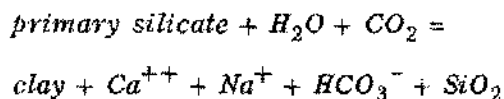


Geochemical Evolution of Closed Basin Water in the Western Great Basin

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ABSTRACT

The composition of saline waters in inland basins is largely the result of weathering processes accompanied by simple evaporative concentration and selective mineral [solid] precipitation. In the absence of older chemogenic deposits in the drainage basin to provide solutes by simple solution, water compositions are related primarily to three major types of inorganic reactions: (1) silicate hydrolysis, (2) uptake of CO₂ from the atmosphere and/or of sulfate from oxidation of sulfides, and (3) precipitation of alkaline earth compounds. Silicate hydrolysis reactions are typically combined with aqueous CO₂ uptake schematically as follows:



With increasing solution concentration, calcium is precipitated first as calcite and then, with rising salinity and sulfate content, as gypsum. However, if silicate hydrolysis proceeds more rapidly than CO₂ uptake, either because of highly reactive phases or the limited access of ground water to atmospheric or soil CO₂, the pH of the solution rises. This pH rise is accompanied by decreased calcite solubility, and further concentration provides more complete precipitation of calcium as CaCO₃. These processes ultimately lead to sodium carbonate or (with extensive mineralization in the area) sulfocarbonate waters. The rate of silicate hydrolysis is dependent on the original silica-bearing phase and the grain size. Glasses or fine-grained silicates formed at high temperatures are much more soluble in water than are quartz or clay minerals, and they are more reactive than coarse-grained silicates; indeed, the silica content of many alkaline waters is apparently related to the solubility of cristobalite or silica gel. Thus waters containing the highest carbonate or sulfocarbonate concentrations are found in basins where the major drainage areas are underlain by volcanics, fine-grained intrusives, or sedimentary materials derived from such rocks. Secondary modification of lacustrine saline water composition is brought about by CO₂ release and sulfate reduction accompanying organic decay.

The occurrence and interaction of all the aforementioned processes are well illustrated by data from several intermontane areas of the western Great Basin.

INTRODUCTION

The development of saline waters in interior basins is essentially a simple function of solute supply and subsequent concentration by evaporation. The geochemical evolution of closed basin waters can thus be described in terms of solution, transport, and mineral precipitation reactions arranged in a sequence controlled by the basin hydrology. Primary solute composition is set for the most part by the reaction of natural waters with the basic lithologies underlying each drainage basin. Secondary modifications are closely tied to hydrologic setting and process.

Because of the normal heavy dominance of sodium among the cations of continental saline waters (Truesdell, Jones, and Van Denburgh, 1965), classification or trends in compositional evolution are most succinctly described in terms of the major anions. The Great Basin waters have been subdivided on the basis of the most characteristic anion in the saline lake or playas of the major intermontane drainages. Thus, chloride is by far the most dominant dissolved species in the Bonneville Basin, whereas relatively high carbonate concentrations distinguish saline waters of the Lahontan and adjacent territories. Sulfate is characteristic of some of the smaller individual basins, as in parts of the Mojave Desert and areas immediately north. Outside the Great Basin, sulfate is the predominant anion in the saline lakes of the glaciated regions of North Dakota and Washington State.

OBSERVED TRENDS

Hutchinson (1957, p. 565) has utilized a triangular plot of anions in waters from the Lahontan Basin and adjacent areas to illustrate a general compositional trend from inflow to lake or playa waters, as shown in Fig. 1. He has suggested that the nature of such a trend may be distinctive

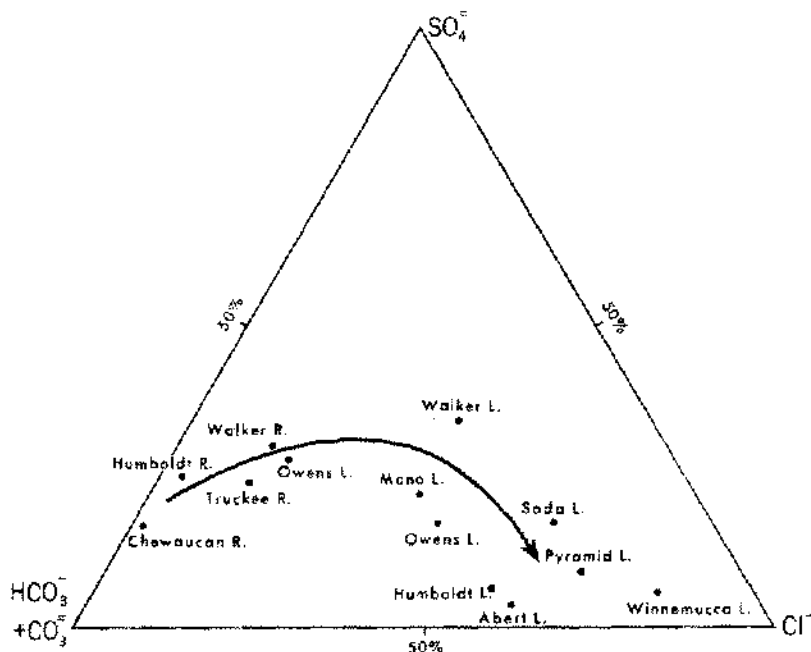


Figure 1. Anionic compositions of rivers and lakes in the Lahontan Basin and in closed basins to the north and west, after Hutchinson (1957), p. 566. Data are from Clarke (1924, pp. 166-168). All locations but Soda Lake are further discussed herein.

for particular regions, but that "the great variation in composition of the individual waters... makes it impossible to follow... a process in the data." Though Hutchinson was certainly correct in detail when pointing to "the complexity of processes occurring even in the simplest cases," it appears possible to make some generalizations based on a few fundamental processes and basic types of solute source.

In the evaporation and concentration of sea water, the trend in anionic composition is severely restricted by the high proportion of chloride and small quantity of carbonate species, because of concentration processes that have already occurred. Precipitation of calcium sulfate enriches the brine in chloride until saturation with halite is achieved and a marked reversal toward higher proportions of sulfate takes place. However, for the first tenfold increase in total salinity, the anionic proportions change less than 10 per cent. In contrast, plots of the major anion distribution in both inflow and lake or playa waters from the major closed basins in the western Great Basin reveal the large-scale changes and distinctive trends which accompany an entire course of concentration. There is significant overlap in the anion composition of initial inflow, but definite differences may characterize the waters of intermediate areas as well as the end products of interior drainage. These differences are illustrated not only for basins where one specie (carbonate, sulfate, or chloride) is heavily predominant, but they can also be distinctive for waters of intermediate anionic type.

In the trilinear plots utilized herein to illustrate major anion composition, total dissolved solids content generally increases in the direction of the chloride apex for each individual drainage basin, but this certainly is not always the case. The location of the major drainage units of the western Great Basin to be discussed is given in Fig. 3. Previously unpublished analytical data from the area are given in Table 1. Methods of analysis were generally those given by Rainwater and Thatcher (1960). Reference to analyses available in other publications is given in the explanation of the figure where the data is utilized. It must be borne in mind that the diversity of sources and of methods employed even by the same laboratories or investigators over the course of time has produced results of variable quality. The very generalized trilinear method of presentation utilized herein serves to minimize the influence of such analytical inconsistencies.

Chloride type.

The Great Salt Lake may be taken as the best example of an interior basin of the chloride type. Hahl and Langford (1964) have compiled estimates of dissolved solids contributions by surficial inflow to the lake for the water years 1960 and 61 and have calculated the percentage contributed by each major source to the total dissolved constituents. Taken in conjunction with the few special analyses presented for the area by Whitehead and Feth (1961), the trend in anionic composition for the bulk of the inflow (> 76 per cent) is directly from the dilute carbonate waters of the Weber River and east shore mountain streams, through the chlorocarbonate Bear River composition, to the very low carbonate, 5-10 per cent sulfate, waters of the lake itself (Fig. 2). The end point of this trend in solution composition is represented by the pure chloride interstitial brines of the Bonneville Desert. The Jordan River and, to a lesser extent, the artificial drains and canals which discharge to the lake have a notably higher sulfate content than other Great Salt Lake inflow as a consequence of human influences. Thus, consideration of the anionic proportions in "average inflow" would offset the general trend toward that presented by Hutchinson for the major drainages of the western Great Basin; there is considerable justification, however, for regarding this offset as artificial. In either case, the course and final result of compositional change is distinctive when compared to that for other Great Basin areas.

Carbonate type.

Though many writers have taken waters of the Lahontan Basin as typical of the carbonate type, the most extreme example of the type actually lies in the Alkali Valley of central Oregon, which is some distance north of the farthest extension of pluvial Lake Lahontan (Fig. 3). Here, in a playa of approximately 5 square miles total area, numerous circular depressions known as pot-holes (Allison and Mason, 1947) contain carbonate brines which vary considerably in total dissolved solids concentration, but much less in anionic proportions. The pot-holes are apparently fed by artesian waters evaporating at a rate roughly equivalent to discharge. The anionic composition of dilute water from a nearby well, which is probably representative of inflow to the pot-holes themselves (Fig. 4). Waters from this area afford the minimum change in anion composition with increased concentration.

Table 1. - Chemical analyses of waters from the western Great Basin
/Chemical analyses in parts per million/

No. on tag-ure	Source	Location ¹	Date of collection	Water temperature (°F)	Silica (SiO ₂) (Oz)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO ₃)	Carbonate (CO ₃)	Sulfate (SO ₄)	Chloride (Cl)	Boron (B)	Dissolved solids	pH
1.	Alkali Valley, Oreg. ² Rotholz nr. log roadway on SW side of Alkali Lake playa.	36/23-18dd	8-13-63	87	842	--	--	117,000	8,850	2,510	91,400	46,300	45,700	185	314,000	10.1
2.do.....do.....	8-13-63	96	1130	--	--	105,000	5,420	45,400	113,000	18,600	18,600	274	271,000	9.9
AW	Flowing 8" well at log roadway, SW side of Alkali Lake playa.	8-13-63	8-13-63	55	65	--	--	163	16	148	94	34	38	.77	484	9.7
1.	Abert Summer lakes basin, Oreg. ² NE end Abert Lake, 0.3 mi. from east shore. ³	33/23-db	8-7-63	75	--	--	--	14,600	522	3,640	6,980	744	12,900	33	37,600	9.7
2.	Abert Lake at gage ³	34/21-24dc	1-12-62	33	144	1.4	.6	22,000	712	5,930	9,460	960	19,300	--	55,900	9.6
C2.	Chewaucan R. at mouth ³	35/21-21bd	6-12-62	69	26	20	5.3	36	5.5	162	0	12	7.0	--	193	7.6
C3.do..... ³do.....	8-7-63	77	30	11	3.7	10	3.2	76	0	5.0	1.5	--	102	7.5
E1.	2.7 mi. NE of Valley Falls, Oreg. Chewaucan R. estuary. ³	35/21-21cd	8-8-63	75	30	10	4.0	45	4.6	115	0	5.0	34	--	190	8.1
E2.	2.8 mi. NE of Valley Falls, Oreg. Chewaucan R. estuary. ¹do.....	8-8-63	75	32	10	4.0	251	12	188	79	15	216	--	715	9.6
11.	Seepage into pit dug in muds at edge of brine pool. ¹	33/21-35bd	8-12-63	77	898	--	--	38,000	1,480	9,680	16,100	3,240	33,400	56	97,800	9.4
12.	Brine pool, west part of salt flat north of Abert Lake. ³do.....	8-12-63	63	645	--	--	119,000	3,690	0	80,300	9,230	115,000	469	309,000	9.8
13.	Seepage from pit dug in playa muds of east part of salt flats north of Abert Lake. ³	Sec. 7, T33S, R22E	7-22-64	83	83	--	--	31,800	1,450	4,090	6,830	2,250	39,300	53	84,000	9.45
31.	Abert Lake, north shore; center Bog spring feeding brine pond. ¹	33/21-35bd	8-13-63	59	52	8.0	4.9	104	14	196	16	28	45	.52	369	8.5
32.	Spv. SW of Abert Lake ¹	35/21-21ba	8-9-62	66	65	9.5	7.5	290	14	282	0	47	285	--	867	8.1
P1.	Poison Creek just above Hwy bridge, Lake Co. ¹	35/22-1ba	7-26-64	66	30	7.5	4.7	5.9	2.5	59	0	1.6	2.0	0.19	64	7.15
12.	Spv. at corral on toe of Poison Creek fan, Lake Co.	35/22-1bb	7-26-64	53.5	14	14	8.5	18	1.1	77	0	15	24	.01	156	6.65
33.	Summer lake Hot Spring ¹	33/17-12ac	10-8-48	116	96	1.4	.4	389	6.8	374	30	111	285	--	1,120	8.5
2.	Summer Lake ³	32/16-2abd	4-25-61	68	110	5.5	13	2,830	115	1,880	1,230	368	1,600	--	7,200	9.6
1.	Ana River ¹	30/17-6dd	4-25-61	58	36	5.0	2.3	38	3.6	91	0	5.6	12	--	158	8.6
Surprise Valley																
1.	Middle Alkali Lake, Modoc Co. ⁴	42/16-2N	9-17-53	55	37	17	6.2	2,330	9.0	1,010	325	510	2,360	.31	6,150	9.2
2.do..... ⁴	42/16-3R	5-5-54	75	28	17	8.9	3,180	7.5	1,300	363	576	3,330	.38	8,200	9.1
6.	Rt. 84 middle of levee Middle Alkali Lake. ⁴	42/16-2ca	3-25-59	--	36	11	31	4,080	11	1,410	664	900	4,110	.35	10,600	9.2
8.	Middle Alkali Lake, at causeway nr. center of north end of lake. ⁴do.....	8-15-63	87	39	14	.7	1,340	5.3	830	148	134	1,280	.17	3,400	9.0
	Liskey Hot Spr., Modoc Co. ⁴	42/16-8c	3-25-59	90	103	22	3.2	269	5.5	46	17	293	187	4.1	932	8.7
	Rt. 84 E side of lake, hot spring inflow to Middle Alkali Lake. ¹	42/16-12bd	3-25-59	--	79	50	6.1	562	18	151	0	597	432	7.5	1,840	7.5

See footnotes at end of table

Table 1. - Chemical analyses of waters from the western Great Basin--Continued

No. on fig-ure	Source	Location ¹	Date of collection	Water temperature (°F)	Silica (SiO ₂) (Ca)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO ₃)	Sulfate (SO ₄)	Chloride (Cl)	Boron (B)	Dissolved solids	pH
1.	Honey Lake														
1.	Honey Lake, 1.5 mi. WSW of Wendell ⁴ ...	29/15-26d	3-23-56	--	54	28	14	62	5.2	199	11	50	.40	342	8.6
2.	Honey Lake, east side at northern boundary of Herlong Ordnance Depot, 100 from shore. ¹	28/16-17cc	8-2-63	77	69	12	1.9	450	26	848	26	138	1.0	1,270	8.3
11.	Honey Lake had interstitial brine from 2 ft. pit on east side at northern boundary of Herlong Ordnance Depot 12 from edge of water. ²do.....	8-3-63	77	88	--	--	9,320	191	2,830	5,320	4,150	190	23,900	9.8
12.	Honey Lake--Continued Bag pit, Honey Lake, bottom of hole ca. 30' from lake shore. ³		8-3-63	77	85	--	--	11,900	248	3,840	6,160	4,870	44	31,700	9.7
13.	Honey Lake had, interstitial brine from 2' pit 30' from edge of water nr. inflow area of Amecdes Hot Spring. ⁴		8-2-63	82	55	--	--	18,300	1,830	5,490	8,029	12,100	44	52,900	9.7
1.	Amecdes Hot Spgs., outflow downstream from central orifice on east side Honey Lake. ²	28/16-8ac	8-6-63	87	--	10	--	249	5.6	52	0	309	--	780	7.8
2.	Honey Lake bed, interstitial brine from 2.5 ft. pit at limit of vegetation nr. inflow area of Amecdes Hot Spgs. ⁴	28/16-7dd	8-4-63	77	5.7	32	270	9,830	372	1,690	426	11,300	43	29,800	8.7
	Pyramid Lake ⁴ Pyramid Lake beach, west shore at Sutcliffe, Nev.		3-26-59	--	13	7.2	117	1,430	120	929	214	274	--	4,820	8.9
1.	Winemucca Lake basin ⁵														
1.	Winemucca Lake Valley, spring.....	27/23-27a	6-18-59	--	69	14	2.3	31.2	97	--	--	12	9	185	7.8
2.do.....	27/23-26c	6-22-59	--	38	23	3.3	849	744	--	--	149	775	2,220	7.5
3.	Winemucca Lake Valley, well, 2' deep.	26/23-11	6-24-59	--	14	28	9.3	1,695	708	--	--	305	1,790	4,040	9.3
4.	Winemucca Lake Valley, well, 12' deep.	25/23-23c	6-17-59	--	11	4.2	4.5	4,350	744	--	--	918	5,290	11,100	8.7
4.	Humboldt Sink ⁷ Humboldt Sink, Tonolow Lake.....	25/29-24dd	3-27-59	--	21	28	134	3,880	169	1,040	120	1,740	17	11,200	8.6
5.	Humboldt R. at gage about 3 mi. above Humboldt Sink.	25/31-11bd	3-27-59	--	64	63	36	2,840	52	377	38	570	--	8,100	8.5
2.	Carson Sink ⁴ Carson R. Flats, 5 mi. N of Fallon, Nev.	19/29-3b	3-27-59	--	--	0	3.2	15,900	135	3,310	9,726	8,730	63	41,000	9.9
3.	Slough, E side of Carson sink, N of Stillwater, Nev.	21/31-20	3-26-59	--	17	38	118	1,220	68	566	57	695	5.7	3,930	8.6
4.	Carson sink, 2 mi. SE of Parrau, Nev.	22/29-17b	3-27-59	--	19	201	139	56,800	3,240	322	0	786	123	152,000	7.8
1.	Monc Lake ⁴ Shoreline sample, Mono Lake at Tioga Lodge.		3-30-59	53	14	4.5	34	21,500	1,170	8,410	10,300	7,380	--	56,600	9.6
1.	Shades Marsh ⁴ Well at Old Plant.....	5/33-16	3-27-59	48	49	8.8	2.1	874	30	260	90	850	--	2,540	8.8
2.	Rhodes Marsh nr. Mina, pond in center of marsh.	5/35-15	3-27-59	--	142	17	.5	3,680	102	23	648	2,390	81	10,400	9.5
3.	Spring in center of marsh.....do.....	3-27-59	60	121	15	2.2	2,550	70	115	384	1,830	55	7,210	9.3
	Owens Lake Basin ⁷ Owens Lake, first centrifugal pump, Columbia Southern line.		5-19-61	71	653	--	--	122,000	9,120	--	--	37,900	1,200	310,000	10.3

See footnotes at end of table

Table 1. - Chemical analyses of waters from the western Great Basin--Continued

No. on figure	Source	Location ¹	Date of collection	Water temperature (°F)	Silica (SiO ₂) (mg)	Calcium (Ca) (mg)	Magnesium (Mg) (mg)	Sodium (Na) (mg)	Potassium (K) (mg)	Bicarbonate (HCO ₃) (mg)	Carbonate (CO ₃) (mg)	Sulfate (SO ₄) (mg)	Chloride (Cl) (mg)	Soluble solids (g)	pH
1.	Saline Valley ² Artesian well, 0.30 mi. W of Palm Springs.	14/38-10ab	1-21-63	--	30	34	22	86	8.1	143	0	193	36	--	7.5
2.	Tunco Mine Camp Spr.	14/38-28	1-31-64	71	28	90	35	21	4.9	144	6	264	11	--	8.4
3.	Beaveridge Canyon water.	14/38-17c	2-1-64	48	36	83	10	15	3.7	128	0	153	14	--	7.6
4.	Hunter Canyon Stream.	14/38-28b	1-31-64	51	33	72	8.9	12	2.5	122	2	122	11	--	8.2
5.	Brine from just under crust of Saline V. salt pan, 0.5 mi. N of end of old tramway.	14/38-23cc	1-22-63	--	74	538	438	101,000	1,610	534	0	8,410	158,000	166	7.6
6.	Brine from 3' depth, NW edge of Saline V. playa, 1 mi. from road intersection, N side.	14/38-19ac	2-2-64	48	1.8	477	1,670	33,000	4,560	211	135	39,200	31,500	27	8.2
7.	Brine from 3' depth, 3 mi. N of road along southern edge of playa.	14/38-20bb	1-23-63	--	--	--	--	103,000	5,190	6,200	(?)	31,400	144,000	701	8.28
8.	Surface brine from spr. area 3 mi. N of road along southern edge of playa.	14/38-18da	2-1-64	57	12	9.4	3.5	28,809	1,650	1,510	1,300	10,100	37,400	90	8.55
9.	Brine from 5' depth, NW corner of Saline Valley playa, 1.5 mi. S of road to Palm Sprn.	14/38-12bc	2-7-64	57	--	352	134	9,430	914	156	0	5,590	12,300	2.2	7.75
10.	Surface pool in ephemeral channel, 0.75 mi. E of Sta. 38 Saline V. playa.	14/38-12ad	2-7-64	--	12	378	1,210	23,900	2,860	166	0	7,390	38,900	8.1	7.88
11.	Brine from 4' depth on old tramway rd. 0.25 mi. N of main valley rd.	14/38-25ac	2-9-64	57	51	392	107	4,300	87	133	0	3,960	5,600	10	7.5

¹ Location system the same as that used by Cohen and Lowitz (1964).² Shirley L. Rettig, analyst.³ A. S. Van Denburgh, Solute balance of saline Abert and Summer Lakes, Oreg. (in preparation).⁴ J. Haruhart and R. K. Seaves, analysts.⁵ U. S. Geological Survey, Quality of Water Laboratory, Salt Lake City, Utah.⁶ U. S. Geological Survey, Quality of Water Laboratory, Portland, Oreg.⁷ Carbonate endpoint not discernible when graphed; assumed to be all bicarbonate.

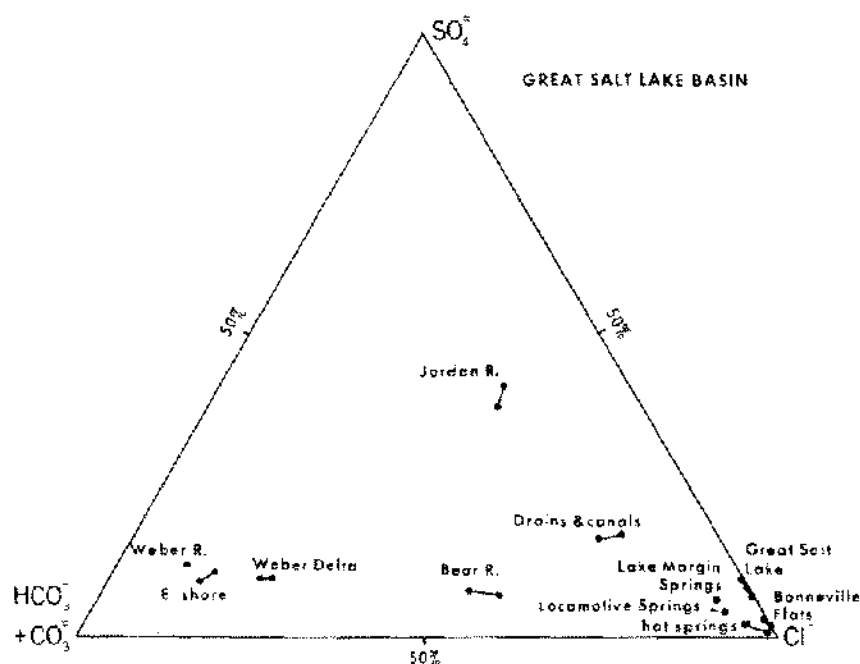


Figure 2. Major anion composition of waters from the Great Salt Lake area, Utah. Most of the points are taken from the analyses of Hahl and Langford (1964, Table 3), with additions from the data of Whitehead and Feth (1961).

Mixed waters.

Drainages included in Hutchinson's plot of anionic composition in the Lahontan adjacent basins (Fig. 3) that show some similarity in hydrochemical evolution are of mixed type, but for most of the basins compositional trends are separate and distinct. South of the Alkali Valley in Oregon, for example, the Abert-Summer Lake area contains "end-point" waters best classified as chlorocarbonate in type. These two bodies of water, both remnants of pluvial Lake Chewaucan, present a distinct contrast in the chemical nature of inflow and lake water (Van Denburgh, 1964). In total dissolved solids concentration and anionic proportions, Summer Lake and its principal inflow, the Ana Springs, are bracketed by the Chewaucan River and Abert Lake (Fig. 4). Some spring inflow suggests slight sulfate enrichment prior to reaching the lakes, but the anion trend for waters of the two adjacent basins is toward increased chloride with nearly constant sulfate content.

The effects of addition of sulfate to basin waters by hot spring systems are shown in the Surprise Valley and Honey Lake Basins of north-east California. Both drainage areas contain playa lakes occupying the downthrown parts of fault block basins. The principal inflow is from

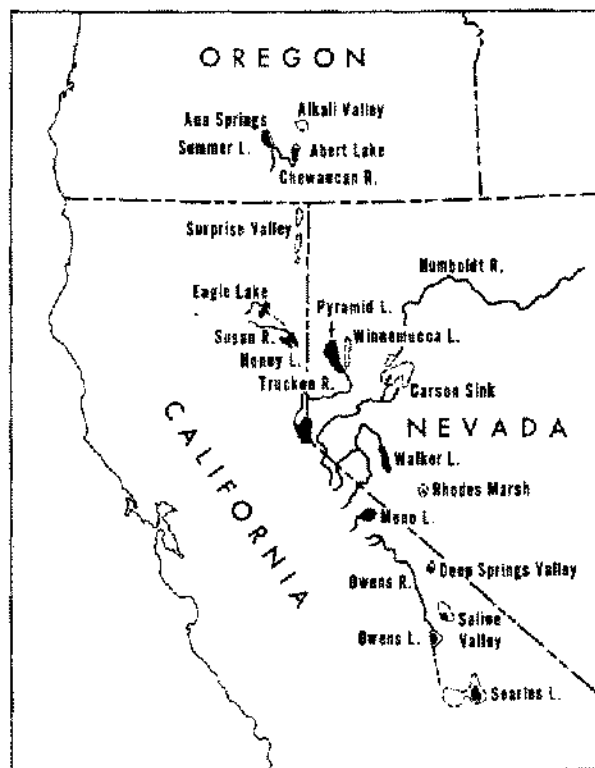


Figure 3. Index map showing the location of some of the principal closed drainage systems of the western Great Basin north of the Mojave Desert.

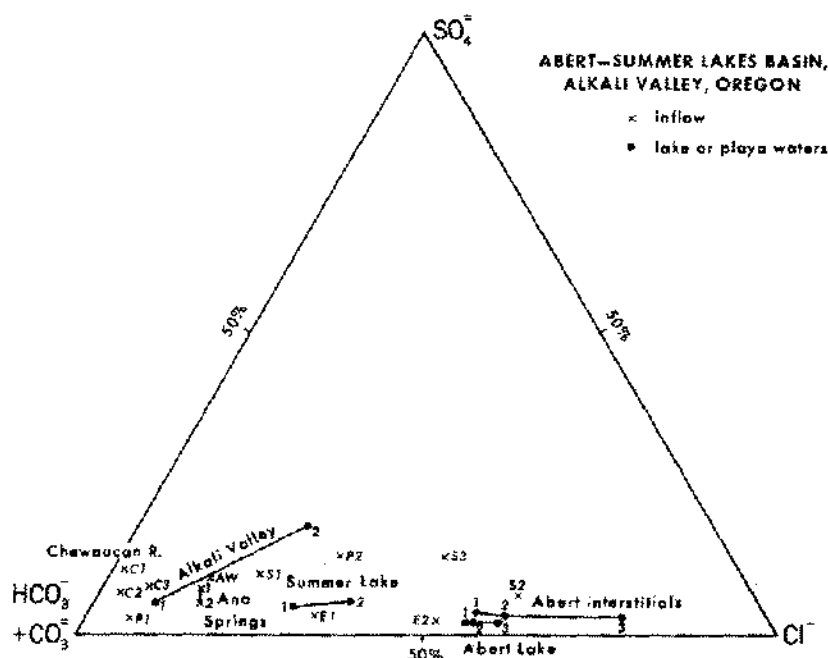


Figure 4. Major anion composition of waters from the Abert-Summer Lakes Basin and the Alkali Valley, south-central Oregon. Analysis number 1 of the Chewaucan River, Ana Springs, Summer Lake, and Abert Lake analysis number 3 all taken from Clarke (1924, p. 163). All other analyses given in Table 2. Most data for the Abert-Summer Lakes Basin is taken from a report in preparation by A. S. Van Denburgh, "Solute balance of the saline Abert and Summer lakes, south-central Oregon."

mountain streams, which are nearly pure bicarbonate in anionic composition. Typical are the waters of the Susan River, and of Eagle Lake, which loses water to Honey Lake by seepage outflow. The result of addition of hot spring inflow varies from the nearly equivalent anionic proportions of sulfate and carbonate in the interstitial brines from the eastern side of the Honey Lake playa, to compositions only slightly higher in sulfate than Abert Lake (Fig. 5). Compared with any of the individual basins herein considered, this trend is the closest to Hutchinson's "average," represented by the arrow in his diagram (Fig. 1) for the western Great Basin.

A significant proportion of sulfate characterizes the only other drainage of the western Great Basin which rivals the Lahontan in area -- the Owens River system. Hutchinson considered only the changes in composition from Owens River to Owens Lake; but as has been discussed by Gale (1915) and Smith (1962), the pluvial Owens River drainage overflowed Owens Lake and carried southward to China Lake, Searles Lake, and at highest stages, onward to the Panamint Basin and probably Death Valley; the Searles Lake Basin with its abundant lacustrine salt deposits (Smith and Haines, 1964) no doubt represented the end point of the Owens River system through most of pluvial times. This relation is further seen in the anion plots for analyses of Owens Lake and the Searles brines (Fig. 6). Older analyses of Owens Lake (Clarke, 1924, p. 162), taken at a time when an extensive body of saline water still covered the basin, plot intermediately between analysis of Owens Lake as it is today, a very shallow body of saturated brine resulting from continued evaporation following nearly complete diversion of the Owens River into the southern California water-supply system, plots very close to recent analyses of the interstitial Searles Lake brines. The closest modern equivalents to the waters of the former Owens Lake are those of Mono Lake. Mono Lake occupies the basin of a larger pluvial ancestor and is fed primarily by Sierra Nevada runoff, which is very similar in composition to tributary streams of the Owens River. Mono Lake and representative surface inflow compositions (Fig. 6) show an anionic trend which is relatively constant in proportions of sulfate.

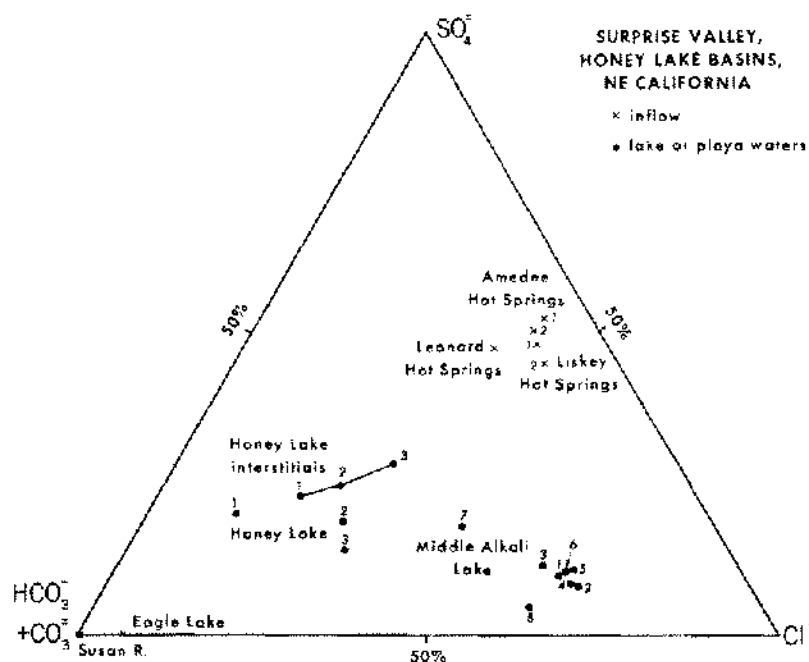


Figure 5. Major anion composition of closed basin waters of northeast California. Susan River analysis from unpublished data, U. S. Geological Survey, 1955. Eagle Lake analysis from Livingston (1963, p. 617). Honey Lake analysis number 2. Middle Alkali Lake analyses numbers 3 and 4, and data for the Leonard Hot Spring from California Department of Water Resources (1960). All other analyses are given in Table 1.

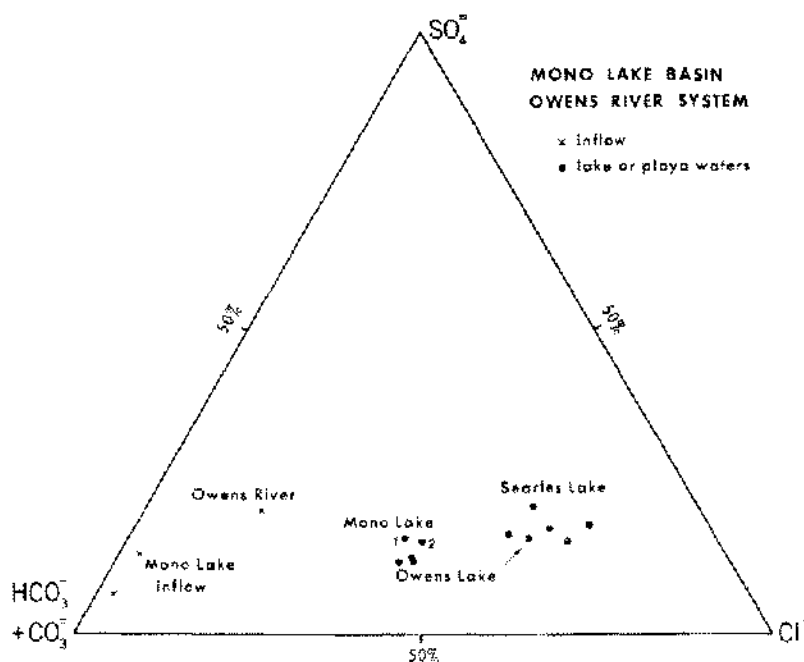


Figure 6. Major anion composition of waters from the Mono Lake Basin and Owens River system of eastern California. Data for Owens Lake and the Owens River prior to diversion are from Clarke (1924, p. 162). Mono Lake analysis number 2 and data for Mono Lake inflow from Whithead and Feth (1961). Analyses of Searles Lake brines from White, Hem, and Waring (1903, p. F56) and unpublished records. Analyses of present-day Owens Lake and Mono Lake are given in Table 1.

D. E. White (personal communication, 1965) has suggested that the Owens River analysis may be higher in sulfate than the general trend because of the influence of hot springs in its upstream drainage, which can account for 80 per cent of the boron carried by the Owens River system. During the Pleistocene, when much of the salt load was actually carried into Owens Lake, the Owens River probably received a greater proportion of its flow from surface waters similar to present Mono Lake inflow. An analysis of the Owens River of Pleistocene time might well plot near a straight line between Mono Lake and its principal inflow.

The most variable and complete range in anionic proportions among the closed basin waters considered by Hutchinson occurs within the central part of the Lahontan area (Fig. 7), although the significance of recent analyses is reduced by complications arising from extensive irrigation. Recent analyses of Pyramid Lake and interstitial waters from the sediments of presently dry Winnemucca Lake contain distinctly lower proportions of chloride than the older analyses of Clarke (1924, p. 160). More recent analyses also make apparent a considerable range in the composition of the Truckee River at successive downstream sites. Modern waters from the Humboldt and Carson Sink areas apparently contain higher quantities of sulfate than previously indicated in Clarke's data. The combined data show that the central Lahontan Basin drainage today exhibits anionic trends not far from the average suggested by the arrow in Hutchinson's diagram for the western Great Basin (Fig. 1).

Sulfate type.

Closed drainage systems of the western Great Basin north of the Mojave region that can be considered of the sulfate type are Rhodes Marsh of western Nevada and the Saline Valley of eastern

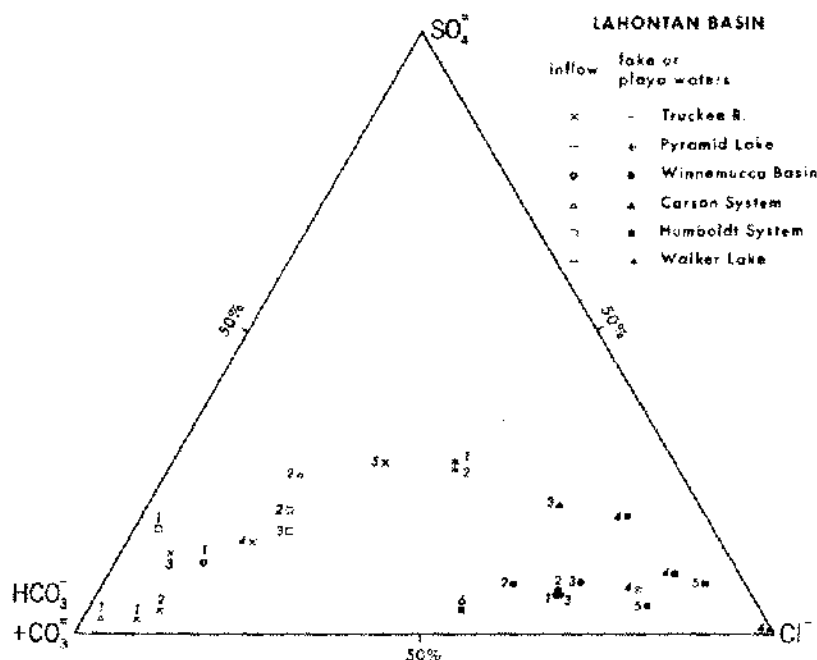


Figure 7. Major anion composition of waters from the Lahontan Basin. Analyses number 1 from the Humboldt River, number 4 from the Truckee River, number 6 from Humboldt sink, number 4 from Pyramid Lake, and number 5 from Winnemucca Lake, all from Clarke (1924, pp. 159-161). Analyses of Walker Lake, Pyramid Lake (number 2), plus the Truckee River at Wadsworth (number 3) and Nixon (number 5), Nevada, from Whitehead and Feth (1961). Other analyses of Pyramid Lake (number 1) and the Truckee River (Lake Tahoe, number 1, and at Farad, number 2) from Livingstone (1963, p. 617). Discharge weighted mean data for the Humboldt River at Rye Patch Dam, Nevada, from U. S. Geol. Survey (1952, 1957). All other analyses given in Table 1.

California. Both these basins contain extensive salt-encrusted playas fed primarily by ground waters. Spring waters collected around the Saline Valley (Lombardi, 1963, Table 3; Hardie, 1965) exhibit a wide range in anionic composition, including high proportions of carbonate, but the bulk of such waters is characterized by high concentrations of sulfate (Fig. 8). Samples of inflow

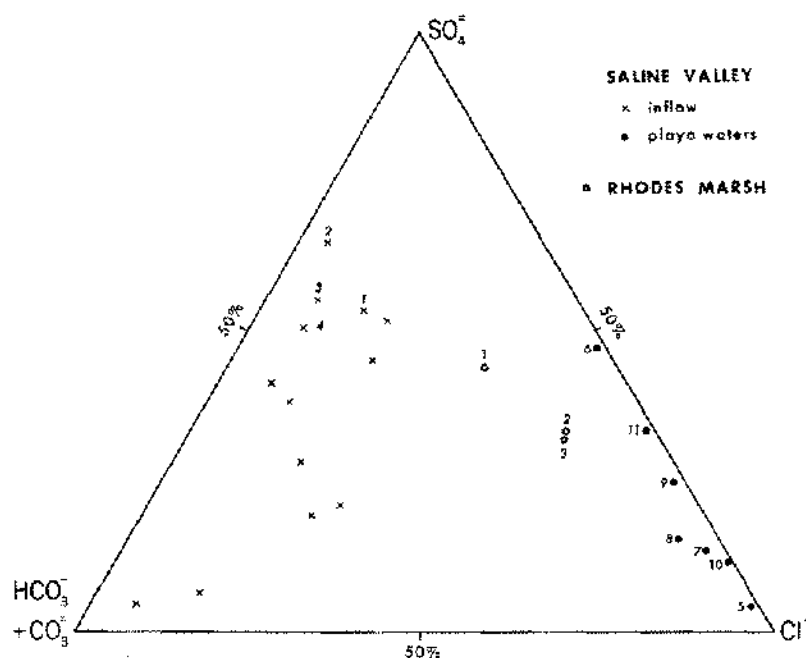


Figure 8. Major anion composition of waters from the Saline Valley, California, with a few points representing inflow in the immediate area of the Rhodes Marsh playa, Nevada. Data for inflow to the Saline Valley from Lombardi (1963, Table 3). Data for Saline Valley brines, selected to give a representative range of anionic composition, from analyses assembled (1965, Table 31).

waters collected in the immediate area of the Rhodes Marsh playa illustrate anionic compositions intermediate between the Saline Valley inflow springs and interstitial brines of the Saline Valley playa. The overall anionic trend accompanying concentration increase from the average Saline Valley spring composition through the Rhodes Marsh solutions to Saline Valley interstitial brines shows the most marked decrease in proportions of sulfate only after the sulfate-chloride edge is approached. Further enrichment in chloride takes place in brines which are nearly carbonate free.

Close to an average trend in anion composition for closed basin waters is provided by analyses of inflow and playa waters from the Deep Springs Valley of eastern California (Fig. 9). In this small intermontane basin, which lies just north of the Saline Valley and east of the Owens River system, salt deposits occur in both a small playa and a nearby fault-trough pond. The area combines an extensive range in lithology with all the natural processes at work elsewhere to give a representative example of compositional evolution in waters of the entire western Great Basin.

PROCESSES RESPONSIBLE FOR THE TRENDS

The primary influence on the initial anion composition of any closed basin water is the gross lithology of the materials with which the water has been in contact. This influence is exerted by two basic mineral-water reactions, solution and hydrolysis. Secondary anionic changes in closed basin waters result principally from the interaction of evaporative concentration with reactions related to organic processes or mineral precipitation. Despite limitations, the trilinear plotting of major anion compositions does reflect these processes, though suggestions made from the

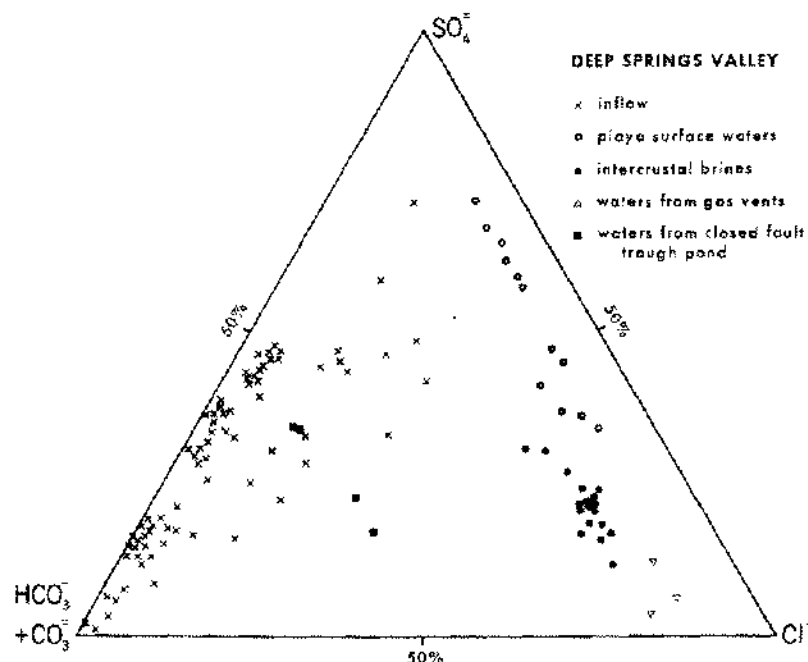


Figure 9. Major anion composition of waters from the Deep Springs Valley, California. Data from Jones (1965, Table 7).

relationships shown must be verified by further evidence (Hem, 1959, p. 183). The primary reactions control the position of points representing basin inflow while secondary processes dictate the anionic trend through the course of evaporative concentration. In general, concentration increase is accompanied by an increase in chloride; and solid precipitation, by a decrease in the appropriate anion. The direction of compositional trends may be similar, but distinct differences in actual path for each of the major drainage areas are established and, to some degree at least, are maintained by the lithologic environment.

Simple solution.

The most straightforward reaction providing solutes to closed basin waters is that of complete solution of readily soluble, simple ionic mineral compounds. Whenever evaporites are present in the drainage area, this process dominates the geochemical evolution of the basin waters. As pointed out by Hutchinson (1957, p. 568), drainage from pre-existing salt beds appears to account for most nearly pure chloride waters. The purest chloride waters discussed herein are the interstitial brines of the Bonneville salt flats. Indeed, it has been postulated that bedded evaporites, primarily halite, have contributed most of the salt load of the Bonneville Basin and the Great Salt Lake (Feth, 1959). Much of the salts in modern inflow to the lake, however, may be simply recycled from older Bonneville sediments.

Another obvious source of the solutes in water is the solution of calcite from limestones. This process exerts a major control on the composition of inflow draining areas underlain by Paleozoic marine strata, as in the immediate area of the Great Salt Lake or parts of the Deep Springs and Saline Valleys.

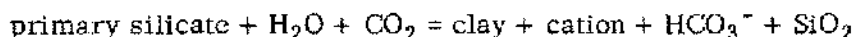
The leaching of ions absorbed or trapped in interstitial fluids in clastic sediments is another solution mechanism providing dissolved components in water. In this way, for example, chloride incorporated in clayey strata by membrane filtration during compaction (White, 1965) might be obtained. The chloride that makes up such a high proportion of the most concentrated brines of the Saline Valley playa may have had such a source. The term leaching may also be used to describe the removal by solutions of the products of oxidation of sedimentary sulfur compounds, largely pyrite. In the western Great Basin it is difficult to differentiate sulfate of sedimentary origin from that associated with areas of hydrothermal alteration without detailed study of each

contributive drainage system (barring possible isotopic differences). Outside the Great Basin sulfate becomes the major constituent of closed basin waters in the glaciated areas of Washington State and the northern Great Plains.

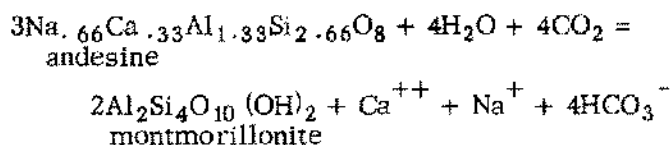
Silicate hydrolysis.

The initial compositions, subsequent evolution, and the importance of carbonate in the major drainages of the western Great Basin are chiefly related to the hydrolysis of primary silicates. The gross effect of such reactions is dependent not only on the quantitative proportions of igneous vs. sedimentary material in contact with basin waters but also on the relative stability of the individual silicate mineral species composing these rocks. In the weathering sequence of clay sized minerals established by Jackson and others (1948) the relative stability of the primary silicates, with the exception of feldspar, increases roughly with decreasing ratios of silica to alumina. This reflects the higher solubility of silica over alumina in natural water, as well as considerations of crystal structure. Preferential attack on mafic mineral phases with high Si/Al ratio further increases the quantity of silica leached by solutions penetrating primary igneous materials. Examination of the detritus in the recent lacustrine deposits of the western Great Basin indicates that feldspars from a wide variety of sources are left intact, while the mafic components of igneous rocks have been extensively altered or completely broken down. The original grain size is an additional factor affecting primary silicate stability; smaller grain size provides additional surface area for solution attack on minerals. An optimum combination for silicate hydrolysis is in pyroclastic deposits. These materials combine metastable molecular structure with maximum granular surface area and, typically, relatively high Si/Al ratios. The highest initial concentrations of silica in natural water can usually be traced to association with such deposits.

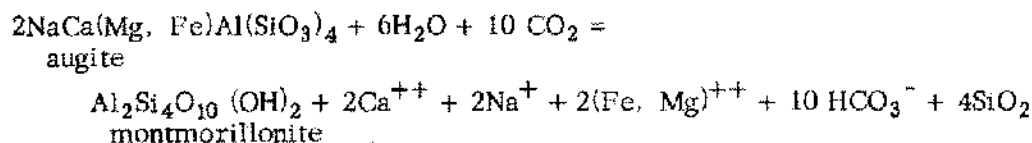
The most common impetus behind the hydrolysis of primary silicates is the reactions of carbon dioxide with water to form carbonic acid. The resulting reactions provide bicarbonate ions in proportion to the release of metallic cations and the solution of silica. Silicate hydrolysis reactions are typically combined with aqueous CO₂ uptake schematically as follows:



Alkali feldspar is most frequently cited as the primary silicate and kaolinite as the clay product in weathering reactions (e.g., Garrels, 1965), but for the more common igneous rocks of the western Great Basin:



This reaction yields no silica, but abundant amounts of SiO₂ can be obtained by mafic mineral alteration, such as¹:

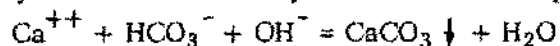


Lesser amounts of silica may be expected from silicic intrusive rocks which bear mafic phases with low Si/Al ratios than from extrusives.

The carbon dioxide for the hydrolysis reactions is derived primarily within soils which support a P_{CO₂} significantly above that of the atmosphere because of biotic activity. Some carbon dioxide may be derived from other sources, as indicated by the high CO₂ content of waters of deep circulation from some fault zones or thermal areas. After steam, carbon dioxide is the next most abundant component of volcanic emanations (White and Waring, 1963). However, the brines of

¹In both equations, the formula for montmorillonite has been idealized to that of pyrophyllite for ease in balancing. In actual fact, divalent cations are in part retained by the clay, thus further enhancing the proportions of alkalis in the solution.

the western United States with the highest carbonate content apparently result from the in situ evaporative concentration of alkaline waters which derive their carbonate content from silicate hydrolysis at the normal temperatures of weathering. The "potholes" of the Alkali Valley in Oregon are fed by seepage which appears to be made alkaline by reaction with lacustrine deposits of re-worked pyroclastics. Similarly, the carbonate brines of the fault trough pond in Deep Springs Valley result from the concentration of dilute, but highly alkaline, seepage inflow. This mechanism apparently operates at points in the Abert, Mono, and Searles Lake Basins also. In any case, silicate hydrolysis in the subsurface has proceeded more rapidly than CO₂ uptake by weathering solutions. This may be because of highly reactive phases (pyroclastic deposits) or restricted contact with the atmosphere or both. Under such circumstances, the participation of CO₂ in silicate hydrolysis reactions such as presented earlier is restricted and OH⁻ substitutes for HCO₃⁻ as a reaction product. Hydroxyl thus released to a normal calcium bicarbonate water by rapid silicate hydrolysis is neutralized by increased calcite precipitation as follows:



This process effectively removes all but traces of the alkaline earths from solution. The amount of silica in solution increases with rising pH, and in the "potholes" and fault trough pond, at least, silica values are above saturation with respect to amorphous silica. With additional concentration the trend of increasing pH and carbonate content continues until the solution becomes saturated with a sodium carbonate phase, as suggested by Garrels (1965). The nature of this phase is related to how high organic matter has maintained the P_{CO₂} in the system (Milton and Eugster, 1959; Jones, 1965; Eugster and Smith, in press).

It should be emphasized that the processes outlined above can be expected to dominate in any area where the drainage is underlain principally by silicic igneous rocks or alluvial deposits derived from such material. Higher dissolved solids content of inflow preceding the onset of evaporative concentration can be expected in areas of pyroclastics or glassy lavas than in normal plutonic terrain, but the prevailing solution compositions are similar in either case.

Silicate hydrolysis proceeds by the same sort of reaction, but even more readily, where oxidation and hydration of sulfides gives sulfuric acid. In areas of extensive mineralization, this process becomes a major factor in determining water composition. Of the basins considered here, the most extensive mineralization in proportion to the total drainage area is within the Saline Valley area, where the famous Cerro Gordo district straddles the southwest drainage divide, and ore deposits occur to the north and east also. It is apparent that mineralized areas contribute much to the drainage around Rhodes Marsh, and, to a lesser degree, the Deep Springs Valley and Owens River system as well. Cohen (1962) has demonstrated the effects of hydrothermal alteration zones on waters of the Truckee Meadows area, and similar conditions locally influence the Carson system.

Silicate hydrolysis processes, whether including either CO₂ as carbonic acid or hydrolyzed sulfides as sulfuric acid, can also be looked upon as a form of low temperature hydrothermal alteration, or "hydrogen metasomatism," as discussed by Hemley and Jones (1964), involving primarily the substitution of H⁺ in silicate phases unstable in the weathering environment.

Hydrologic effects.

The disposition of solutes derived from simple solution or hydrolysis reactions is controlled in large part by hydrologic factors. Of initial importance in any drainage basin is the total and seasonal distribution of rainfall, as reflected in the relative amounts of infiltration versus runoff. Higher infiltration rate and deeper circulation favor more complete reaction of sparingly soluble materials, and enhance the role of hydrolysis reactions. This factor may account in part for compositional differences even within individual spring systems of the Deep Springs and Saline Valleys (Figs. 8 and 9).

The nature and quantity of solutes in spring waters of closed basins often reflect flow patterns which are physically obscure, but these hydrologic routes in large measure dictate the major lithologic influence on compositional trends. A shift in source area with seasonal change in storm patterns may also affect water compositions significantly. Such influences are illustrated at the Buckhorn Springs of the Deep Springs Valley where marked compositional changes reflect

variation in the amounts contributed from areas underlain by igneous as compared to sedimentary rocks (Jones, 1965).

Secondary effects.

Secondary modifications of the anion distribution originally established by primary solution and hydrolysis may not be related solely to evaporative concentration. The most obvious example is the mixing of inflow waters of different composition. This generally is a simple quantitative addition, as illustrated by the Chewaucan River "estuary," where the inflow passes through a straight line transition from the anion composition of the river to that of the lake. Similarly, the composition of some interstitial brines in the Honey Lake Basin appears to be a 1:1 anionic mixture of stream and hot spring waters, and two compositionally distinct spring orifices which supply inflow to Deep Springs Lake provide a compositional intermediate by simple surface mixing proportional to discharge (Fig. 10).

A most important secondary mechanism for modification of closed basin water compositions is the addition of CO_2 to the system by organic respiration and decay. In the Deep Springs Valley, Barnes (1965, p. 100) has suggested that respiration may account for P_{CO_2} levels in Birch Creek well in excess of those in the atmosphere, though more recently Slack (personal communication, 1965) has attributed these levels largely to decay processes. Similarly, significantly higher alkali carbonate content at one orifice of the Corral Springs than at another in the Deep Springs Valley can be attributed to evapotranspiration, respiration, and decay by marsh vegetation flourishing around a spring outlet of very low discharge. The effects of combined biotic activity and evaporative processes on water compositions in the immediate area of low discharge springs is also shown by the increased total dissolved solids (from 257 to 447 ppm) and alkali concentration (from 22 to 37 ppm) in waters from spring orifice as compared to those at the marsh edge in the central Bog Mound spring of the Deep Springs Lake area (Jones, 1965).

The largest contribution of CO_2 to closed basin waters from organic activity is probably the result of anaerobic decay at lake bottoms or interstitially in lacustrine sediments. This is indicated by the higher CO_2 content of interstitial brines obtained from Abert Lake bottom sediments as compared to the immediately overlying lake waters. It is also recorded by nahcolite (NaHCO_3) which occurs in traces in the bottom muds of the closed fault trough pond at Deep Springs and which is abundant in the parting muds of the Scarles saline deposits; nahcolite has been shown (Milton and Eugster, 1959; Jones, 1962, 1965; Eugster and Smith, in press) to require a high P_{CO_2} environment for formation.

Anaerobic decay of organic materials in closed basin waters also gives rise to significant loss of sulfate by bacterial reduction to H_2S , particularly in open bodies of saline waters. The effect of this process is clearly suggested in the trends of anionic composition at Abert, Summer, Honey, Pyramid, and Owens Lakes. The tendency for inflow to increase in sulfate percentage with increasing total dissolved-solids content apparently is abruptly halted upon entry into the lakes proper. In the Abert-Summer and Honey Basins, the sharp shift in trend is more apparent than real because of the effects of diverse sources and large differences in amounts of inflow; but

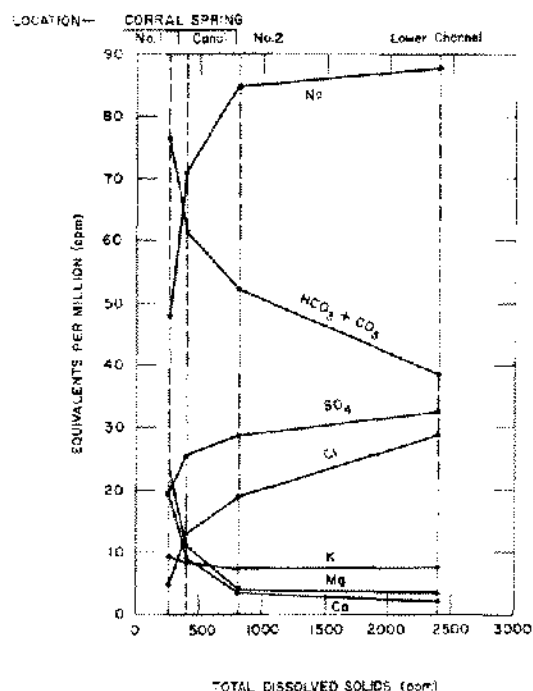


Figure 10. Relation of major ion concentration to total dissolved solids for Corral Springs waters inflow to Deep Springs lake. The waters of the canal represent a simple mixture, proportional to discharge, of waters from Corral Springs Numbers 1 and 2 (from Jones, 1965, p. 38).

the contrast in trend paths between the Pyramid Lake or Mono Lake-Owens River Systems, and the relatively ephemeral Carson or Humboldt sink areas reflects the increased sulfate reduction possible within the permanent lacustrine regime. Further, the proportion of sulfate consistently decreases northward in the permanent lacustrine features of the western Great Basin. This situation conforms well with Jenny's (1941) observation of increased organic matter accumulation with decrease in temperature in soils within belts of uniform moisture conditions and comparable vegetation, although changes in geologic setting suggest that the coincidence is most likely fortuitous.

Mineral precipitation.

The final major reactive process which modifies the anionic composition of closed basin waters is precipitation of solids. As an ordinary fresh water increases in concentration, alkaline earth carbonate is the first material deposited. The extent of calcium removal from solution and the point of initial precipitation in the drainage basin are related to the relative importance of limestone solution vs. silicate hydrolysis in primary solute derivation. The combination of abundant calcite supply with the pH rise and CO₂ uptake accompanying hydrolysis results in the initiation of deposition within drainage lines, such as in the tributaries of the Deep Springs Valley. Quantitatively, carbonate deposition reaches a maximum in the marginal areas of the saline lake or playa, as indicated by the carbonate saturation levels in the springs adjacent to Deep Springs Lake (Table 2). The carbonate chemistry of these springs is suggestive of the favorable inorganic conditions which have permitted the formation of the algal tufa mounds of the Searles (Scholl, 1960), Mono (Scholl and Taft, 1964), and Lahontan Basins.

Table 2. Ion activity products (IAP) of alkaline earth carbonate for inflow from springs to Deep Springs Lake, August, 1961

Locality	Water temperature (°F)	pH	Calcite Keq ¹ x 10 ⁻⁹	Calcite IAP x 10 ⁻⁹	Dolomite ² IAP x 10 ⁻¹⁷
Buckhorn Springs, main channel	68	7.97	5.281	7.906	7.534
Corral Springs, combined flow	72	8.29	4.992	7.212	6.176
Bog Mound Springs, central orifice	55	8.26	6.447	13.50	14.38
central marsh	68	7.95	6.281	36.64	90.06

¹Keq = equilibrium constant.

²Keq for dolomite is probably about 2 x 10⁻¹⁷ (Hsu, 1963).

Compared to basins where solutes are apparently derived in similar amounts by limestone solution and silicate hydrolysis, carbonate deposition is more restricted areally in basins where one or the other process predominates. In the Abert-Summer (pluvial Lake Chewaucan) Basin where inflow is in almost exclusive contact with volcanics and there is a relative paucity of Ca in the water, carbonate deposition is confined to the lake basin. In the Bonneville Basin, where calcite saturation is brought about more by rising salinity than excess alkalinity, carbonate deposits are also confined to the lake or playa areas, but they are very abundant and in the

immediate Great Salt Lake area form widespread oolitic sands (Eardley, 1938). With the near neutral pH and relatively low bicarbonate content of Great Salt Lake and brines from the Bonneville Flats, significant amounts of calcium still remain in solution even after saturation with respect to gypsum has been exceeded.

In contrast to the Bonneville Basin evaporating waters of the Lahontan Basin and adjacent territories continue to deposit carbonate until the alkaline earths in solution are nearly exhausted. Total alkaline-earth content is below detection by titrametric methods in brines from the Alkali Valley, interstitial brines of the Abert Lake and Honey Lake areas, and in Owens Lake, Deep Springs, and Searles Lake brines. These basins all contain alkaline-earth carbonates in lacustrine muds, and at Deep Springs and Searles Lakes varved muds may contain in excess of 75 per cent carbonate in alternating layers composed primarily of aragonite and dolomite (Jones, 1965; Smith and Haines, 1964).

In heavily mineralized regions sulfate substitutes in large measure for bicarbonate as the resultant anion in hydrolysis reactions. Coupled with a predominant solution of alkaline earth from limestone, and P_{CO_2} values restricted to atmospheric levels, carbonate precipitation is overshadowed by gypsum deposition. The "normal" precipitation sequence of calcite and gypsum on evaporation of an "ordinary" fresh water should result, as pointed out by Hutchinson (1957, p. 374), in a water containing chloride as its main anion. Indeed, such is the case with the nearly pure sodium chloride brine in the playa pond of the Saline Valley, but only after considerable precipitation of sodium sulfate (Hardie, 1965). The sodium chloride brines of the Columbus and Silver Peak playas of western Nevada may represent a similar residuum.

Because of the great disparity in solubility between the alkaline earth carbonates or gypsum and the alkali salts, changes in anion proportion of closed basin waters intermediate in concentration can only be attributed to hydrologic or organic effects. Langbein (1961, p. 14) has shown that variation in total concentration of many closed lakes can be related to strictly hydrographic variables including net evaporation, depth, total lake area, and areal variation with time. Such a treatment implies measurable depths, lack of stratification, generally stable anionic proportions, and a solute gain or loss that affects all constituents alike and avoids fractional precipitation. About the only suitable processes are marginal precipitation or insulation through sedimentation. Accordingly, preliminary data indicate significant incorporation of salts in interstitial solutions of closed lake sediments in a number of areas. Although the above criteria appear to hold for many examples treated by Langbein, the shift in anionic proportions brought about by alkali sulfate precipitation at Deep Springs Lake has been demonstrated by Jones (1965), and more subtle changes in anionic proportions at Summer Lake resulting from selective aerosol movement have been shown by Van Denburgh (Written communication, 1964).

Usually the last process to affect the composition of closed basin waters is the precipitation of the alkali salines. In the Great Basin this process takes place both in open bodies of saline water and interstitially in playa sediments. Quantitatively, the most significant saline deposit presently forming is the halite which is precipitating in the northwest arm of the Great Salt Lake. Sodium carbonate (trona and/or natron) is deposited from the open waters of the Alkali Valley "potholes" and playa pond. Further desiccation of Owens Lake will undoubtedly lead to further growth of sulfocarbonate crusts composed primarily of trona and burkeite ($2Na_2SO_4 \cdot Na_2CO_3$). Sodium sulfate is the major precipitate of Deep Springs Lake at low stage, whereas trona is a major constituent of crusts which form at low stage in the closed fault trough pond. Saline deposits from perennial open waters are characterized by crustal layering where more than one salt phase has precipitated. The layering follows the sequence of precipitation expected according to solubility, except where secondary reaction of the saline phase with solution has taken place (Jones, 1965).

Within a "dry lake" or playa environment saline deposition takes place according to the "evaporating dish" principle illustrated by Hunt (1960) for the Death Valley salt pan. In this process, areal shrinkage of a shallow body of water by evaporation results in continuous precipitation of salts in concentric zones from edge inward according to their relative solubilities; alkaline-earth carbonates precipitate in the outermost areas, sulfates in the intermediate zones, and chlorides at the center. Similar salt pan zoning involving somewhat different phases has been recorded at Deep Springs Lake (Jones, 1961), and in the Saline Valley (Hardie, 1965).

Available data are insufficient to illustrate well the effects of precipitation of the alkali salines on trends in anionic composition. Distinct shifts in trend away from the sulfate apex in the central Lahontan Basins and the Saline Valley are correlative with the precipitation of sulfates, but the initiation of this process cannot be definitely pinpointed in most places. This fact is related to the inclusion within the trend sequence of anomalously dilute waters which have picked up salts in proportions which reflect relative position in the whole drainage system. In this way it appears that trends in anionic composition may be as meaningful in ephemeral as in perennial systems.

SUMMARY

In summary, the major drainage units of the Great Basin may be classified according to the major anion in their most saline waters, and each basin is characterized by a distinctive compositional trend from dilute inflow to most concentrated brine. Each of the three major anions in highly concentrated lake or playa waters points to distinctive association of lithology and weathering process within the contributive drainage areas. High percentages of chloride indicate sedimentary rocks or marine origin and solution processes; carbonate reflects igneous lithologies and the hydrolysis of primary silicates; predominance of sulfate suggests ore mineralization and acid alteration. Secondary hydrologic, organic, and mineral precipitation processes can severely alter but do not completely obliterate the initial lithologic control of water composition.

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