

BROMIDE GEOCHEMISTRY OF SOME NON-MARINE SALT DEPOSITS IN THE SOUTHERN GREAT BASIN

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ABSTRACT

The Wisconsin Upper Salt and Lower Salt in Searles Lake regularly contain about 50 ppm Br, compared to a mean of 20 ppm in the Early to Late Pleistocene Mixed Layer in Searles and the correlative salt in Panamint Valley. At least one period of dessication is suggested by high bromide in unit C of the Mixed Layer. Bromide in both the Pliocene Virgin Valley and Avawatz Mountain salt rocks is 6 to 10 ppm. This low range is consistent with derivation from older marine salt rocks eroded from the Colorado Plateau by an ancestral Colorado River.

The Wisconsin salts at Searles accumulated at a rate possibly consistent with the recent flux of chloride in the Owens River, but these rates are several times the present input of chloride into the entire Owens drainage, including atmospheric precipitation and a small contribution from thermal springs. The halides may have been held over in Pliocene sediments such as the Waucobi-Coso lake beds. Various lines of evidence about Pliocene geography of this area admit the possibility that the Waucobi-Coso sediments may also have received some of their halides from an eastern source of marine evaporites either by a westward-flowing river or by westward-moving weather systems.

INTRODUCTION

The general geochemical evolution of lake waters in the Great Basin was first developed by Hutchinson (1957), and with more detailed evidence by Jones (1966). The processes dominant in the alteration of the major ion concentrations are weathering, evaporative concentration, the precipitation of salts and silicates, and losses by wind or by infiltration into lower sediments. Among individual lakes, Searles Lake has probably received the most attention, and in particular, the evaporative history leading to the formation of the upper two salt bodies has been deduced in detail from mineralogical relations by Smith and Haines (1964) and Eugster and Smith (1965). As a supplement to such general studies, the detailed study of a single element is interesting both as evidence for the origin of this element and for its contribution to the history of the brines and salts. As an example, Smith (1966) was able to pinpoint the source of most of the borate in the Searles Lake deposits as the Hot Creek springs at the far north end of the Owens River drainage. Incidental to our study of the distribution of sulfur isotopes in marine evaporites, Holser and Kaplan (1966) measured S^{34}/S^{32} ratios in Searles Lake salts and brines, and suggested considerable loss of sulfate by reduction to hydrogen sulfide. Now I will describe the distribution of bromide beneath Searles Lake, with particular emphasis on the contrast between all the pre-Wisconsin age deep salts, and the better-known Wisconsin and Holocene salt bodies near the top of the section. I will then calculate a geochemical balance of chloride and bromide in Searles Lake, in the Owens River drainage from which it was derived, and in the Panamint Valley into which it overflowed. Finally I will present new data on some other salt deposits in the Great Basin.

CHLORIDE AND BROMIDE IN INTERIOR BASINS

Some important aspects of bromide geochemistry are shown in Figure 1 (Holser, 1966), on a logarithmic plot of Cl/Br ratio. These two elements are of particular interest because by far the largest reservoir of them is the sea itself.

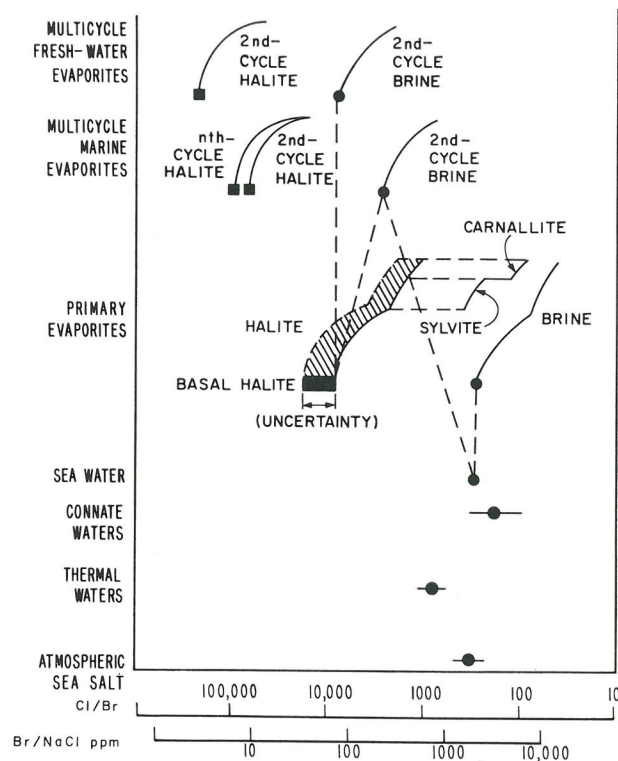


FIG. 1. Summary of the weight ratio Cl/Br in various natural settings, after Holser (1966).

In the main only one thing happens to these elements throughout the whole geochemical cycle: halite is crystallized in evaporite deposits, taking with it a small fraction of the bromide and leaving behind a brine with a lower Cl/Br ratio. If these halite salts are later redissolved by either ocean water or fresh water, the new brine will have a markedly higher Cl/Br ratio, and the salts precipitated from it in a second cycle are even more purified, with an extremely high Cl/Br ratio. The bromide concentrations in marine salt rocks are in the range of 50-200 ppm, and, for halites en-

tirely derived from these by a cycle of fresh water solution and crystallization, are in the range 5–20 ppm.

Inasmuch as the sea is the main reservoir for chloride and bromide, interior basins must ultimately derive these elements from that source. The route may be fast and direct as when spray is carried up from the present ocean and later falls with precipitation or as dry fallout from the atmosphere into the basin. The Cl/Br ratio of atmospheric ("cyclic") salts so far as it is known, is near the same value of 300 found in the ocean. A second route from the sea to a

playa lake is by the inclusion of connate waters in ancient marine sediments that were later uplifted and drained. Cl/Br in connate waters is usually a little lower than sea water, around 200, possibly because of concentration of bromide in, and later release from, organic matter in sediments. A third and very important route for halides is precipitation as marine evaporites and later uplift and erosion by desert streams. As indicated on Figure 1, such material will have a very high Cl/Br. Finally, volcanism, and especially hot springs, are an important source of the halides.

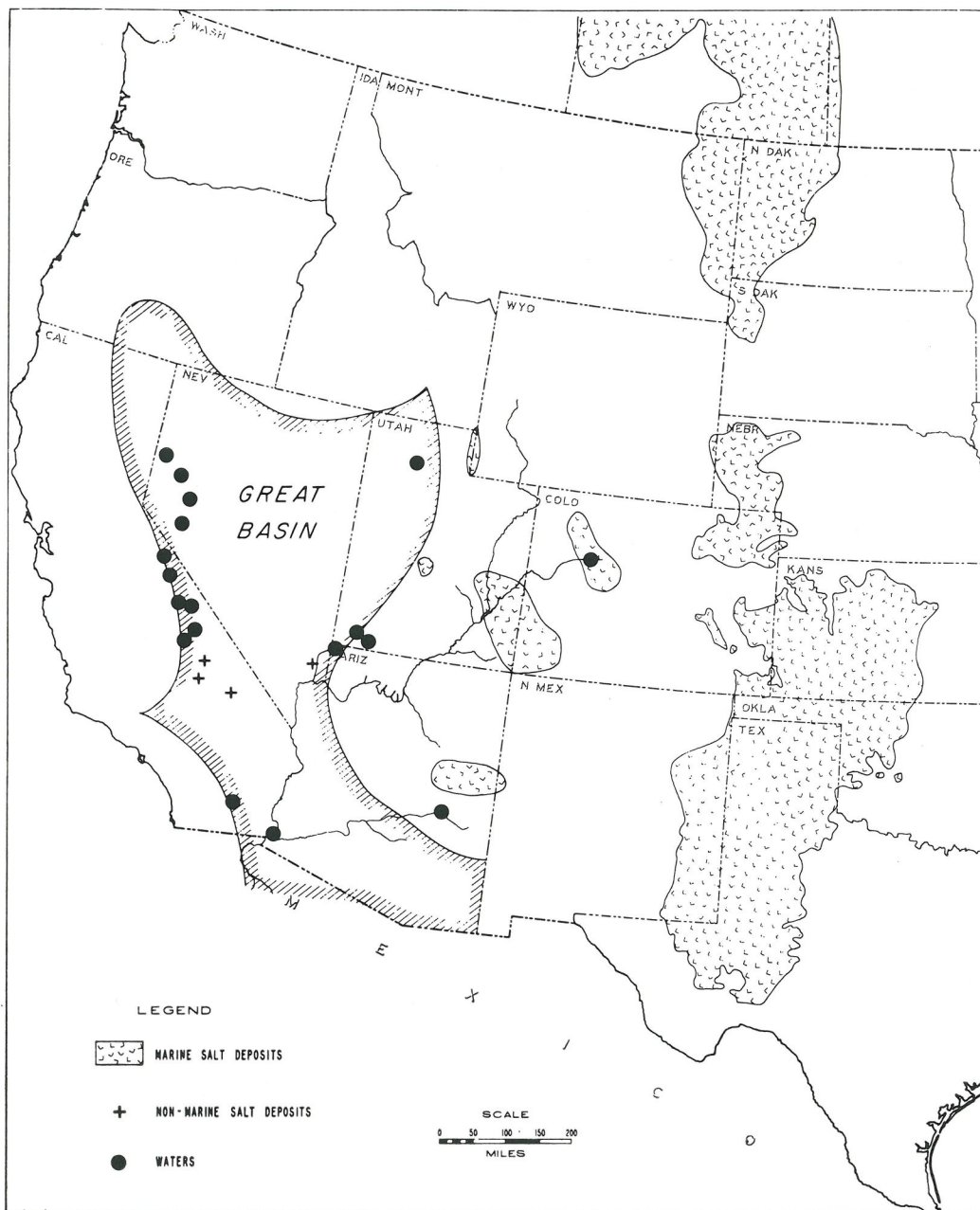


FIG. 2. The Great Basin in relation to marine evaporites [after Le Fond (1969) and McKee, *et al.* (1967)]. Location of samples analyzed for Cl/Br of non-marine salt rocks are shown by crosses, and of associated waters by circles.

Although it seems likely that most volcanic halides also came from earlier sediments, their ultimate origin is really not clear. In any case, most halides closely associated with volcanic activity have Cl/Br 2-5 times higher than sea water, although the data are still very scarce.

It is not usually appreciated that in the Basin Range Province, despite the extensive area it covers, very few marine evaporites are known. The distribution of marine salt deposits, as shown in Figure 2, is for the most part east of the Rocky Mountains, with the major exception of the Paradox Basin section, of Pennsylvanian age, on the Colorado Plateau. A minor amount of Jurassic Arapien salt outcrops in the Sevier Valley at the very eastern edge of the Basin. In southwestern Utah and southeastern Nevada beds of gypsum are common in the Triassic Moenkopi Formation (McKee, 1954) and in the Permian Toroweap and Kaibab Formations (*e.g.* McKee, 1952) extending far north in Nevada as the Arcturus Group (*e.g.* Bissell, 1964). Salt rock has not yet been found in those rocks, but most areas are known only in outcrop, where collapse breccias (Bissell, 1964) indicate possible salt at depth. No marine evaporites at all are known farther west in the Great Basin, and in this respect it is almost unique among sedimentary basins of the world.

As shown in Figure 3, the ultimate source of halides in the Great Basin lakes must be: (1) from atmospheric sea salt transported over the Sierra Nevada by wind; (2) by erosion off the Colorado Plateau of marine salts or connate waters; (3) thermal waters; or perhaps (4) by some mechanism of deflation out of the salts and connate waters east of the Rocky Mountains. The possibility of undiscovered marine evaporites closer to the present basins must also be considered, directly or as an ultimate source of (3). The nonmarine salt deposits that will be discussed are shown by crosses on Figure 2: Searles Lake, Panamint Valley, Avawatz Mountains, and Virgin Valley. Supplementary analysis of various brines and fresher waters are shown by circles both as a result of this work and that of Whitehead and Feth (1961).

ANALYTICAL METHODS

Salt rocks were analyzed by our usual colorimetric procedures (Holser, 1966) by Mr. Gale Baker and Mrs. Vina Spiehler at Chevron Oil Field Research Company. The presence of even a moderate amount of trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) gave a solution of high pH which had to be acidified to a pH of 5 before the colorimetric analyses could proceed.

Some waters were analyzed by the above colorimetric procedure. Others were analyzed by neutron activation analysis. Prof. R. H. Filby analyzed some at the Nuclear Radiation Center, Washington State University, Pullman, Washington. Samples and standards were irradiated for 4 hours in a thermal neutron flux of 8×10^{12} n/cm² sec. About a week following irradiation, after Na activity had decreased sufficiently, samples were counted for 36-hour Br⁸² at 0.777 MeV, using a Ge-Li crystal detector. Other samples were analyzed at Gulf-General Atomic, Inc., San Diego, California, irradiating for 30 minutes at flux of 1.8×10^{12} n/cm²

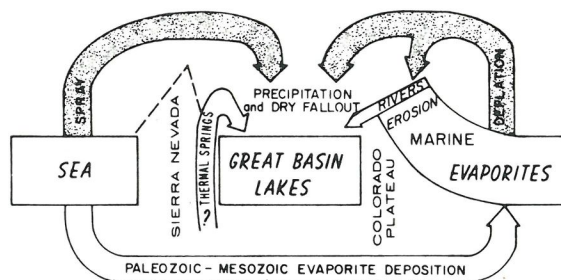


FIG. 3. Possible paths of chloride and bromide from the sea into the Great Basin.

sec., and counted with an NaI(Tl) scintillation detector. The latter procedure included undetermined amounts of interference from activity of Sb and As.

OWENS RIVER DRAINAGE

Searles Lake Salts. The geology of the Searles Lake evaporites has been described by Smith (1962, 1966, 1968). During the Pleistocene, Searles Lake received drainage from the old Owens River system, as shown in Figure 4 (Gale, 1914b, Blackwelder, 1954; Blanc and Cleveland, 1961). Although much of the clastic sediment load of this system remained in the Owens and China basins, most of the soluble material reached the Searles Lake basin and much of that precipitated there during desiccation stages of that lake. Occasional overflows spilled into Panamint Valley and even into Death Valley (Gale, 1914b). Figure 2 also shows locations in which the present water supply of the Owens River system has been sampled.

A section of the sediments in Searles Lake is given in Figure 5, generalized from a core log published by Haines (1959) for the upper part of the section, and by Smith and Pratt (1957) for a core penetrating to 875 feet. These cores were made available for examination and sampling by the U. S. Geological Survey in 1959.

The principal features for our purposes are the beds containing halite, shown in white on Figure 5, which occur intermittently from the bottom of the core to the surface itself. The most important stratigraphic change in the sequence occurs within the interval known as the Bottom Mud of early Wisconsin age; salts older than this are mainly trona and halite, with lesser amounts of gaylussite and pirssonite; above the Bottom Mud the salts also contain burkeite, borax, hanksite, and the other complex carbonates and sulfates for which the deposit is famous. The latter much-studied Middle Wisconsin to Holocene section is divided by the Parting Mud into the Lower Salt and the Upper Salt; thinner mud layers further subdivide the lower of these sections. Below the Bottom Mud, the Mixed Layer also shows alternations of mud, trona, and halite, and some of these mud layers are probably as important and continuous as the younger mud units.

Halite is by far the dominant halide mineral in the Searles Lake section, although northupite ($\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot \text{NaCl}$) is a minor constituent of the salts and muds, and hanksite ($9\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3 \cdot \text{KCl}$) is important

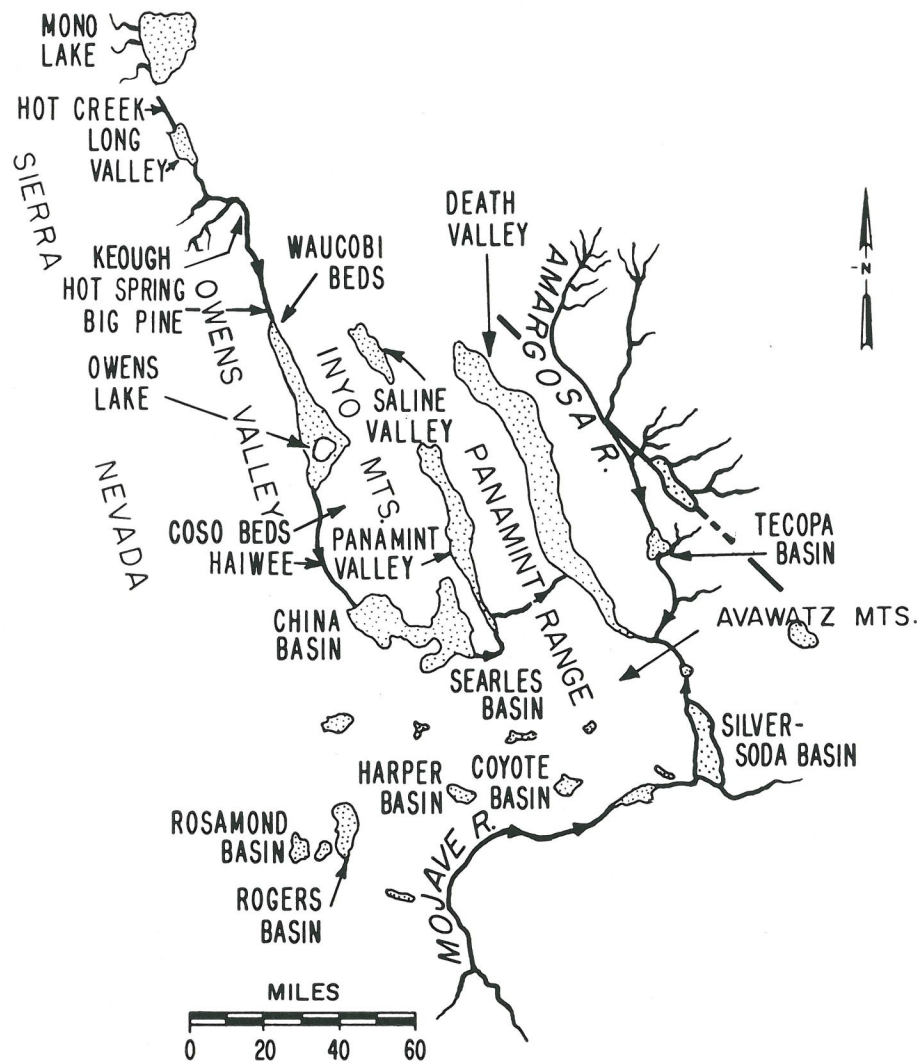


FIG. 4. Possible Pleistocene drainage systems in the southwestern part of the Great Basin, modified from Cleveland (1961).

in some beds of the Upper Salt. Most of my samples were chosen from halite-rich zones. The samples were dissolved in water, recrystallized by evaporation and then thoroughly remixed. Therefore, the analyses actually represent bromide content of water-soluble salt in each sample, mostly halite and the remainder trona.

Bromide analyses and detailed sample descriptions are shown in Table 1. The profile of bromide values (Fig. 5) shows two features of particular interest. Firstly, nearly all the samples of the Upper and Lower Salts lie within the range 40–60 ppm Br (weight fraction of soluble salt), with a mean of 50 ppm, when the analyses are weighted by the thickness of halite in each part of the section, whereas in the Mixed Layer Br concentrations are mostly in the range 10–20 ppm, with a mean of 20 ppm. The second feature is extreme irregularity; several samples contained more than 100 ppm Br, whereas others were near zero. In order to study this feature further, 13 samples were analyzed at

close intervals within on bed of halite in Unit C of the Mixed Layer, as shown in Figure 6. Within this 10-foot bed, Br ranged from 6 to 180 ppm. Samples from different parts of the core diameter (which was only 5 cm) gave about the same values, although samples a few centimeters up and down the core were different by a factor of 30. These facts, and extensive experience with bromide profiles of older salt rocks, indicate that these vertical variations are real, and neither an artifact of the analyses nor a random variation in space. They probably represent real bedding features. Within this set of detailed samples, the wild variations in bromide content could not be correlated with grain size of the halite, the amount of fluid inclusions, or the associations of trona and clay.

In general, one expects bromide to increase in halite as the bromide is left behind and concentrated in brine during advanced stages of evaporation. The highly irregular variation in bromide content, particularly in Units D and E of

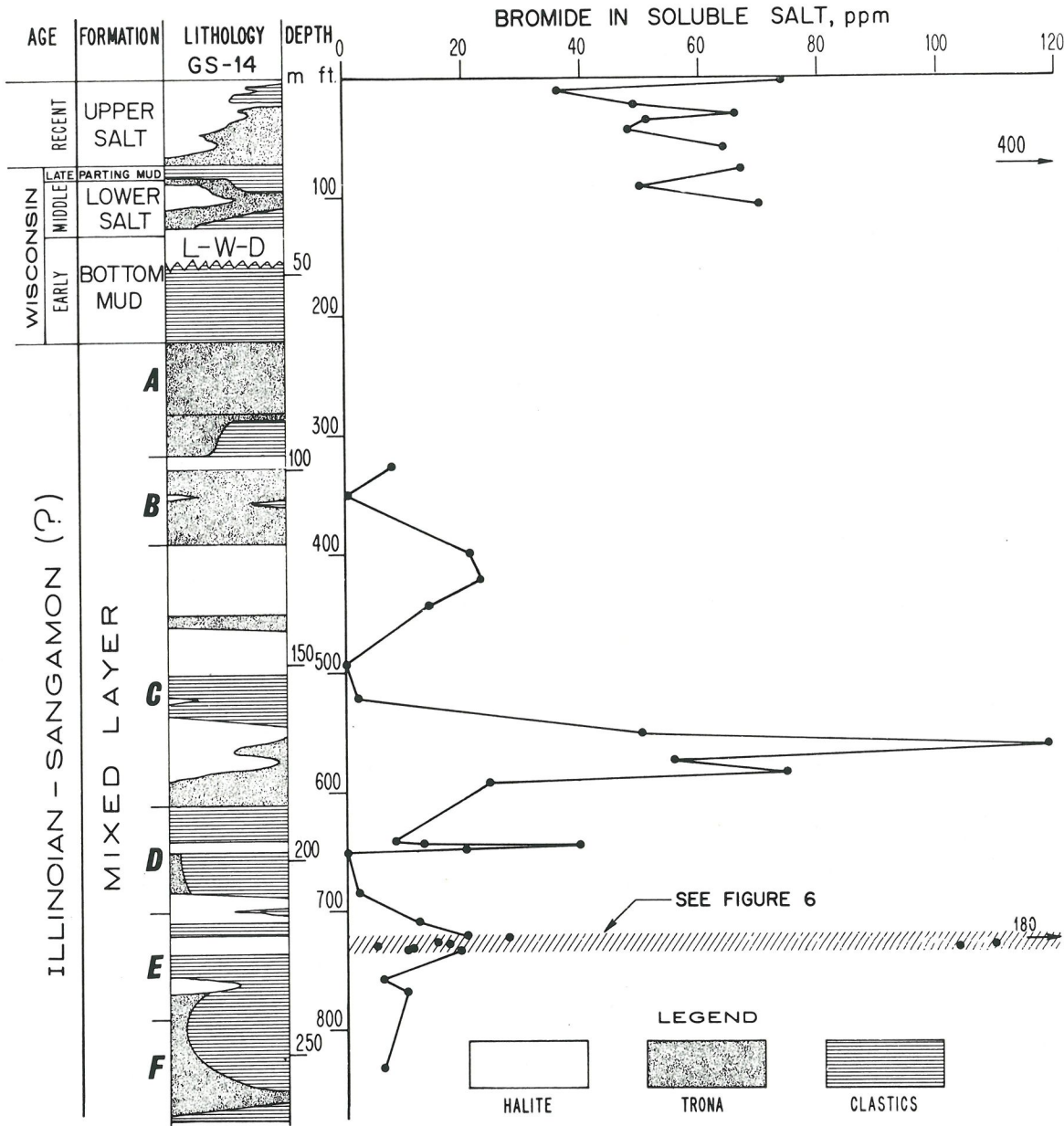


FIG. 5. Bromide profile of Searles Lake salts.

the Mixed Layer (Figure 5), therefore suggests short periods of near desiccation of small amounts of brine that failed to mix with the main brine body. These could have been very local, in both vertical and horizontal dimensions. The irregular rise toward a peak at 560 feet in Unit C suggests, on the other hand, a gradual net increase in the extent of evaporation of a larger body of brine, with which the surface evaporating layer occasionally mixed. Conversely, the return to extremely low values of bromide in the upper part of Unit C and Unit B should indicate a new inflow of water with the very high Cl/Br ratio that seems to be characteristic of this entire early period.

Interpretation of these bromide profiles in terms of the march of evaporation, as is customary in dealing with thick sections of marine salt, is possibly not warranted; many of these layers of salt could have been deposited by a brine that was isolated by intervening mud layers from previously concentrated brines, therefore, the mean level of bromide content in each layer would indicate the Cl/Br level of the source at that particular time, but be unrelated to the extent of desiccation of previous layers.

The peak of the bromide profile in Unit C occurs just below where Hay and Moiola (1963) found unusual concen-

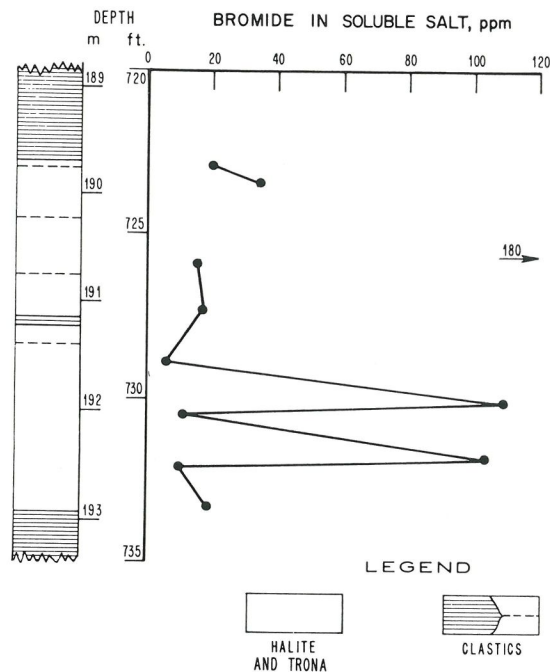


FIG. 6. Details of bromide distribution in one salt layer of Unit C of the Mixed Layer.

trations of boron as searlesite and potassium as K-feldspar. A few individual high bromide analyses are also found in Unit F, where Hay and Moiola found additional concentrations of searlesite and K-feldspar. Taken together, these facts suggest some concentration, by evaporation, of Br, B, and K at these times in the history of the lake, but without formation of borate and potassium salts such as prevail in the Upper and Lower Salts. Eugster and Smith (1965) analyzed the salt mineralogy in terms of activities of H_2O and CO_2 , and show (Eugster and Smith, 1965, Fig. 22) highs for both activities at 540–570 feet. A high a_{H_2O} generally corresponds to a low salinity, which would contradict the above conclusion. However, G. I. Smith points out in personal discussion that his conclusions were based on negative evidence, and that below the lowermost occurrence of gaylussite at 545 ft, a_{H_2O} may indeed have been low.

Panamint Valley. The location of Panamint Valley east of Searles Lake is shown in Figure 4. Three cores through its sediments were described by Smith and Pratt (1957 p. 57–62) and were made available for sampling by the U. S. Geological Survey. Salt, almost entirely halite, occurs at depths of 70–260 and 430–530 feet, in only one of the holes.

Samples were analyzed for bromide at six depths between 100 and 530 feet (Table 1). All showed bromide between 5 and 11 ppm, with a mean of 7 ppm.

Overflow water from Searles Lake into Panamint Valley occurred most extensively during deposition of the Bottom Mud in Searles Lake although some overflow occurred during deposition of the Parting Mud (Smith, 1966, 1968).

TABLE 1. BROMIDE ANALYSES OF SALT IN THE WESTERN INTERIOR U.S.

Sample No.	Depth, Ft.	Br in Soluble Salt, ppm ^a	Remarks ^b
<i>Searles Lake, Drill Hole GS-14, in Central Facies (Eugster and Smith, 1965, p. 481) logged in Haines, 1959, p. 227–244.</i>			
16662-1	4.0	44	Yellow-green clay. (31 ppm)
		74	10-mm halite cubes.
-2	10.8	36	Halite and [10%] clay.
-3	22.1	49	Halite [75%] and trona [25%] (59 ppm).
-4	25.6	3.4	Hanksite, $9Na_2SO_4 \cdot Na_2CO_3 \cdot KCl$
-5	30.2	66	Halite.
-6	35.6	51	Halite and hanksite.
-7	44.5	48	Halite (45 ppm).
-11	59.9	64	Halite.
-13	62.2	52	Halite and trona. (102, 97 ppm).
-14	62.9	55	Halite and trona. (50 ppm)
-17	64.1	52	Halite and trona. (59 ppm)
-19	72.9	400	Clay [and 20% pirssonite].
-20	78.2	67	Clay
-21	92.0	50	Halite and trona.
-25	106.3	70	Halite and trona.
<i>Searles Lake, Drill Hole GS-10, in Central Facies, Lower Salt, logged in Haines, 1959, p. 196.</i>			
16662-28	101.6	34	Trona and [10%] northpote, $MgCO_3 \cdot Na_2CO_3 \cdot NaCl$
<i>Searles Lake, Drill Hole LWD, all in Mixed Layer; logged in Smith and Pratt, 1957, p. 25–51.</i>			
16658-11	326.9	8	Halite, massive, near base of 10-ft halite bed at top of Unit A.
-10A	350.8	1	Coarse halite crystals in trona-halite aggregate; center of Unit B.
-10B		4	Mud in same sample.
-9	398.2	21	Halite coarse crystals [10%] mud; top of 50-ft. halite bed, top of Unit C.
-6	422.5	23	Halite, coarse crystals, with a little trona; middle of same halite bed.
-5	443.3	14	Halite, coarse crystals; bottom of same halite bed.
-4	491.6	3	Halite, coarse crystals; at base of 30-ft. halite bed near center of Unit C.
16658-2	521.7	2	Halite in coarse crystals with [30%] clay, at top of 70-ft sequence of halite interbedded with trona and clay, lower part of Unit C (19 ppm).
-45	551.0	49	Halite, medium-grained, same sequence.
-44	561.6	118 ± 3	Trona and halite, same sequence (130 ± 5, 135 ± 5).
-43	574.0	55	As above.
-42	583.8	74	Halite and a little trona, same sequence.
-41	590.4	24	Halite, medium-grained, base of same sequence, near base of Unit C.
-40	640.3	8	Halite, coarse crystals at top of 10-ft halite bed in middle of Unit D.
-39	642.5	13	Halite, same bed.
-38A	645.0	39	Halite crystals, same bed.
-B		43	Mud in same sample.
-37	647.5	20	Halite, same bed.
-36	650.0	4	Halite, base of same bed.
-35	684.9	2	Halite with a little trona [and pirssonite], at top of 20-ft halite bed on boundary units D and E.
-30	709.0	12	Halite, medium-grained, and clay, at base same bed.
-29	722.9	20	Halite, in clear coarse cubes in light green clay [with some pirssonite], near top of 10-ft salt bed near middle of Unit E.
-28	723.4	27	Halite, medium-grained irregularly intergrown crystals with disseminated clay inclusions; same bed.
-27	725.6	180	Halite, as above, with somewhat irregular 2-mm bands of clay spaced 25 mm; same bed.
-26	725.9	15	Halite, coarse-grained, clear, with fluid inclusions; same bed.
-25	727.3	17	Halite, coarse-grained clear cubes and octahedrons in clay matrix; same bed.
-24	728.9	6	Halite, clear, with coarse, irregularly intergrown crystals; same bed.
-23	730.1	109	Halite, in medium-grained, translucent white intergrown crystals; same bed.

(TABLE 1-(Continued))

Sample No.	Depth, Ft.	Br in Soluble Salt, ppm ^a	Remarks ^b
16658-22	730.5	11	Halite, in very coarse clear intergrown crystals; same bed.
-21	730.8	103	Halite, in medium-grained, clear, intergrown friable aggregate; same bed. [northupite reported]
-20	732.1	10	Halite, medium-grained, gray-green, with [20%] disseminated clay; same bed.
-19	733.3	19	Halite, coarse-grained, clear, partly cubic; base of same bed.
-18	757.2	6	Halite, coarse-grained, with 5% clay; near top of 12-ft sequence of interbedded halite and [pirssonitic] clay, near base of Unit E (6).
-15	768.2	10	Halite, medium-grained, with 20% clay; base same sequence.
-14	832.0	6	Trona with a little halite, fine-grained and faint clay bands; a 2-ft bed halfway between top of Unit F and bottom of hole (14).
<i>Panamint Valley, Drill Hole 3, logged in Smith and Pratt, 1957, p. 57-62.</i>			
16659-2	102.8	5	Halite with some silt interbeds; and minor calcite and gypsum, 30-ft below top of uppermost, 140-ft thick salt bed.
-5	120.0	5	As above, near middle, same bed.
-7	200.0	5	As above, near base, same bed.
-11	263.0	11	As above, at base of second, 40-ft thick salt bed.
-13	438.0	8	As above, near top of third, 70-ft thick salt bed.
-21	530.0	7	As above, at base, same bed.
<i>Virgin Valley, Nevada, outcrop in Pliocene Muddy Creek Formation at Salt Cove described by Mannion, 1963, p. 171.</i>			
18862-1		6	Salt rock, coarse, brown, [with some glauconite].
<i>Virgin Valley, Nevada, Drill Hole SSC-1, as above.</i>			
18861-1	2119.4	5	Salt rock, as above, in salt beds from 2070 to 3058 ft depth.
-4	2587.8	7	Salt rock, as above.
-2	2587.8	6	Salt rock, as above.
-3	3034.0	6	Salt rock, as above.
<i>Avawatz Mts., California. Pliocene (?) lake beds described by Ver Planck, 1958, p. 29-31.</i>			
17798-1		9	
-2		9	
<i>Redmond, Utah, Jurassic Arapien salt in outcrop described by Pratt, Heylman and Cohenour (1966).</i>			
19233		17.9	Salt rock, coarsely crystalline, red with intermixed silt.

^a Mostly in halite.

^b Parentheses indicate our other probably less reliable analyses. Brackets indicate information from the published core logs.

The uppermost salts in the Mixed Layer of Searles Lake contained 1-8 ppm Br (Fig. 5; Table 1). The bromide analyses are consistent with this time of inflow.

Unfortunately no cores are still available to test the bromide content of the salt bodies underlying Death Valley (Gale, 1914a) at the end of this drainage system.

Geochemical budget of halides in the Owens system. During much of its history, Searles Lake received waters through a series of overflowing basins reaching back to the Owens Valley (Figure 4). The following calculations are an attempt to find out where, within this system, the halides originated during the Wisconsin-Holocene (Lower and Upper Salt) stages of the lake. Calculating from published

data, Table 2, and summing both Upper and Lower Salts, the total mass of chloride is estimated at 48×10^7 T. Most of this is in halite of the Upper Salt. Using the extensive Cl^{14} data, and including the underlying muds during which halides were accumulating but not depositing, the rate of Cl accumulation was about 21,000 T/yr for Late Wisconsin-Holocene time, and 2400 T/yr for the Early and Middle Wisconsin.

Turning now to the source of the halides, data from the Owens River is pertinent, but it is preferable to look at measurements made before the Owens River was emaculated by the aqueducts of the Metropolitan Water District, early in this century. Such data are available only for chloride. In 1908 (Table 3) the Owens River at Big Pine passed 8700 T/yr Cl; so the amount of chloride flowing in the Owens River was of the right order of magnitude to account for the Wisconsin-Recent salt in Searles Lake. At Round Valley it was 4400 T/yr, and these two values are reasonably consistent with an estimate of present Aqueduct flow of 6000 T/yr.

Flow of chloride characteristic of the Owens River in the last half century therefore is able to account for less than half of the chloride accumulated in the Upper Salt and Parting Mud considered as one unit. If all of Wisconsin time is considered together, the present flow is sufficient. That would mean a carry-over of chloride in the lake from the Bottom Salt to the Parting Mud, which could have been effected by either re-resolution of a large volume of salt, or mixing of interstitial brine into the overlying lake brine. Alternatively, flow of chloride down the Owens River system would have had to be more than twice as large during Late Wisconsin time.

Even if the present flow accounts for the chloride, the question remains as to its ultimate source. Smith (1966) calculated that the thermal springs still flowing at Hot Creek above Long Valley (Figure 4) could account for most of the borate in the Wisconsin salts of Searles Lake, but only for about 5 percent of the chloride. Other data (White, Hem and Waring, 1963, p. F42; Cleveland, 1962, p. 18, 20) could be used to reduce this figure by a large factor, and on the other hand at least three more thermal areas should be added (Table 3, Figure 4): Keough Hot Spring, Coso Hot Springs, and Little Lake (Waring, 1965). In any case, it is evident that the present flow of thermal springs in the Owens drainage does not make a substantial contribution to the total flow of chloride. Volcanic activity in Owens Valley has been much greater in the recent past; for example, Pakiser, Kane and Jackson (1964, p. 61) estimated 200-300 cubic miles of volcanic material in Mono Basin and Long Valley. A large increase in flow of chloride along with volcanism is conceivable, although such an origin only further begs the question as to how the chloride got into the area of the basin.

Another source of chloride that must be considered is atmospheric precipitation, which in this basin is principally snow. Data were integrated (Table 3) over the Owens River drainage to get a total water input of 2.3×10^9 T/yr.

TABLE 2. HALIDES IN SEARLES LAKE, IN METRIC TONS

	Upper Salt	Lower Salt	Upper Salt and Lower Salt
Volume of salt formation (including intercalated muds), measured from Haines (1959, pl. 5-6).	$11.9 \times 10^8 \text{m}^3$	$8.4 \times 10^8 \text{m}^3$	
Volumes at 40% porosity, of brine	$4.8 \times 10^8 \text{m}^3$	$3.4 \times 10^8 \text{m}^3$	
Volumes at 40% porosity, of rock	$7.1 \times 10^8 \text{m}^3$	$5.0 \times 10^8 \text{m}^3$	
Mass of brine at $\rho = 1.3$	$6.2 \times 10^8 \text{T}$	$4.4 \times 10^8 \text{T}$	
Volume fraction of halite in formation (G. I. Smith, pers. commun.)	0.45	0.30	
Volume of halite	$3.2 \times 10^8 \text{m}^3$	$1.5 \times 10^8 \text{m}^3$	
Mass of halite at $\rho = 2.17$	$7.0 \times 10^8 \text{T}$	$3.3 \times 10^8 \text{T}$	
Mass of Cl, in brine (analyses Table 4)	$5.8 \times 10^7 \text{T}$	$3.6 \times 10^7 \text{T}$	$9.9 \times 10^7 \text{T}$
Mass of Cl, in halite	$43 \times 10^7 \text{T}$	$20 \times 10^7 \text{T}$	$63 \times 10^7 \text{T}$
Total	$48 \times 10^7 \text{T}$	$24 \times 10^7 \text{T}$	$72 \times 10^7 \text{T}$
Br in brine (analyses Table 4)	$53 \times 10^4 \text{T}$	$25 \times 10^4 \text{T}$	$78 \times 10^4 \text{T}$
Br in halite at 50 ppm	$3.5 \times 10^4 \text{T}$	$1.7 \times 10^4 \text{T}$	$5.2 \times 10^4 \text{T}$
Total	$56 \times 10^4 \text{T}$	$27 \times 10^4 \text{T}$	$83 \times 10^4 \text{T}$
Cl/Br	860	870	870
Time of deposition including underlying "mud" (Smith, 1962)	23,000 yrs	$\sim 100,000$ yrs	$\sim 125,000$ yrs
Rate of Cl accumulation	21,000 T/yr	$\sim 2,400$ T/yr	$\sim 6,000$ T/yr

Direct analyses of this water are not available, even for chloride content. However, Feth, Rogers and Roberson (1964) find a mean of 0.5 ppm Cl for Sierra Nevada snowfall, and this order of magnitude is substantiated by two new analyses of fresh waters from Sierra lakes (Table 4). The total of about 1000 T/yr Cl in precipitation is rather

short of the present flow of Cl in the Owens system. It is similarly short of requirements of Searles Lake, although the higher precipitation (4 to 6 times as much—see below) during pluvials would have meant a similar increase in chloride input, as chloride concentration in inland rainfall seems to be independent of the amount of precipitation (Junge and Gustafson, 1957, p. 167).

TABLE 3. CHLORIDE SOURCES ON OWENS DRAINAGE, METRIC TONS/YEAR

Sources	T/yr
Precipitation in Owens Valley ^a , 2.3×10^9 T, at Cl=0.5 ppm (mean of Sierra snow: Feth, Rogers and Roberson, 1964, Table 2)	1200
Hot Creek Springs, 1.7×10^6 T/yr (Waring, 1965) at Cl=200 ppm (White, Hem, and Waring, 1963, p. F42)	340
Owens R. at Round Valley, 1908, 2.1×10^8 T/yr at Cl=21 ppm (weighted mean from data in Van Winkle and Eaton, 1910, p. 119)	4400
Keough Hot Springs, 1.6×10^6 T/yr (Waring, 1965) at Cl=180 ppm (Table 4)	290
Owens R. at Big Pine, 1908, 2.7×10^8 T/yr at Cl=32 ppm (weighted mean from data in Van Winkle and Eaton, 1910, p. 121)	8700
Aqueduct at Haiwee, 3.5×10^8 T/yr attributable to Owens Valley sources ^b , at Cl=17 ppm ^c	6000

^a Integrated from isohyetal maps for mean precipitation for 1895-1941 (Rantz, 1969) supplemented by the detailed hydrologic survey of Lee (1912) and mean snow survey data for 1931-1960 (Calif. Dept. Water Resources, 1965).

^b Current normal runoff, personal communication, 1969, from Byron Weinstein, Los Angeles Department of Water and Power.

^c 1960-61 average of all aqueduct water, personal communication, 1961, from D. W. Graham, Los Angeles Department of Water and Power.

An important possibility is that chloride input by precipitation has been held back during earlier times of sediment accumulation, particularly in lakes, to be delivered during times of erosion.¹ This process concentrates the chloride from a possibly much longer time span. Unconsolidated sediments fill the Owens Valley and Long Valley to depths of as much as 1000 feet, and consolidated Tertiary sediments fill Owens Valley to 5000 feet and Long Valley to 10,000 feet (Pakiser, Kane, and Jackson, 1964). To the extent that chloride was deposited with such sediments, as is commonly the case in a desert climate, a change to conditions in which they were eroded or flushed (including by thermal springs) would add their chloride to the water flow of a later time.

Bromide analyses of Owens Valley waters. Some analyses (Table 4) were made of waters in the present Owens Valley River drainage, in an attempt to corroborate the mass balance calculations made for chloride. Waters of the Owens River, Owens Lake, and the total for Searles Lake were all in the general range of Cl/Br 500-900, somewhat higher than sea water and lower than marine salt rock.

¹ This idea was developed as a result of discussions with George I. Smith.

TABLE 4. CHLORIDE AND BROMIDE IN WATERS OF THE OWENS SYSTEM

Location	Cl, mg/l	Br, mg/l	Cl/Br	Reference
Florence Lake (west side of Sierra Nevada; 9/7/65)	0.38 ^a	<0.003 ^a	>130	Holser
Hot Creek (5/17/57)	200	0.7	285	White, Hem & Waring, 1963
Pine Creek, at Pine Lake (8/1/65)	0.11 ^a	<0.003 ^a	>35	Holser
Pine Creek, at Rock Creek (8/1/65)	4.4 ^a	<.017 ^a	>260	Holser
Keough Hot Spring (7/30/65)	180	.11 ^b	1700	Holser
Owens River at Big Pine (8/1/65)	10.7	.022 ^b	490	Holser
Aqueduct at Haiwee (7/30/65)	8.7	.017 ^b	520	Holser
Owens Lake (9/27/58)	138,000	280	500	Holser
Searles Lake—Upper Brine	121,000	860	140	White, Hem & Waring, 1963
Searles Lake—Lower Brine	105,000	580	180	White, Hem & Waring, 1963
Searles Lake—total of both brines and both salts			870	Table 2

^a Neutron activation analysis by Gulf-General Atomic.

^b Neutron activation analysis by R. H. Filby.

Bromide could not be detected in the samples analyzed from the fresh headwaters of the Owens River, but the lower limits established for Cl/Br are also consistent with this value. Analyses from the hot springs are still in question. A more extensive program of sampling, with evaluation of possible modern contamination, will be required to accurately define the bromide geochemistry of the Owens Valley drainage.

BROMIDE DATA FROM OTHER PARTS OF THE GREAT BASIN

Other sampling in the Great Basin is shown in Figure 2. The crosses are salt rocks, and in addition to Searles and Panamint basins in the ancestral Owens River system, they include the Avawatz Mountains south of Death Valley and the Muddy Creek formation near Overton, Nevada. These analyses are supplemented by a few water analyses from the Colorado River drainage and by analyses of lakes in the western Great Basin, mainly from data published by Whitehead and Feth (1961). A large amount of Cl/Br data has been accumulated for the Great Salt Lake-Bonneville system, by J. H. Feth, B. F. Jones, and me, and will be published elsewhere.

Avawatz Mountains. Lake beds containing halite, whose age is possibly Pliocene, have been described from the Avawatz Mountains south of Death Valley by Ver Planck (1958, p. 29-31) and by others. Although it has not been possible to untangle the complicated local structure of these deposits, data on the bromide content of the salt were important to the overall picture of the Great Basin. Samples of halite from outcrop and drill cores were all near 10 ppm (Table 1), not unlike those of the Mixed Layer at Searles Lake. The Avawatz Mountains deposit is probably older than the oldest Searles Lake deposit, surely from a different drainage, and did not contain trona. The drainage system from which the Avawatz Mountains salt was derived is unknown, so this material cannot be compared with present water analyses.

Virgin River Area. One section of salt rocks accessible to

analysis was the several thousand feet of halite in the Pliocene(?) Muddy Creek Formation near Overton, Nevada. It was described by L. E. Mannion (1963, see also Longwell, 1936), to whom I am indebted for both core and outcrop samples. These were also all very low in bromide, having only 5-7 ppm (Table 1).

The drainage source of these deposits is not certain. Upstream now is the Virgin River, for which some analyses are shown in Table 6. It has Cl/Br of 1400, and much of the halide load is contributed by La Verkin Hot Springs along the Hurricane Fault at Hurricane, Utah. Halides in this spring are probably derived, at least in part, from previously undetected salt rock in the underlying Triassic Moenkopi Formation, which is known to contain gypsum over a wide area (McKee, 1954). Other parts of the Colorado River drainage show a very high Cl/Br associated with buried salt deposits: U. S. Geological Survey data at Glenwood Springs, Colorado, and Salt Banks, Arizona have Cl/Br of 8000-9000 (Table 4), possibly from solution of the Pennsylvanian Eagle and Permian Supai marine salt rocks, respectively. The entire Colorado River has been calculated to derive 98 percent of its chloride by erosion (Van Denburgh and Feth, 1965). Similar solution by a river drainage from the Paradox or Eagle evaporites of the Colorado Plateau, along the direction of the present Colorado River, could have supplied the interior basin in which the Muddy Creek evaporites were formed.

Other Great Basin Lakes. Table 5 reviews some Cl/Br ratios published for some other lakes of the Great Basin. Much more detail is available on the drainage areas of the Great Salt Lake and Salton Sea (Table 6), but will be discussed elsewhere. Of particular importance is the thorough study by Hardie (1968) of the brines permeating the desiccated playa of Saline Valley, just east of Owens Valley. Only the mean is given here, but the Cl/Br varied extremely among brines from various parts of the playa body, which Hardie has found to have originated in different terrains of the drainage. The other lakes analyzed, which lie north of Owens Valley in the western Great Basin and none of which are desiccated, have Cl/Br of several hundred.

TABLE 5. CHLORIDE AND BROMIDE IN SOME GREAT BASIN LAKES

Location	Number of Samples	Mean Values, ppm			Reference
		Cl	Br	Cl/Br	
Saline Valley (1963-64)	34	73,000	200	625 ^a	Hardie, 1968
Mono Lake (8/19/58)	1	14,300	57	250	Holser
(3/26/57)	1	14,500	35	410	Whitehead & Feth, 1961
Walker Lake (11/20/58)	2	1,640	3.5	470	Whitehead & Feth, 1961
Big Soda Lake (8/28/58)	1	7,570	18	420	Whitehead & Feth, 1961
Fernley Sump (4/23/59)	1	25,200	32	790	Whitehead & Feth, 1961
Pyramid Lake (10/22/58)	1	1,920	5.4	360	Whitehead & Feth, 1961
Great Salt Lake (4/6/58)		140,000	86	1600	Whitehead & Feth, 1961

^a Mean of ratios, *not* ratio of means.

ANALYSIS AND DISCUSSION

General sources of chloride and bromide. Flow in the present Owens River can possibly account for the chloride in the Wisconsin-Holocene section of Searles Lake, but only about a sixth of that flow can be attributed to input to the basin from current atmospheric precipitation. I have suggested above that chloride could have been held in the basin in older sediments, and released by erosion or leaching (including thermal springs) in more recent times. Similarly, while mass balance calculations for other Great Basin lakes were interpreted by Broecker and Walton (1959) in terms of atmospheric input and output, Feth (1959) pointed out the probable importance to the mass balance of salt held in earlier lacustrine sediments.

The bromide data suggest that such halides may not only have been held over in older sediments, but that they may not have come directly into the older basins as atmospheric sea salt. Present meteorological conditions in all of the Great Basin are clearly dominated by storm tracks (Klein, 1967) that come directly over the Sierra Nevada from the Pacific Ocean. Meager data from Hawaii (Duce, *et al.*, 1963) show Cl/Br of 190 ± 40 in rainfall and 420 ± 100 in aerosols aloft. Compared with Cl/Br of 870 in Searles Lake (Table 2), and even with 400-600 in nondesiccated lakes of the western Great Basin (Table 6), these data sug-

gest a significant contribution by other halides, such as those recycled from marine salt deposits (Fig. 1).

The older salt rocks, of Pliocene and early Pleistocene age, must have derived an even larger proportion of their halides from such second-cycle sources. The Mixed Layer at Searles Lake, the correlative salt in Panamint Valley, and the salt beds in the Avawatz Mountains and Virgin Valley, all have very low bromide, in the range 6-20 ppm. Analyses and amounts of brine are not available with which to calculate directly the overall Cl/Br of the input responsible for these older salts. However, the distribution relations between brine and salt, as shown schematically in Figure 1, indicate that a Br content of 10 ppm in halite must correspond to a Cl/Br in the source of at least 2000 even if the ratio of unevaporated brine to precipitated halite is very large.

An ancient Colorado River as source of the Virgin Valley and Avawatz Mountain salt. Some waters of the present Colorado River drainage that may be closely associated with older marine salt rock deposits have such an expectedly high Cl/Br (Table 5). Mannion previously suggested (1963) that the Virgin Valley evaporites originated by solution of older marine evaporites underlying the Colorado Plateau, carried by an early form of the Colorado River,

TABLE 6. CHLORIDE AND BROMIDE—COLORADO RIVER BASIN

	Cl	Br	Cl/Br
Springs, Glenwood Springs, Colorado (9/9/57):			
White, Hem and Waring, 1963)	290	0.03	9700
Virgin River, Virgin, Utah (3/30/67)	26	<0.1	>260
La Verkin Springs, Hurricane, Utah (3/30/67)	3,650	3	1200
Virgin River, below Hurricane (3/30/67)	414	0.2	2000
Virgin River, Littlefield, Arizona (3/30/67)	436	0.32	1400
Colorado River, Lake Mojave, Arizona (4/6/59):			
U. S. Geol. Surv., unpubl.)	78	.0	>800
Salt River (3/3/59; Feth and Hem, 1963)			
Salt River, above Salt Banks, Arizona	843	0.1	8400
Springs, Salt Banks, Arizona	13,000-20,000	6-9	2000
Salt River, Roosevelt, Arizona	794	.0	>8000
Colorado River, Yuma (12/7/62)	140	.07	2000
Salton Sea (1963-1965)	14,600-15,700	8.1-10.8	1500-1900

that ended in an interior basin where the extensive series of salts were evaporated. According to Longwell (1954) the Colorado River did not go through to the Gulf of California until after Muddy Creek time. The bromide data are consistent with this conclusion. Furthermore, similar values for the salt deposits of the Avawatz Mountains, which may also be of Pliocene age, suggest that such drainage may have extended somewhat further west. The history of structure and geomorphology of the area, as summarized for example by Eardley (1962, p. 497), is also consistent with this picture, as block faulting and development of closed basins continued all through the period in which the Muddy Creek Formation was being deposited.

Immediate source of the Searles Lake halides. Another question concerns the ultimate origin of the salts that ended in Searles Lake and Panamint Valley. The suggestion was made in an earlier section that at least the Wisconsin-Holocene part of the Searles Lake section was derived in large part from salts held in older sediments of the Owens Valley drainage. Can a similar source account for the older Mixed Layer at Searles Lake and the correlative salts of Panamint Valley?

In Searles Lake the most recent such salt is perhaps 150,000 years old, and the core bottoms in salt that may be as much as 700,000 years old (Smith, 1968). Hay (1966, p. 34) has correlated two tuffs in the lower part of this section with two at depths of 400 and 600 feet in Owens Lake, and this lies within the approximately 1000 feet of "younger Cenozoic deposits" that Pakiser, Kane, and Jackson (1964 pl. 3; p. 53) trace by seismic sections up the Owens Valley, to where it includes the Bishop tuff of 700,000 years of age (Bateman, 1965, p. 151).

These sediments in Owens Valley are underlain by a thick section of high-velocity and presumably more consolidated sediments, designated "older Cenozoic deposits" by Pakiser, Kane, and Jackson (1964). Along the eastern edges of Owens Valley sediments of the Coso beds (Hopper, 1947, p. 417) southeast of Owens Lake have been dated at 2.1–2.3 m.y. (Evernden, *et al.*, 1964, p. 177, 189) and of the Waucobi beds (Walcott, 1897; Nelson, 1966) east of Big Pine have been dated at 2.3 m.y. (J. F. Evernden, in Hay, 1966, p. 20), which is late Pliocene (Ericson and Wolin, 1968). On the basis of these dates, I suggest that both are correlative with part of the "older Cenozoic deposits" of the Owens Valley fill. Both Waucobi and Coso sediments are in part lacustrine, and Hay (1964, p. 1370) mapped zeolites showing two episodes of high salinity in the central portion of the Waucobi Lake, although no crystalline salts have been noted in either Waucobi or Coso sediments. Leaching or erosion of such older sediments could have been the intermediate source of salts in any part of Searles Lake.

Ultimate source of the Searles Lake halides via a westward Pliocene drainage. The Waucobi-Coso sediments probably cover a sufficient span of time to account for the halides in the whole Searles Lake Section simply by the

accumulation of atmospheric precipitation. However, that still leaves the problem as to why the Mixed Layer salts in Searles Lake and the correlative salt in Panamint Valley have a low bromide content like the Pliocene salts of Virgin Valley and Avawatz Mountains. The Waucobi-Coso beds, which I have suggested as an intermediary for the Searles Lake salts, are of about the same age as the Virgin Valley salts. Is it possible that halides trapped in the Waucobi-Coso beds also were derived in part from a river eroding marine salt from the Colorado Plateau?

The Avawatz Mountains are only 30 percent farther from the Paradox Basin salt rocks than the Virgin Valley, and Owens Valley is 50 percent farther than Virgin Valley. The Coso beds were deposited on a surface of low relief (Hopper, 1947) at an elevation of only 1,000–1,500 feet (Axelrod and Ting, 1960). The major deformation that blocked out the basins and ranges, and that would have cut off such long range westward-flowing drainage, was probably correlative with the Sierra Nevada scarp that has been dated as 1–2 m.y. B.P. (Dalrymple, 1964). Although the Waucobi beds were usually considered (Knopf and Kirk, 1918, p. 52; Hay, 1964) to have been deposited in the Owens Valley at the foot of the Inyo scarp, the relatively old radio metric date for the beds requires renewed consideration of Walcott's (1897) original suggestion that westward dips of 3 to 10 degrees may have been due to a westward tilting of the Inyo Range; the beds may lie on a warped mountain front similar to those mapped on the west side of Owens Valley (Bateman, 1965, p. 174). Thus even Waucobi beds may have been in a position, in Pliocene time, to receive inflow from outside the area. To answer the question framed above, an ultimate origin for part of the Searles salts, through erosion and drainage from the Colorado Plateau, is barely possible, if the unknown Pliocene topography was favorable.

The lower bromide content of the earlier Searles Lake (Figure 2) would then be explained as a larger contribution of such salt, relative to the atmospheric sea salt, a certain amount of which would always have been entering the basin.

Ultimate source of the Searles Lake halides via easterly storms. An alternative route for old marine salt into the western Great Basin is through atmospheric precipitation (Figure 3). This would require a substantial alteration from the present climatic pattern, which is essentially winter precipitation brought on by low-pressure systems associated with the westerly jet stream. Although a *major* change of this atmospheric circulation can be ruled out on theoretical grounds (Sawyer, 1966), a precipitation regime dominated by summer storms from the southeast is now found as far west as central Arizona (Bryson, 1957). A shift to this regime in earlier times could have carried salt dust high in Cl/Br from areas of Permian marine salt rock (Figure 2). In the Wisconsin section at Searles Lake Smith (1968; see also Smith, Friedman and Matsuo, 1970) found that some saline beds must have crystallized during rela-

tively dry winters, suggesting that, "... A significant difference in atmospheric circulation was responsible." In making detailed calculations of climatic factors affecting Pleistocene lake levels in the Great Basin Snyder and Langbein (1962) assumed that the seasonal distribution of rainfall was the same in Pleistocene pluvials as it is today. Recalculation assuming that summer precipitation was dominant ("seasonal factor" of say 0.75) gives precipitation/evaporation ratios of 0.75 to 0.95 necessary to maintain Pleistocene pluvial lakes in Deep Springs, Mono and Lahontan basins. Floral evidence from the southwestern Great Basin indicate precipitation in the range 30 to 40 in/yr (compared to 4 to 8 in/yr today), and cooler summers with "... Summer rains present in moderate amount ...", for both late Pliocene (Coso: Axelrod and Ting, 1960) and early Pleistocene (Chagoopa: Axelrod and Ting, 1961); during the Pleistocene winters were wetter and cooler than during the Pliocene. These considerations all indicate the possibility of an eastern source for some of the atmospheric precipitation of this area during the Pliocene-Pleistocene, but whether this would have substantially altered the nature of halide input to the basin is still conjectural.

CONCLUSIONS

1. Chloride accumulated in Searles Lake at a much greater rate than present input into the Owens Valley drainage from both atmospheric precipitation and thermal springs. Much of it may have come into the basin in Pliocene time and been held over in sediments like the Late Pliocene Waucobi-Coso lake beds.

2. Bromide in the Pliocene salt rock at Virgin Valley and the Avawatz Mountains is so low that most of it must be second-cycle, probably eroded from the Colorado Plateau and deposited in these interior basins by an earlier course of the Colorado River.

3. Bromide in the Early to Middle Pleistocene Mixed Layer at Searles Lake, and the correlative salt in Panamint Valley, are similarly low in bromide; the Wisconsin-Holocene section is higher in bromide but still somewhat short of that expected from atmospheric sea salt. If both have their immediate origin in Pliocene sediments, as postulated in (1) above, such sediments may have also had a dominant contribution of bromide from the Colorado Plateau, via either a river or an altered wind pattern.

4. In attributing low bromide in ancient salt rocks to a second cycle of erosion of older marine salt rocks (Holser, 1966; 1970), the possibilities have to be considered of transport over long distances, and intermediate holdover in other sediments; both may have been operative in the more recent examples studied here.

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