

The Role of Pore Fluids in Evaporitic Basins

Ronald J. Spencer

Department of Geology and Geophysics
University of Calgary
Calgary, Alberta, Canada

ABSTRACT

Two closed basin systems in the western United States (Great Salt Lake, Utah, and Walker Lake, Nevada) are used to emphasize the importance of pore fluids in evaporitic basins. Pore fluids in these systems behave primarily as mass transport media. As a result of diffusive flux, pore fluids may act as major sources or sinks for dissolved constituents and form a bridge between surface brine bodies and subsurface diagenetic environments. In addition, pore fluid composition is much more sensitive to mineral reactions than is the sediment mineralogy; in this respect they provide an important tool in studying modern systems.

Differing hydrologic conditions in the two basins in the past are reflected in the pore fluid profiles at Great Salt Lake and Walker Lake. Deeper portions of each basin are underlain by salts. Dis-

solved constituents (Na^+ , SO_4^{2-} at Great Salt Lake; Na^+ , K^+ , Cl^- , SO_4^{2-} , CO_3^{2-} at Walker Lake) derived from these salts are transported toward the lakes through the pore fluids. In those portions of the lakes not underlain by salts and for dissolved species not present in the salts the pore fluids act as a major sink.

Pore fluids are also useful in pinpointing diagenetic reactions. At Walker Lake precipitation and dissolution of calcium carbonates and the uptake of Mg^{2+} in the sediment are evident from the pore fluids. At Great Salt Lake reactions involving gypsum, mirabilite, halite and Mg-silicates are interpreted using the pore fluids. These reactions are communicated to the lakes by diffusion through the pore fluids.

INTRODUCTION

The evolution of closed basin brines has been described in terms of two phases. The first phase is concerned with the acquisition of solutes through interaction of rainwater with bedrock and/or soils. Solute acquisition has been discussed by Jones (1966) and Garrels and Mackenzie (1967). Additionally, significant solute influxes from pore fluids and hydrothermal systems have been identified in the Walker Lake and Great Salt Lake systems (Spencer 1977, 1982).

The second phase of closed basin brine evolution is concerned with evaporative concentration and subsequent precipitation of salts from the evaporating brine body. The general nature of salt precipitation has been discussed by Jones (1966) and Garrels and Mackenzie (1967). Detailed predictions of brine evolution paths for closed basin systems have been presented by Hardie and Eugster (1970) and Eugster and Hardie (1978). This second phase evaporitic concentration model has also been carried and applied to the sea water system (Harvie et al.; 1980, 1982).

A third phase of closed basin brine evolution, or evaporitic basin evolution, has been employed by Benson and Spencer (1983) and Spencer (1977, 1982). This third phase includes diagenetic reactions and their relation to

open brine body compositions and the consideration of pore fluids as important sources and sinks for major elements. Mass flux through the pore fluids acts as a bridge between surface brine bodies and the shallow diagenetic environment.

The Walker Lake and Great Salt Lake brines, when compared to the inflow compositions, contain a deficit of K^+ , Mg^{2+} and SO_4^{2-} relative to Cl^- . These ions (K^+ , Mg^{2+} and SO_4^{2-}) are for the most part conserved in solution in the two brine bodies at present, although Na^+ — SO_4^{2-} salts have precipitated from both systems in the past. Even allowing for the precipitation of these salts, a SO_4^{2-} deficit remains. Removal of K^+ , Mg^{2+} and SO_4^{2-} from solution does occur within the pore fluids.

Examination of the removal mechanisms for Mg^{2+} and SO_4^{2-} is hoped to yield some insight into what Braitsch (1971) described as "MgSO₄-deficient" marine evaporites and the formation of "altered sea water." One explanation for such deposits appears to lie in the alternative that they formed from sources deficient in MgSO₄; e.g., they are non-marine (Hardie, 1978). Braitsch (1971) discusses several mechanisms which might lead to "MgSO₄-deficient" brines, including dolomitization, sulfate reduction and clay mineral formation. By considering diagenetic reactions and their effect on evaporating brine bodies, the

extent of brine evolution as a result of such syndepositional processes may be evaluated more carefully.

Basin Hydrology

The Great Salt Lake and Walker Lake occupy positions in lower portions of the Bonneville and Lahontan Basins, respectively. Large fluctuations in lake elevation have occurred within the last 30,000 years. During the last 100 years numerous workers have examined both basins in an attempt to reconstruct the Late Pleistocene and Holocene history of each basin. The models presented here, in terms of lake elevation through time (Figure 1), are from Benson (1978) and Spencer (1982) for Walker and Great Salt Lakes.

Great Salt Lake has been a perennial body of water for the last 32,000 years. Prior to that time an ephemeral lake-

playa system existed in the basin. The lake rose and freshened in a series of steps and overflowed into the Snake River drainage briefly about 15,000 years ago. The lake elevation dropped sharply and has remained nearly constant since that time. The major contributors to Great Salt Lake inflow and dissolved species are direct precipitation, dilute $\text{Na}^+\text{Ca}^{2+}-\text{HCO}_3^-$ river waters and Na^+-Cl^- -rich hydrothermal spring waters (Spencer, 1982).

Walker Lake is believed to have desiccated between 9,050 and 6,400 years B.P. and to have risen to levels at or above that of the present lake (Benson, 1978). The major source of inflow and dissolved species to the Walker Lake system is the Walker River, which is a $\text{Na}^+-\text{Ca}^{2+}-\text{HCO}_3^-$ water.

With the exception of the brief overflow at Great Salt Lake, both systems have remained hydrologically closed during the periods of interest for their evolution. In closed systems the effect of short term (hundreds of years) dilute inflow is insignificant to the total mass of salt in the system. Lake volume or elevation are therefore inversely proportional to the concentration of conservative dissolved species. In the longer term (thousands of years) dilute inflow increases the mass of salt in the system. Assuming an accurate inventory can be made of sources and sinks through a given period, mass balances for various species may be made. Salt budgets presented by Spencer (1977) for Walker Lake over the last 8,000 years and Spencer (1982) for Great Salt Lake over the last 32,000 years balance extremely well.

Pore Fluids as Mass Transport Media

The first question to address is what do the pore fluids represent? The composition of pore fluids extracted from cores at both Walker Lake and Great Salt Lake do not reflect the original lake water composition at the time of deposition (Figure 2). This is illustrated well in the pore fluid chloride profiles of cores GSLC and GSLF from Great Salt Lake. The chloride profiles are shown on Figure 3 as a function of depth and stratigraphy. Core GSLC penetrates all five stratigraphic units described by Spencer (1982), while core GSLF is entirely within the upper saline stage. The estimated chloride concentration of the lake waters inversely proportional to lake elevation as a function of time and stratigraphy (Spencer, 1982). The data for core GSLF indicate chloride near that expected in the lake at the time of deposition; the data for core GSLC vary significantly, especially in stratigraphic unit III. Estimated lake chloride during unit III deposition is about 300 mg/kg; pore fluids in unit III sediments contain about 110 g/kg.

The remarkable similarity of the chloride profiles from cores GSLC and GSLF with depth, without regard to stratigraphy, indicates the profiles to be the result of relatively recent phenomena. The pore fluid profiles may be modeled using fickian diffusion equations and the pore fluids ap-

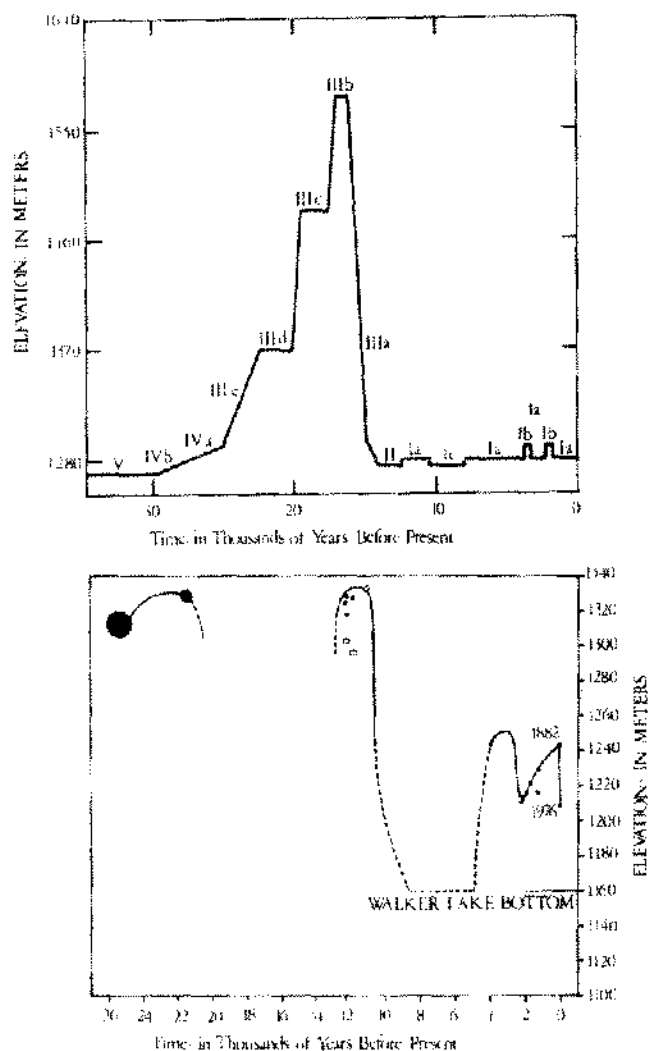


Figure 1. Elevation vs. Time. Lake elevation of Great Salt Lake (top) and Walker Lake (bottom) after Spencer (1982) and Benson (1978). Lake elevation is inversely proportional to salinity in each basin.

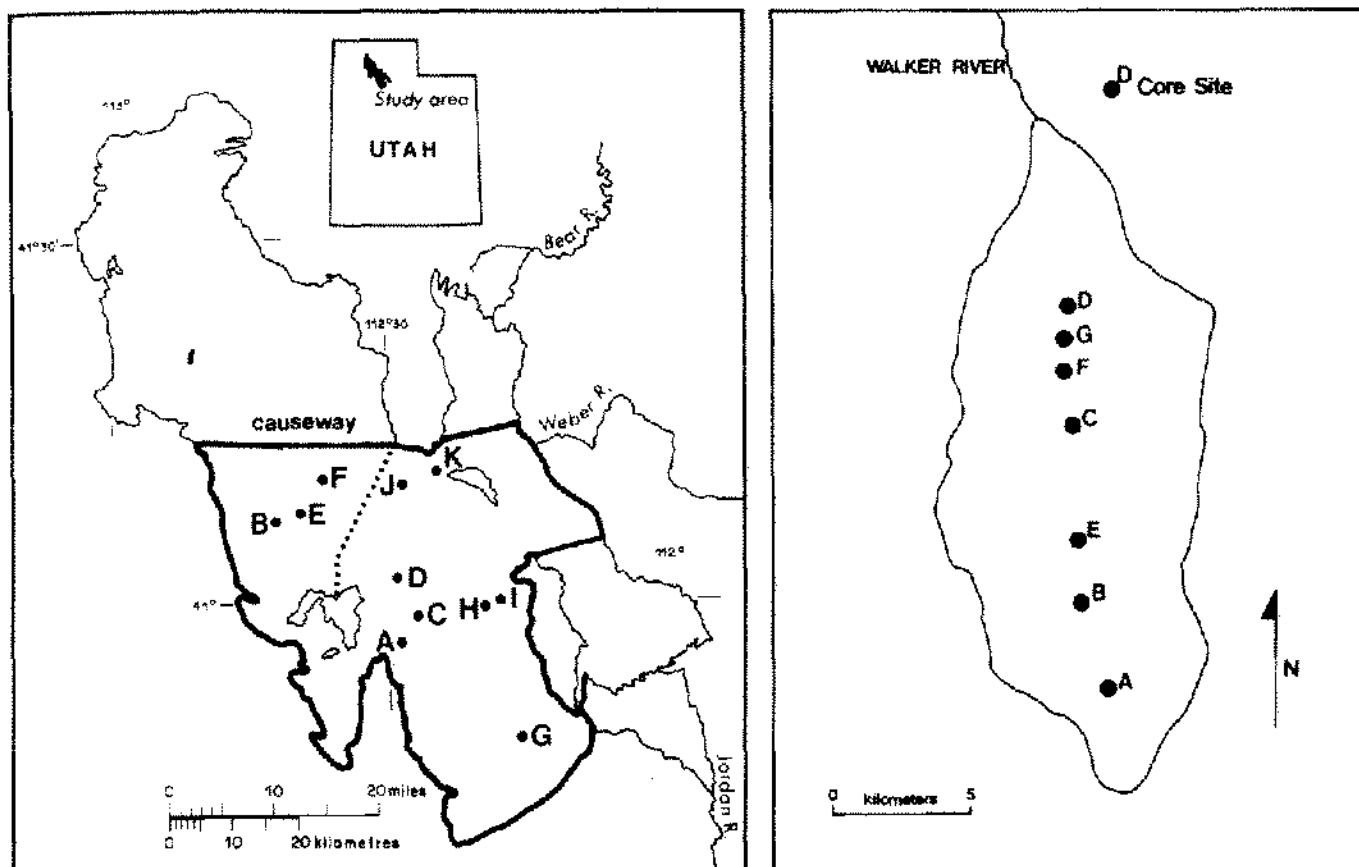


Figure 2. Core Location. Location of cores collected at Great Salt Lake (left) and Walker Lake (right).

pear for the most part to behave as diffusive media. The diffusion model is based on the selection of appropriate boundary conditions and mathematical solutions of one-dimensional diffusion equations.

The mathematical solutions used in the diffusion models below are based on the random motion of particles (Crank, 1979, p. 1) and are modeled in terms of concentrations. To simplify, I have not considered the charge balance constraints which must apply during mass transport but have modeled only individual ions.

The first problem is to assign a set of boundary conditions which will be used as a basis for the mathematical solution. Consider the Cl^- profile for core GSLF (Figure 4); in this case a bed of halite is present below the sediment-water interface. This bed acts as a buffer to the Cl^- concentration at the bed; holding it near halite saturation (150 g/kg). Halite appears to have been present at the site since 1933 (Spencer, 1982). A boundary condition at depth equal to zero (bottom of the halite bed) from time equal to 0 to 47 years (1933–1979) of 150 g/kg is therefore used.

The second boundary condition necessary is that of Cl^- concentration with depth at time zero (1933). Prior to 1933 the lake elevation fluctuated; however, the average composition appears to be near 120 g/kg Cl^- (the 1930 lake

composition) during the 1850 to 1933 historic period. A curve is fitted through the data points below 2.5 metres and the 1930 lake composition; this yields a linear profile, used to satisfy the initial boundary condition.

Using these two boundaries, the present profile is fit, using a solution for diffusion in a semi-infinite medium with a fixed concentration at depth equal to zero given by Crank (1975, p. 21) as

$$C_{in} = C_0 \operatorname{erfc} \frac{d}{2\sqrt{D^*t}} \quad \text{or} \quad \Delta C = \Delta C_0 \operatorname{erfc} \frac{d}{2\sqrt{D^*t}}$$

where

- $C_0 = \text{Cl}^- \text{ at } d = 0$
- $C_0 = 150 \text{ g/kg at } d = 0 \text{ from } t = 0 \text{ to } t = 47 \text{ yrs}$
- $C_{in} = \text{initial Cl}^- \text{ as f(d)}$
- $C_{in} = 120 - .02d \text{ at } t = 0$
- $d = \text{depth (cm)}$
- $t = \text{time (sec)}$
- $D^* = \text{apparent diffusion coefficient (cm}^2/\text{sec)}$.

The profile at time equals 47 years is then fit (Figure 4) and a solution for D^* obtained. In the case of core GSLF, D^* is approximately $3.8 \times 10^{-5} \text{ cm}^2/\text{sec}$.

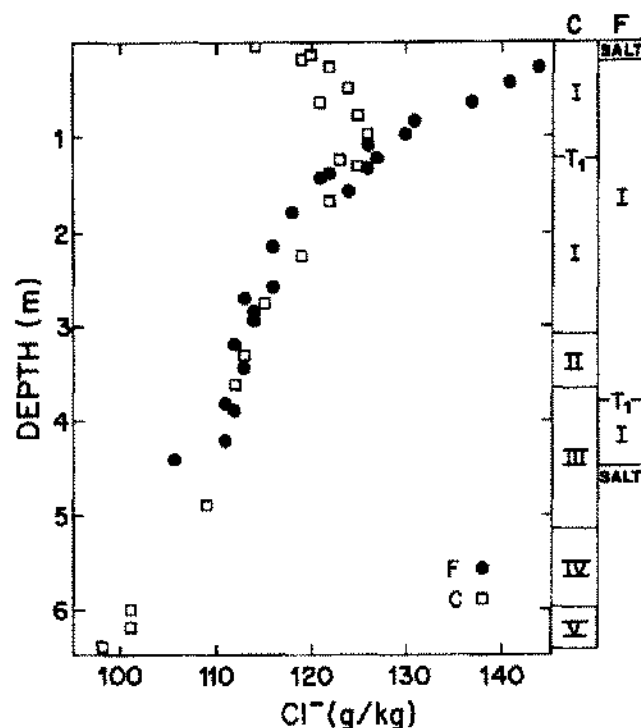


Figure 3. Cl^- vs. Depth, Great Salt Lake. The Cl^- pore fluid profiles for cores C and F are shown as a function of depth below the sediment-water interface. The stratigraphy of the two cores is also shown and may be compared to lake elevations on Figure 1. Core F is entirely within the upper saline unit (I), while core C contains all five stratigraphic units including the fresh water interval (III).

Mathematical solutions for cores GSLC, GSLG, GSLH and GSLI are obtained in a similar manner. The initial boundary conditions as a function of depth are estimated from the 1930 lake composition and the profile below 2.5 m in the same manner as those for core F. The boundary conditions at the sediment-water interface have changed with time at these locations. Using the lake composition data discussed by Spencer (1982), it is estimated that at location G, halite precipitated in 1933 and bottom waters remained at 150 g/kg Cl^- until 1969. From 1969 to 1975 the estimated Cl^- concentration is 120 g/kg, and from 1975 to 1979 115 g/kg. The diffusion solution is therefore

$$\Delta C = \text{erfc } x_1 - 30 \text{erfc } x_2 - 5 \text{erfc } x_3$$

where

$$x = \frac{d}{2\sqrt{D^*t}}$$

$$\begin{array}{ll} \text{for } x_1 & t = 47 \text{ yrs} \\ x_2 & t = 11 \text{ yrs} \\ x_3 & t = 4 \text{ yrs.} \end{array}$$

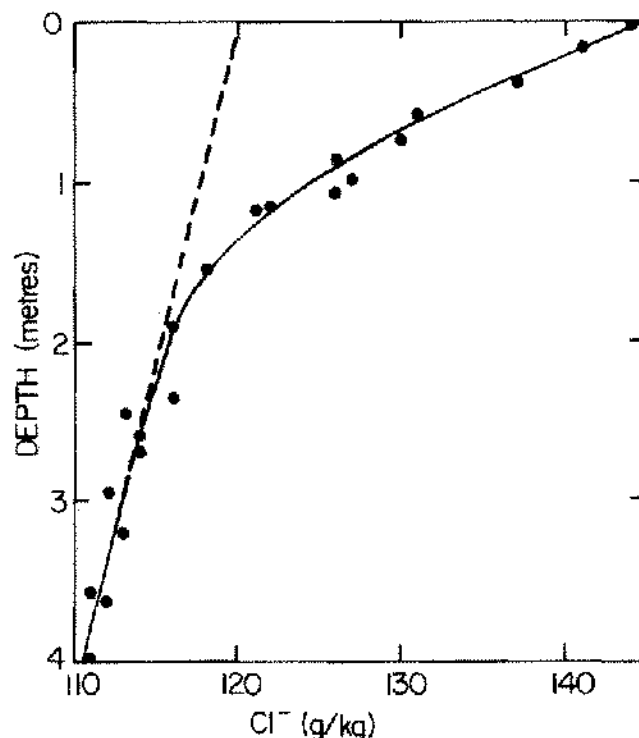


Figure 4. Cl^- Diffusion Profile. The Cl^- pore fluid profile for core F at Great Salt Lake fit using the diffusion model in the text (solid curve). Dashed curve is the estimated 1933 profile.

The fit of this curve (using D^* from core GSLF) for the data points from core GSLG is shown in Figure 5.

The curves for cores GSLC, GSLH and GSLI are also constructed using the boundary conditions estimated from the past lake composition at these locations. There are 150 g/kg Cl^- from 1933 to 1956, 115 g/kg from 1956 to 1960, 135 g/kg from 1960 to 1964, 120 g/kg from 1964 to 1975 and 115 g/kg from 1975 to 1979. The equation used is

$$\Delta C = 30 \text{erfc } x_1 - 35 \text{erfc } x_2 + 20 \text{erfc } x_3 - 15 \text{erfc } x_4 - 5 \text{erfc } x_5.$$

$$\begin{array}{ll} \text{For } x_1 & t = 47 \text{ yrs} \\ x_2 & t = 24 \text{ yrs} \\ x_3 & t = 19 \text{ yrs} \\ x_4 & t = 15 \text{ yrs} \\ x_5 & t = 4 \text{ yrs.} \end{array}$$

The curves on Figure 5 for the most part fit the data quite well.

The apparent diffusion coefficient calculated for the Cl^- profiles of $3.8 \times 10^{-6} \text{ cm}^2/\text{sec}$ may be compared with published values measured for Cl^- tracer diffusion. Robinson and Stokes (1970) cite a value of $1.42 \times 10^{-5} \text{ cm}^2/\text{sec}$ for the diffusion coefficient of Cl^- in a 3 molar NaCl solution. This is a reasonable approximation of the Great Salt Lake system over historic times. Because in a

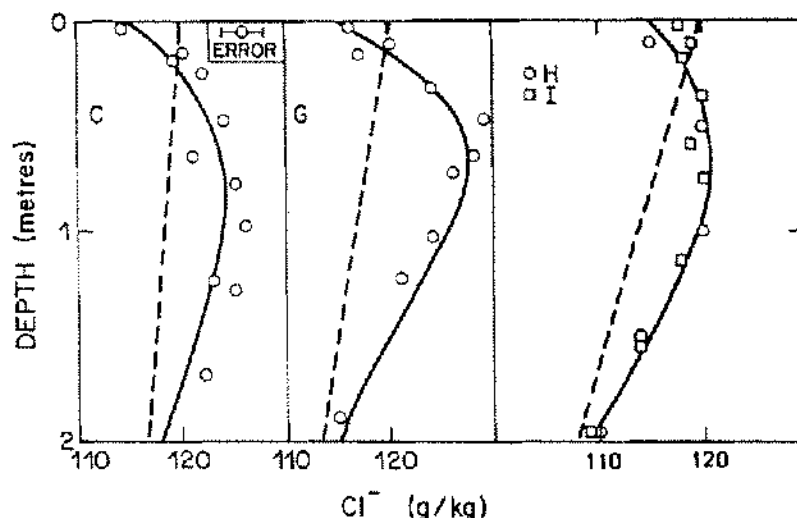


Figure 5. Cl^- Diffusion Profiles. The Cl^- pore fluid profiles for cores C, G, H and I at Great Salt Lake and calculated profiles from the diffusion model in the text (solid curves). Dashed curves are the initial (1933) estimated profiles; below 2 m the data follow the initial curves.

porous medium the apparent diffusion coefficient will differ from that in a pure solution by the hydraulic conductivity (K) of the media

$$D = KD^*$$

using the values of D and D^* above, K is calculated to be 0.26, which appears to be a reasonable value for a porous sand-mud mixture (see Lerman and Weiler [1970] estimated K range 0.1–0.5). The Cl^- pore fluid profiles therefore are consistent with a diffusion model, the major controls on which are 1) the Cl^- concentration of the lake waters over long periods at the site which is manifested in the profile below ~ 2 m and is not terribly sensitive to short term fluctuations; 2) the Cl^- concentration of the lake mass at the site over shorter periods, which in this system is largely controlled by the presence or absence of halite. Fluctuations occurring over a period of about 50 years are recorded within the upper 2 m.

The pore fluids at Walker Lake also behave as mass transport media (Benson and Spencer, in press). Diffusion into the sediment occurs in shallow areas of the lake, as in the Cl^- profile for WLB, Figure 6, as a result of the increase in concentration of the lake waters due to elevation decrease (Figure 1). In deeper portions of the lake a negative concentration gradient is present as in WLG, Figure 6. This is interpreted as due to the dissolution of salts or mobilization of brines produced during the last desiccation of Walker Lake (Spencer, 1977; Benson, 1978; Benson and Spencer, 1983).

Pore Fluids as a Diagenetic Bridge

Through mass transport the pore fluids form a bridge between the lake brines and the diagenetic environment.

The flux of components is a function of the concentration gradient as shown by the simple one-dimensional diffusion equation

$$J_i = -D_i^* \frac{\partial C_i}{\partial x}$$

where

- J_i = flux of species
- D_i^* = effective diffusion coefficient ($D_i K$)
- C = concentration of species
- x = distance.

The removal of species from solution causes an increase in the concentration gradient ($\partial C_i / \partial x$) accelerating the flux of that species. Diagenetic reactions involving carbonates, clays and more saline minerals have been pinpointed in the Great Salt Lake and Walker Lake systems (Spencer, 1977, 1982); these reactions are summarized below.

Carbonates. Dissolution of calcium carbonate hydrate (monohydrocalcite) occurs in the upper few metres of Walker Lake sediments. The dissolution is seen in terms of local maxima in the pore fluid Ca^{2+} concentration due to the relatively low (10 mg/kg) background. The alkalinity is not affected; the dissolution is masked by the high (2900 mg/kg as HCO_3^-) background. The Ca^{2+} released is relatively insignificant in solution but is exchanged for Na^+ on clays within the sediments. Reactions involving carbonates have not been identified in the Great Salt Lake sediments.

Clays. Two types of clay-solution interactions occur within the lake sediments. Cation exchange reactions affect Na^+ , Ca^{2+} , K^+ and Mg^{2+} , while alteration of clay structures and/or authigenic clay formation involves

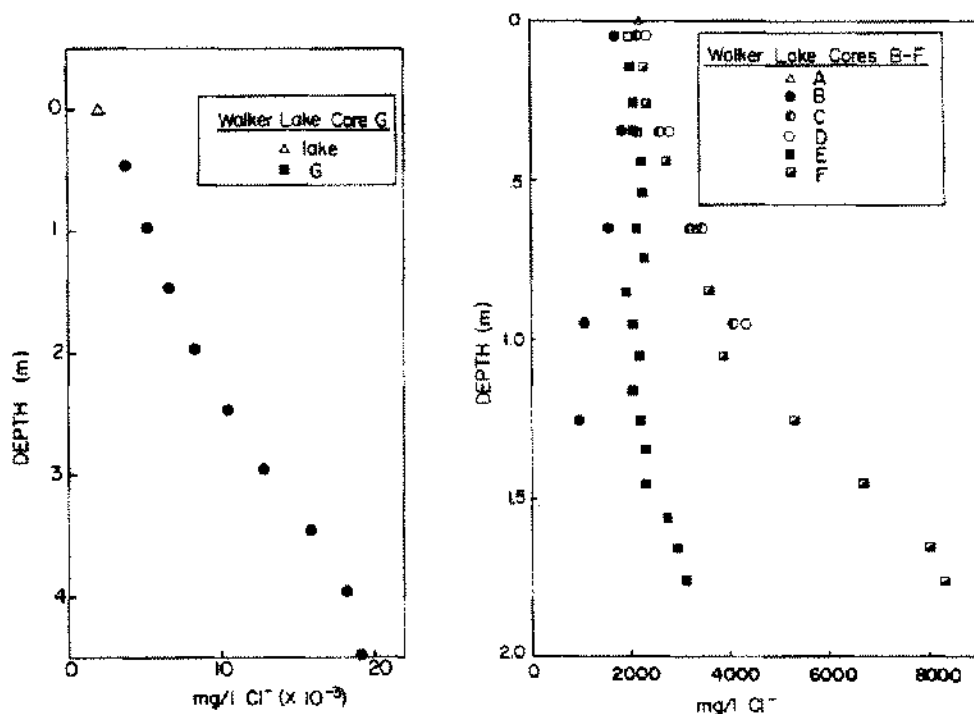


Figure 6. Walker Lake Pore Fluid Cl^- . The Cl^- gradient in cores C, D, F and G indicates transport of Cl^- toward Walker Lake, while in core B it is away from the lake. Saline pore fluids or buried salts beneath the central portion of the lake (below cores C, D, F and G, Figure 2) are a source of Cl^- , SO_4^{2-} , HCO_3^- , Na^+ and K^+ to the lake.

Mg^{2+} . Exchange reactions may have a significant effect on brine composition. Dilute inflow waters tend to have relatively high $\text{Ca}^{2+}/\text{Na}^+$ in solution, and therefore relatively high Ca^{2+} on exchange sites (Figure 7). As a result of carbonate precipitation in the lakes, $\text{Ca}^{2+}/\text{Na}^+$ in solution is low; Na^+ is therefore exchanged for Ca^{2+} on the clays. A large detrital clay influx may significantly increase Ca^{2+} in the system; at Walker Lake about 10% of the Ca^{2+} in the system appears to have been derived in this manner. Removal of K^+ by fixation occurs both in the lake and sediment. Increased layer charge leads to higher exchange capacity followed by K^+ fixation and lower exchange capacity (Figure 8).

Removal of Mg^{2+} from solution through alteration of detrital clays or formation of new material is important in both systems. This is especially seen in the pore fluid Mg^{2+} profiles from Walker Lake (Figure 9), where Mg^{2+} removal from solution is nearly quantitative. Removal of Mg^{2+} from solution appears to be a function of increased salinity in both systems. Although the detrital clays from the two systems differ from one another, original detrital clays appear similar for each system as a function of stratigraphic position, as seen in the proportions of Fe/Al (Figures 10 and 11). The Mg/Al content of the clays varies stratigraphically (Figures 10 and 11). At Great Salt Lake a large increase in the proportion of Mg in the clay fraction is observed in the saline perennial lake sediments (units I, II,

III), relative to river, fresh water (unit III), or playa (unit V) clays. Increased Mg is also found in Walker Lake clays related to the present low stand and a similar low stand about 2,000 years B.P. (Figures 1 and 10). The major removal appears to occur in the upper few centimetres of sediment but may continue in the upper few metres.

Saline Minerals. At Great Salt Lake gypsum, mirabilite and halite are present in some intervals within the sediment. Core F contains gypsum, mirabilite and halite in the salt in the upper 25 cm and mirabilite at the bottom of the core (Figures 3 and 12). At location G three intervals containing gypsum were cored (Figure 13).

The effect of the salts at the top of core F on both the Cl^- (halite) and SO_4^{2-} (mirabilite) pore fluid profiles are shown in Figures 3 and 12. The lack of halite in the salts at the base of core F and presence of mirabilite are also seen in the contrasting Cl^- and SO_4^{2-} profiles on Figures 3 and 12. The presence of saline minerals results in high local concentrations of the components of the salts in solution and transport of these components away from the source through the pore fluids.

The SO_4^{2-} , Ca^{2+} ion activity product ($\text{Ca}^{2+} \cdot \text{SO}_4^{2-} \cdot \text{H}_2\text{O}^2$) and location of gypsum in Great Salt Lake core G are shown on Figure 13. The SO_4^{2-} profile is the result of diffusion with the upper boundary condition fluctuating. The pore fluids near the sediment-water interface are undersaturated with respect to gypsum, while the lower two

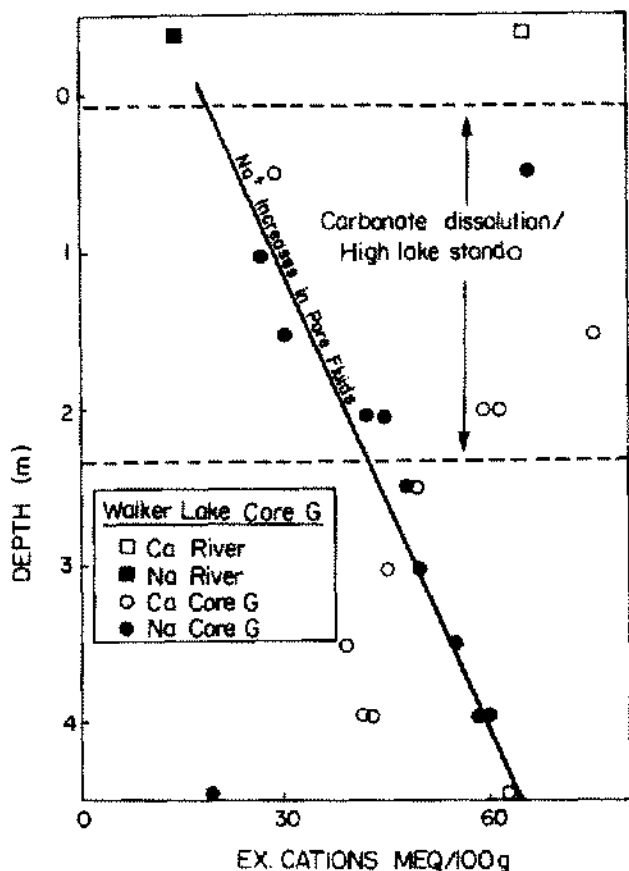


Figure 7. Exchangeable Na^+ and Ca^{2+} ; Walker Lake Clays. Exchangeable Na^+ and Ca^{2+} on Walker River and Walker Lake clays; river clays are high in Ca^{2+} and low in Na^+ ; in the lake and sediment Na^+ on the clays tends to increase as Na^+ increases in the pore fluids (samples at 0.4 and 4.5 m are exceptions). The relatively high Ca^{2+} on exchange sites between 1.0 and 2.0 metres may be the result of calcium carbonate dissolution in the interval, or original high exchangeable Ca^{2+} during higher lake stands.

intervals containing gypsum approach saturation. The Ca^{2+} profile contains maxima at the upper and lower gypsum intervals, indicating a source of Ca^{2+} to solution, and a minimum at the middle gypsum interval, indicating possible Ca^{2+} removal from solution. The gypsum in the upper and lower intervals appears to be dissolving, supplying Ca^{2+} for gypsum precipitation in the middle interval.

Saline minerals were not found at Walker Lake. However, the pore fluid profiles from the mid lake cores indicate a possible buried source of salts. The Cl^- , SO_4^{2-} , HCO_3^- , Na^+ and K^+ diffusing toward the lake may be present due to saline pore fluids stored during the desiccation of Walker Lake, to salts formed at the time, or both.

Pore Fluids as Sources and Sinks

As a result of diffusion, large quantities of dissolved species which are conserved in solution are transported

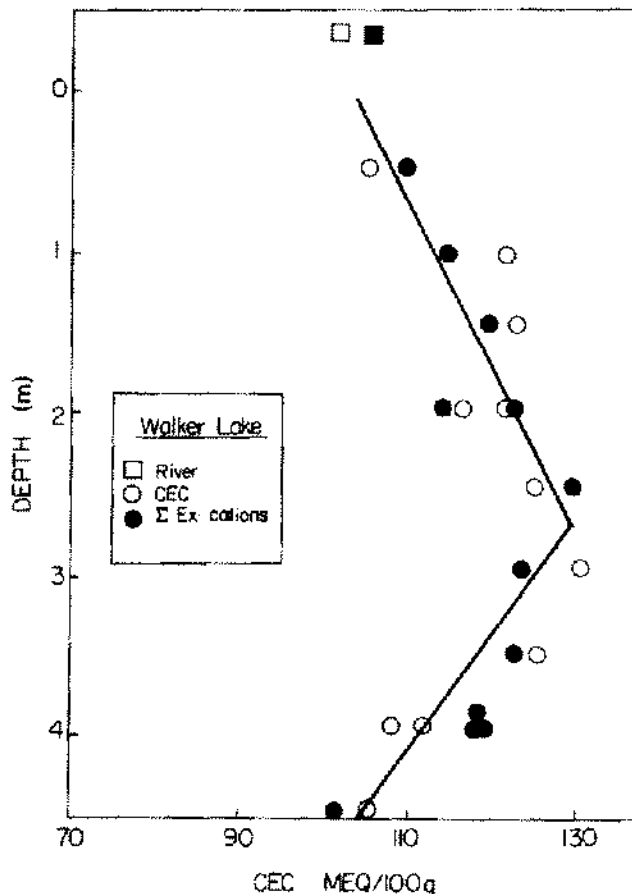


Figure 8. Cation Exchange Capacity; Walker Lake Clays. The cation exchange capacity of Walker Lake clays increases steadily in the upper 3 metres. Below this the exchange capacity decreases, apparently due to fixation of K^+ resulting from increased charge imbalance in the structural clay sites.

into and from both lake water bodies. Dissolved species which react to form less soluble salts or clay minerals are removed from solution in either the lake body or pore fluids. Pore fluids are not effective sources and sinks for these species. More conservative species, however, are lost to or supplied from the pore fluids, which are significant sources, and/or sinks. The direction of transport appears to be a function of the hydrologic changes within the basins.

During stages of pronounced evaporative concentration, dissolved species diffuse into the pore fluids. At Great Salt Lake significant quantities of Cl^- , SO_4^{2-} , Na^+ , K^+ and Mg^{2+} are present in the pore fluids (Table 1). These species have diffused into the pore fluids during the Holocene as a result of the low stand and high concentration of the lake.

During stages of freshening or lake level rise, these species present in high concentrations in the pore fluids flux toward the lakes. The modern Walker Lake system exemplifies this. The estimated Cl^- input to the lake

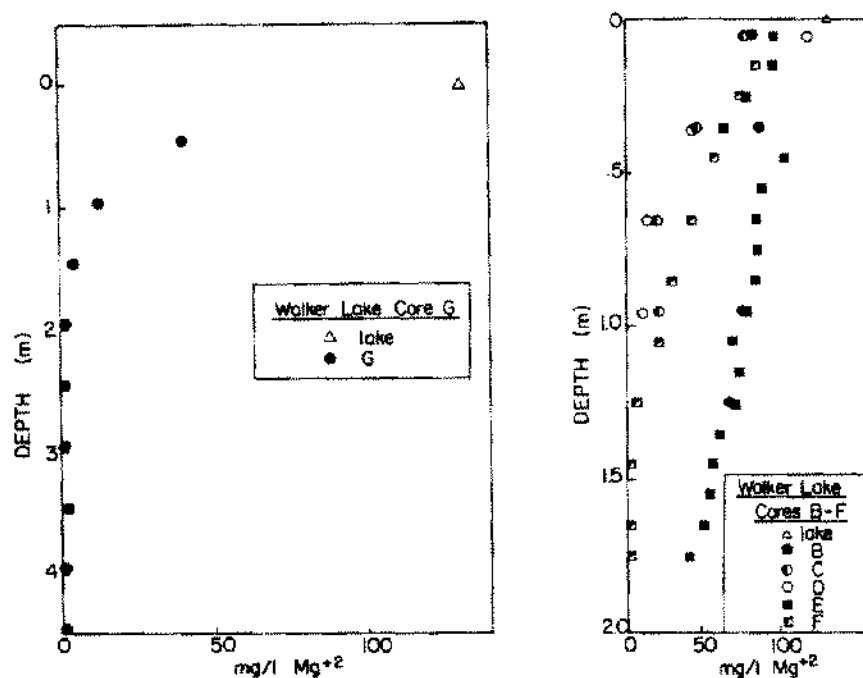


Figure 9. Mg^{2+} Pore Fluid Profiles; Walker Lake. A sharp decrease in Mg^{2+} is seen in the pore fluids at Walker Lake. The more saline pore fluids (cores C, D, F and G) appear to have stronger losses than do the fresher pore fluids.

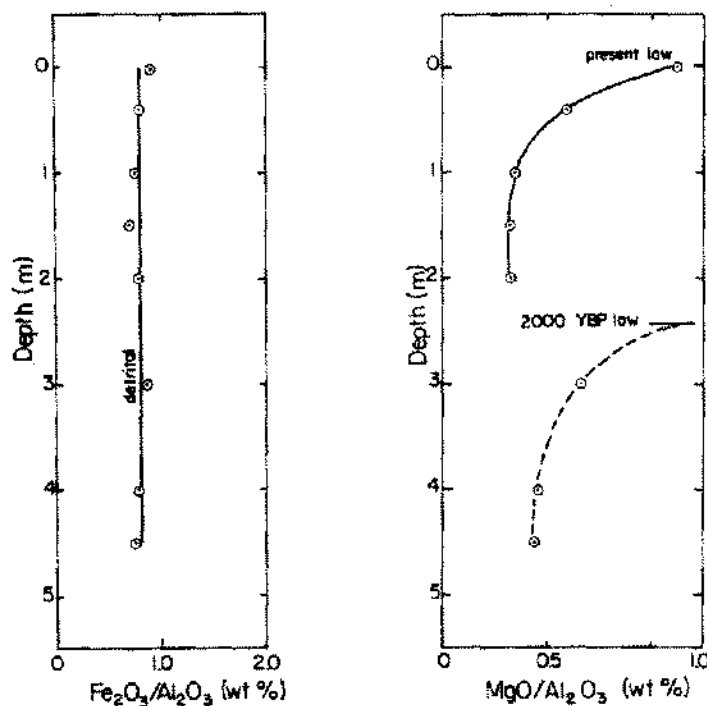


Figure 10. Clay Chemistry; Walker Lake. The composition of Walker Lake clays in terms of Fe/Al and Mg/Al are shown as a function of depth. The constant Fe/Al ratio is taken as an indication of a relatively constant detrital source. The sharp increase in Mg in the upper metre of sediment is due to Mg^{2+} removal from the pore fluids (Figure 9) into the clays during the present low stand. The increased Mg in the clays at about 3 metres is interpreted to be the result of similar removal during the low stand about 2,000 years B.P. (Figure 1).

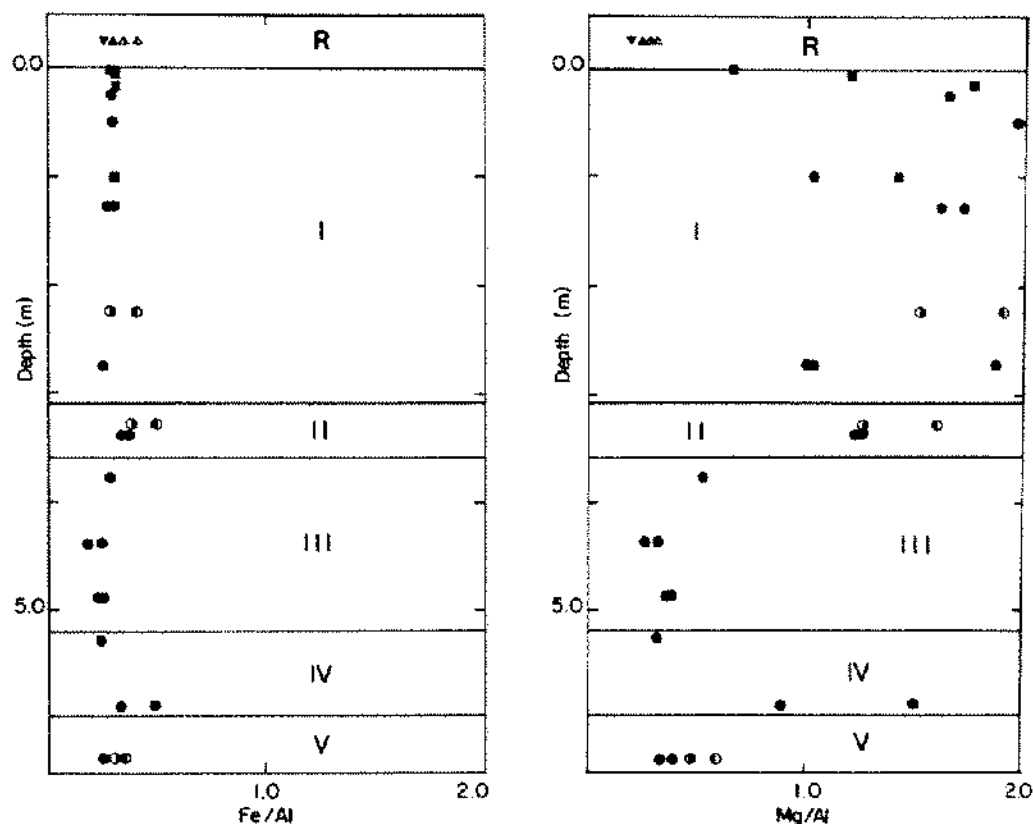


Figure 11. Clay Chemistry: Great Salt Lake. As in the case of Walker Lake clays, the Great Salt Lake clays appear to have had a similar detrital input on the basis of the Fe/Al content. Magnesium is enhanced in the clays deposited under saline lake conditions (I, II and IV, see Figure 1). The fresh water sediments (III) are similar to the river clays, as are the playa clays (V).

waters from the pore fluids is nearly twice that of the surface water input (Table 1).

Major Dissolved Species

The behavior of individual major dissolved species in both the Great Salt Lake and Walker Lake systems is summarized below. Emphasis is placed on pore fluid contributions. The salt budgets presented in Table 1 differ for the two systems. For Great Salt Lake the total sinks in the system (lake brines + pore fluids + solids) are compared with the net aqueous input over the last 32,000 years. For Walker Lake the masses accumulated within the lake and/or pore fluids are compared with the estimated net aqueous input for the last 8,000 years, solid sinks have not been estimated directly.

Chloride. Within the Great Salt Lake system Cl^- may be enhanced or depleted in various brines. Fluctuations of the lake volume have caused halite precipitation and dissolution to occur during the historic period, but for the most part Cl^- is conserved in solution.

The pore fluid Cl^- concentrations are a result of mass transport. The upper boundaries are controlled by conditions within the lake and are especially affected by the

presence or absence of halite and/or stratified brines. In the absence of buried halite beds, the major removal of Cl^- from the lake is diffusion into the pore fluids, which accounts for about 50% of the Cl^- in the system.

Conditions similar to those at Great Salt Lake today existed at Walker Lake from 5,000 to 10,000 years ago. The relatively higher lake stands during the last 2,000 years have resulted in mobilization of Cl^- stored in salts or pore fluids toward the lake. It is estimated that about 65% of the Cl^- input to Walker Lake was supplied by upward diffusion through the pore fluids, and that about 2% of the total Cl^- has been lost by downward diffusion.

Sulfate. The behavior of SO_4^{2-} within the Great Salt Lake system is more strongly influenced by solid phases than that of Cl^- . The precipitation of mirabilite and gypsum has removed about 40% of the SO_4^{2-} from solution; an additional 20% has been removed through reduction to form sulfides. Of the SO_4^{2-} remaining in solution, about 37% is in pore fluids and the remainder in the lake brines. The inflow ratio of SO_4^{2-} to Cl^- at Great Salt Lake is 0.34, while the ratio in the lake is 0.09.

At Walker Lake SO_4^{2-} has also been removed from solution to a large extent. The ratio of SO_4^{2-} to Cl^- in the

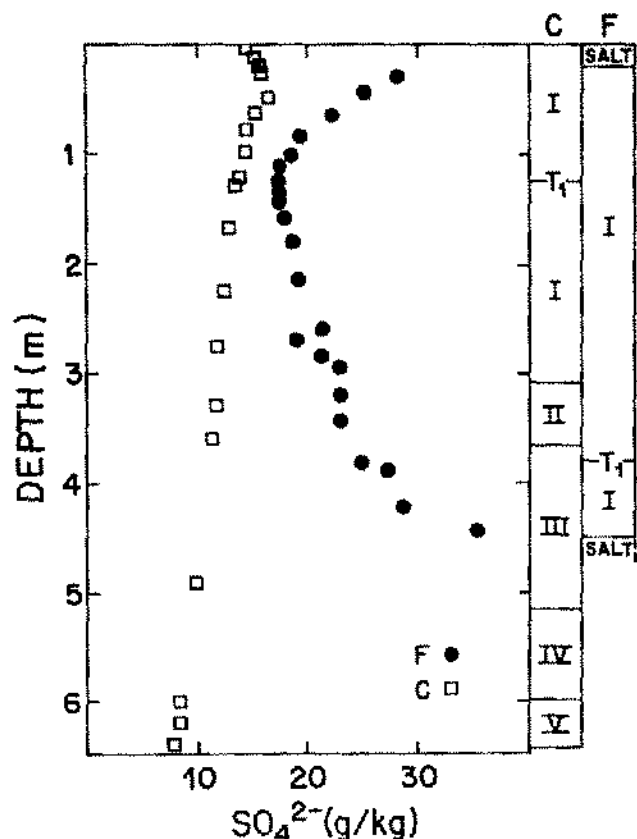


Figure 12. Pore Fluid SO_4^{2-} , Great Salt Lake. The SO_4^{2-} profiles of cores C and F from Great Salt Lake are shown as functions of depth and stratigraphy. Core F contains salts at the top and bottom of the core. The lower salt layer consists of mirabilite, while the upper layer contains halite, mirabilite and gypsum. No salts are present in core C.

Walker Lake inflow is 2.6, while in the lake waters it is only 0.9. A portion of the removal may be due to the precipitation of sulfate salts, such as mirabilite and gypsum, which formed during the mid Holocene low stand or desiccation of Walker Lake. The deepest pore fluids analyzed (4.5 m, WLG) contain a SO_4^{2-} to Cl^- ratio of 0.65; as pore fluid diffusion is a major contributor to the dissolved salts in Walker Lake and diffusive flux is dependent on concentration gradient, less SO_4^{2-} is supplied to the lake. Reduction of SO_4^{2-} also occurs within the sediments, most noticeably in the shallower portion of the lake where it is removed almost quantitatively from solution.

Carbonate Alkalinity. Carbonate alkalinity accounts for only a very small portion of the anion content of both Great Salt Lake brines and pore fluids. As a consequence of the near equality of Ca^{2+} and HCO_3^- (on an equivalence basis) in the inflow waters, removal of HCO_3^- (or CO_3^{2-}) during the precipitation of calcite and aragonite in the lake is nearly quantitative.

Carbonate precipitation also occurs in the Walker Lake waters. The Walker Lake inflow contains HCO_3^- in excess of Ca^{2+} ; therefore, HCO_3^- and CO_3^{2-} remain in solution. Like Cl^- , the carbon species diffuse both toward the lake (in the deeper portion) and away from the lake (in the shallower portion) through the pore fluids. The inflow waters contain of 25.8 HCO_3^- to Cl^- , while the lake and deeper pore fluids contain ratios of 1.28 and 0.94, respectively.

Sodium. At Great Salt Lake Na^+ is for the most part conserved in solution. About 15% of the total Na^+ to have entered the system has been removed in solid phases (~12% in halite and mirabilite, and ~3% exchanged on clays). About half the remaining Na^+ is contained in pore

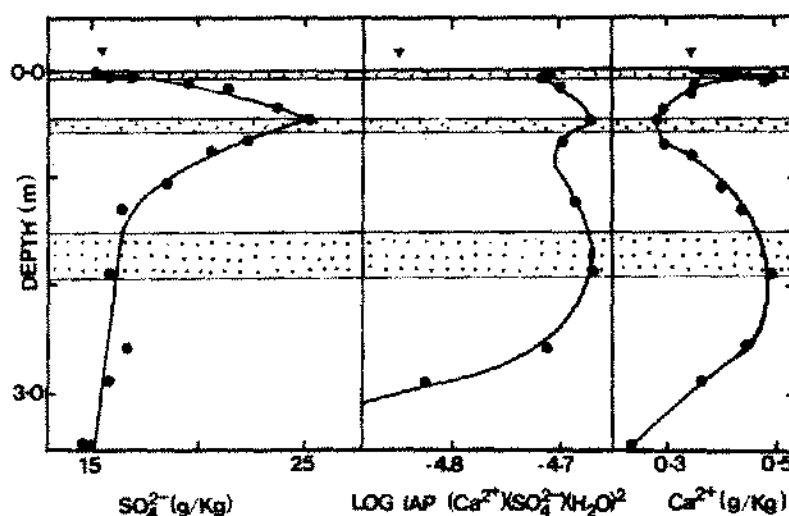


Figure 13. Gypsum. Intervals of Great Salt Lake core G which contain gypsum are stippled. The SO_4^{2-} , Ca^{2+} and ion activity product ($a_{\text{Ca}^{2+}}$) ($a_{\text{SO}_4^{2-}}$) ($a_{\text{H}_2\text{O}}^2$) for the pore fluids (circles) and immediately overlying lake brines (triangles) are also shown.

TABLE 1
Salt Budgets

	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
<i>Great Salt Lake</i>							
Lake	2.65	0.25	0.005	1.53	0.07	0.005	0.13
Pore Fluid	2.70	0.15	0.005	1.50	0.08	0.005	0.10
Salts	0.21	0.80		0.53			
Sediment		0.40	22.	0.13	0.04	7.4	0.64
Total Input	6.90	2.36	12.26	4.54	0.36	3.52	0.87
Overflow Loss	1.12	0.45	0.24	0.74	0.08	0.10	0.19
Net Input	5.78	1.91	12.02	3.80	0.28	3.42	0.68
Total Sinks	5.56	1.60	22.01	3.69	0.19	7.41	0.87
<i>Walker Lake</i>							
Lake	0.80	0.73	1.02	1.10	0.06	0.004	0.05
Pore Fluid	0.99	0.79	1.05	1.26	0.04	0.002	0.001
River Input	0.33	0.86	8.45	1.30	0.19	1.06	0.35
Pore Fluid - Flux	0.02	ND	ND	0.015	ND	ND	ND
Pore Fluid + Flux	0.63	ND	ND	0.20	ND	ND	ND
Net Input	0.95	ND	ND	1.515	ND	ND	ND

Great Salt Lake masses in grams $\times 10^{-15}$ Walker Lake masses in grams $\times 10^{-13}$

fluids, with the balance in the lake brines. The pore fluids are therefore a sink for about 40% of the Na⁺ in the Great Salt Lake system.

At Walker Lake Na⁺ diffuses toward the lake in the deeper portion and away from the lake in shallower portions. Removal of Na⁺ from solution as a result of clay exchange accounts for about 3% of the Na⁺ in the system. The inflow ratio of Na⁺ to Cl⁻ is about 4.0, while the lake ratio is 1.37, and the deeper upward diffusing brines have a ratio of 1.20. The major removal of Na⁺ from the system is probably the result of precipitation of salts and diffusion into the sediment during the mid Holocene low stand.

Potassium. At Great Salt Lake 15% to 20% of the K⁺ has been removed from solution onto clays. The fixation of K⁺ appears to occur on detrital clays with high exchange capacities as they enter the lake. The K⁺ remaining in solution is present both in pore fluids (53%) and the lake brines.

The K⁺ remaining in solution in Walker Lake is only about 50% of the estimated river input. As is the case with Na⁺, Cl⁻, SO₄²⁻ and the carbon species, K⁺ diffuses toward the lake in the deeper portion. It appears that greater than half of the K⁺ entering the system in solution has been removed by reactions involving clay minerals.

Calcium. In terms of the total Ca²⁺ budget, both lake and pore fluids are insignificant in Great Salt Lake and Walker Lake. The Ca²⁺ is removed nearly quantitatively as a result of carbonate mineral precipitation. Reactions involving Ca²⁺ do occur in the sediments of both systems; at Great Salt Lake local dissolution and precipitation of gypsum occur, while at Walker Lake dissolution of carbonate and clay exchange occur locally.

Magnesium. The diffusion of Mg²⁺ into Great Salt

Lake pore fluids is accelerated by the removal of Mg²⁺ from solution into the clay fraction of the solids. Less than 35% of the Mg²⁺ estimated to have entered the system remains in solution. The major portion of the Mg²⁺ removal appears to have occurred during saline lake stages.

Removal of Mg²⁺ from solution at Walker Lake is even more dramatic than at Great Salt Lake. Only about 15% of the estimated river input of Mg²⁺ remains in solution. The pore fluid Mg²⁺ concentration is near the detectable limit as a result of removal from solution into the clay fraction.

SUMMARY

Consideration of three phases of the geochemical evolution of closed basins or evaporating brine bodies allows for a better understanding of such systems. The first phase in understanding modern systems is to define the input to the system. Secondly, reactions occurring within the standing water column need to be considered. The evolutionary pathways of brines from these processes are removal of Ca²⁺, during carbonate precipitation (Figure 14), and in highly saline systems removal of Na⁺ from salt precipitation. Removal of HCO₃⁻, during carbonate precipitation, may also be traced in the water column (Figure 15), along with SO₄²⁻ and Cl⁻ removal during saline stages. Complete understanding of the evolutionary paths on Figures 14 and 15 for the Walker Lake and Great Salt Lake systems also requires consideration of pore fluid processes.

The pore fluids in evaporitic basins are a significant portion of the system. Pore fluids may act as significant sources and/or sinks for the components of more soluble salts. Mass transport through diffusive flux is important

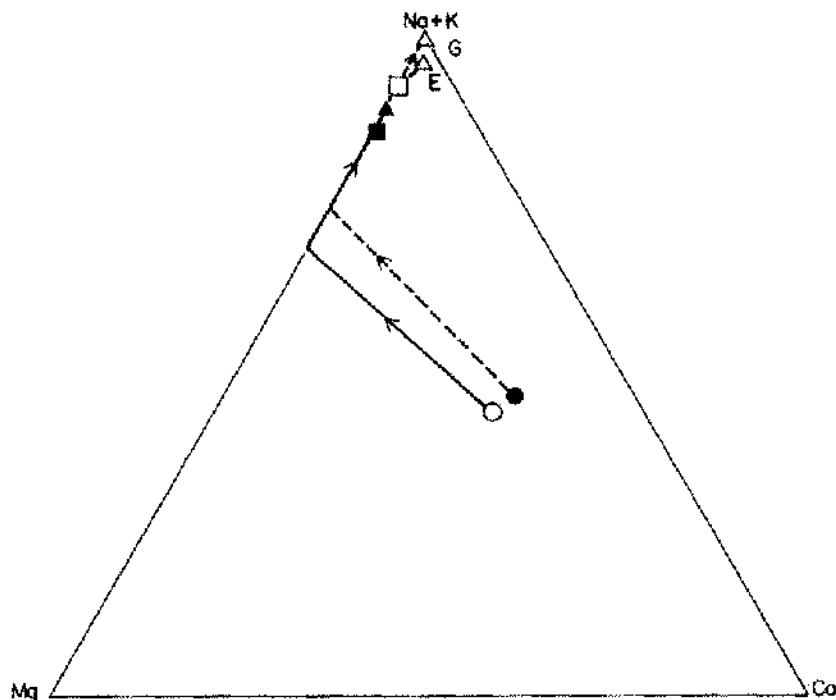


Figure 14. Cation Mole Fractions. The mole fraction of the major cations in the Great Salt Lake inflow (solid circle), lake brines (solid square) and pore fluids (solid triangle) are shown along with the Walker Lake inflow (open circle), lake (open square) and pore fluids from cores E and G (open triangles). Within the lakes Ca^{2+} is removed during carbonate precipitation, driving the compositions away from the Ca^{2+} corner. Removal of Mg^{2+} occurs within the pore fluids of both systems.

as a mechanism to create sources or sinks, and also serves as a bridge to communicate diagenetic reactions in the sediment to the evaporating surface waters. Reactions which occur within the upper few metres of sediment affect the composition of the surface waters; as a result, these should be considered as part of the syndepositional processes. Reactions which occur within the pore fluids are significant in terms of altering the subsequent precipitation paths of evaporating brines.

Components, such as Cl^- , which are conserved in solution may be removed in large quantities from evaporating brine bodies through diffusion during cycles of increased concentration. This tends to deplete the components of more soluble salts from a brine body relative to the less conservative species. During periods of freshening, these more conservative species diffuse toward the evaporating brine body. In contrast, dissolved species which react within the evaporating water mass to form solids may be removed almost entirely from solution. The role of pore fluids is of little consequence for these species.

The diffusive fluxes of components, which are relatively unreactive in the evaporating brine bodies but react within the sediment to form solid phases (most notably Mg^{2+} , K^+ and SO_4^{2-}), are enhanced as a result of increased concentration gradients. The removal of Mg^{2+} , K^+ or SO_4^{2-}

are independent of one another; the possibility exists for accelerated depletion of one, two or all three species. The positions of the inflow, lake brines and pore fluids from Walker and Great Salt Lakes, along with sea water, are shown on the mole fraction diagram in Figure 16. The various lake and pore fluid brines have moved in different directions with respect to the inflow compositions or lake brine source as described below:

1. Great Salt Lake brines are slightly enhanced in Mg^{2+} and K^+ with respect to SO_4^{2-} relative to the inflow. Although all three are removed to some extent diagenetically, the major SO_4^{2-} removal resulted from mirabilite precipitation from the lake brines during early Holocene low stands.
2. The composition of Great Salt Lake pore fluids shows a slight enhancement in Mg^{2+} and K^+ . This is due in part to removal of SO_4^{2-} as mirabilite but also to SO_4^{2-} reduction. Relative to the inflow, the lake composition has been "dragged" in the direction of the pore fluids due to the communicative diffusive flux.
3. The composition of Walker Lake waters is the result of mixing of upward diffusing SO_4^{2-} -rich pore fluids with the dilute inflow, plus removal of Mg^{2+} and K^+

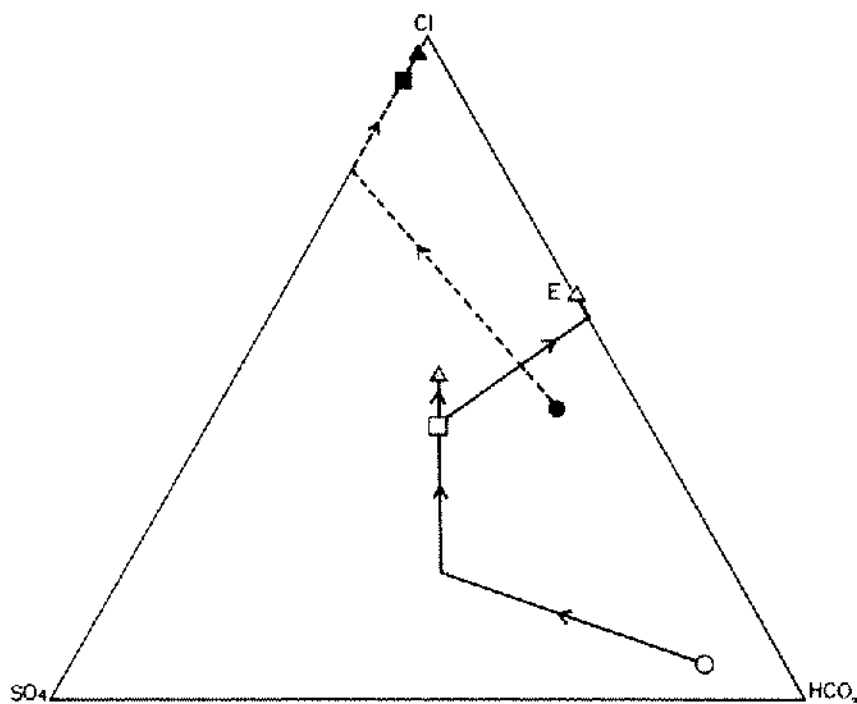


Figure 15. Anion Mole Fractions. The mole fraction of the major anions in the Great Salt Lake inflow (solid circle), lake brines (solid square) and pore fluids (solid triangle) are shown along with the Walker Lake inflow (open circle), lake brines (open square) and pore fluids from cores E and G (open triangles). Precipitation of carbonates within each lake pushes the compositions away from the HCO_3^- corner. Precipitation of mirabilite and SO_4^{2-} reduction lead to Cl^- enrichment in Great Salt Lake brines and pore fluids. Walker Lake brines receive much of their Cl^- from upward diffusion through pore fluids; the resulting lake brines are formed through mixing of material transported through the pore fluids with dilute inflow which has precipitated carbonate minerals.

on clays, and reduction of SO_4^{2-} . The result is seen primarily as an increase of SO_4^{2-} .

4. The upward diffusing pore fluids at Walker Lake were probably derived from compositions similar to the present inflow. The upward diffusing pore fluids are highly enriched in SO_4^{2-} and slightly enriched in K^+ relative to Mg^{2+} ; the Mg^{2+} has been almost completely removed from solution.
5. Shallow areas of Walker Lake are underlain by more dilute pore fluids. These pore fluids are almost totally devoid of SO_4^{2-} as a result of reduction to S^{2-} . Extensive removal of Mg^{2+} from solution into the clay fraction of the solids also occurs. Although K^+ removal from solution occurs, it is lesser than that of SO_4^{2-} or Mg^{2+} , resulting in strong enhancement of K^+ in the pore fluids.

Removal of SO_4^{2-} , Mg^{2+} and K^+ from solution occurs in the pore fluids of both Great Salt and Walker Lakes. In the absence of salts containing SO_4^{2-} , Mg^{2+} or K^+ the major removal mechanisms are SO_4^{2-} reduction, Mg^{2+} incorporation in authigenic or detrital clays and K^+ fixation

by detrital clays. The three processes occur to differing extents in the pore fluids of the two lakes.

Reduction of SO_4^{2-} is most pronounced in the fresher portion of the Walker Lake pore fluids, where SO_4^{2-} is almost entirely removed from solution. The upward diffusing SO_4^{2-} in more concentrated brines is removed to a lesser extent relative to the mass in solution. The Great Salt Lake system appears to follow the same trend; SO_4^{2-} reduction occurs within the saline pore fluids, but the proportion of SO_4^{2-} removed from solution is relatively small. The mass of solid sulfides within the sediments at Great Salt Lake is greater within or just below the fresher water intervals. It appears that both the amount of sulfide formed and the proportion of SO_4^{2-} removed are inversely proportional to the concentration of the brines. Reduction of SO_4^{2-} is therefore expected to exert a dominant control in relatively early stages of evaporative concentration and a lesser control as concentration increases.

Removal of Mg^{2+} from solution occurs primarily as a result of detrital clay alteration or authigenic clay formation. The mass of Mg found in the clay fraction of sediments at both Great Salt Lake and Walker Lake increases

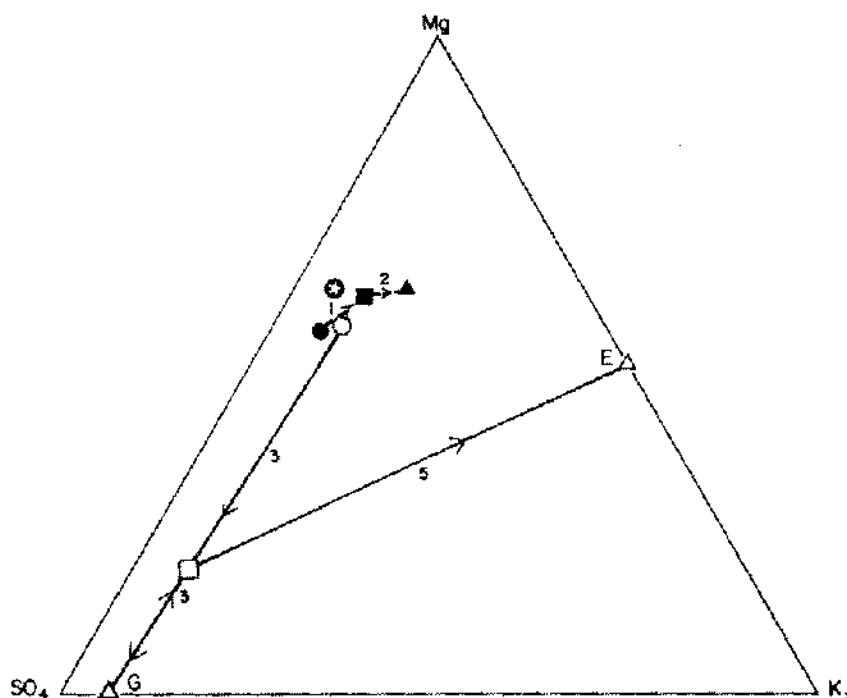


Figure 16. Mg—SO₄—K₂ Equivalence Diagram. Within both systems Mg²⁺ and K⁺ are conserved in solution in the lake brines, SO₄²⁻ has been precipitated at Great Salt Lake, all three participate in diagenetic reactions involving the pore fluids. The Great Salt Lake inflow (solid circle), lake brines (solid square) and pore fluids (solid triangle) are shown along with the Walker Lake inflow (open circle), lake brines (open square) and pore fluids from cores E and G (open triangles), sea water (star) is shown for reference.

in the sediments deposited during more saline stages. The mass of Mg²⁺ removed, therefore, appears to be proportional to the concentration of the brines. Removal of Mg²⁺ from Walker Lake pore fluids is nearly quantitative, while at Great Salt Lake the Mg²⁺ content of the brines, although depleted, remains significant. There appears to be an inverse correlation of the proportion of Mg²⁺ removed from solution and brine concentration.

Fixation of K⁺ on detrital clays or diagenetically altered clays occurs in both systems. The removal of K⁺ from solution is relatively minor and therefore the brines are somewhat enhanced in K⁺ relative to Mg²⁺ and SO₄²⁻. It therefore appears that syndepositional processes acting within the upper few metres of sediment may result in "MgSO₄-deficient" brines enriched in K⁺. Pore fluids may serve as a bridge to alter the composition of standing brine bodies as a result of the diagenetic reactions. In order to identify this type of brine alteration, masses of Mg (as clays) and S (as sulfides) are expected to be found in close proximity to other deposits of evaporated brine bodies.

REFERENCES

- Benson, L. V. 1978. Fluctuation in the level of pluvial Lake Lahontan during the last 40,000 years. *Quat. Res.* v. 9:300-318.
- Benson, L. V. and R. J. Spencer. 1983. A Hydrochemical Reconnaissance Study of the Walker River Basin, California and Nevada. U.S. Geol. Surv. Open-File Report 83-740.
- Braitsch, O. 1971. *Salt Deposits: Their Origin and Composition*. Springer-Verlag, New York.
- Crank, J. 1975. *The Mathematics of Diffusion*. 2nd edition, Clarendon.
- Eugster, H. P. and L. A. Hardie. 1978. Saline lakes. In: *Lakes: Chemistry, Geology, Physics* (A. L. Lerman, ed.), pp. 237-294.
- Garrels, R. M. and F. T. Mackenzie. 1967. Origin of the chemical composition of some springs and lakes. In: *Equilibrium Concepts in Natural Water Systems*. Amer. Chem. Soc., Washington, D.C., pp. 222-242.
- Hardie, L. A. 1978. Evaporites, rifting and the role of CaCl₂ hydrothermal brines. (abstr). *Geol. Soc. Amer. Abst. Prog.* 10, (7), p. 416.
- Hardie, L. A. and H. P. Eugster. 1970. The evolution of closed-basin brines. *Min. Soc. Amer. Spec. Pap.* 3, pp. 273-290.
- Harvie, C. E., J. H. Weare, L. A. Hardie and H. P. Eugster. 1980. Evaporation of seawater: calculated mineral sequences. *Science* v. 208:498-500.
- Harvie, C. E., H. P. Eugster and J. H. Weare. 1982. Mineral equilibria in the six-component seawater system, Na—K—

- Mg—Ca—SO₄—Cl—H₂O at 25°C. II: Compositions of the saturated solutions. *Geoch. Cosmo. Acta* v. 46:1603-1618.
- Jones, B. F. 1966. Geochemical evolution of closed basin waters in the western Great Basin. 2nd Symp. Salt, Ohio Geol. Soc., Cleveland, Ohio, v. 1:181-200.
- Lerman, A. L. and R. R. Weiler. 1970. Diffusion and accumulation of chloride and sodium in Lake Ontario sediment. *Earth and Planetary Sci. Letters*, v. 10:150-156.
- Robinson, R. A. and R. H. Stokes. 1970. *Electrolyte Solutions*. Butterworths Scientific Publ., 559 pp.
- Spencer, R. J. 1977. Silicate and carbonate sediment-water relationships in Walker Lake, Nevada. Masters Thesis, Univ. of Nevada, Reno, Nevada, 98 pp.
- Spencer, R. J. 1982. The geochemical evolution of Great Salt Lake, Utah. Ph.D. Dissertation, The Johns Hopkins University, Baltimore, Maryland, 309 pp.