or have been contaminated by the brine remains undetermined. The evolution of Clayton Valley suggests strongly that the composition of the brine has been derived in large part from the leaching and the weathering of lithium-rich Tertiary sediments.

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