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BEHAVIOR OF MAJOR SOLUTES DURING CLOSED-BASIN BRINE EVOLUTION†

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ABSTRACT. The pronounced chemical fractionation that takes place in hydrologically closed basins between dilute inflow and concentrated brines can be accounted for by a variety of mechanisms. These include mineral precipitation, selective dissolution of efflorescent crusts and sediment coatings, sorption on active surfaces, degassing, and redox reactions. Major solutes are differentially affected by these mechanisms, and their response may differ from basin to basin. Using data from Lake Magadi, Kenya; Lake Abert, Oreg.; Devils Lake, N. Dak.; Deep Springs Lake, Calif.; Basque Lake, British Columbia; and Great Salt Lake, Utah, some of these differences can be delineated. In most of these systems, chloride behaves as a conservative element and can be used to monitor the progress of evaporative concentration; (Ca + Mg) are removed from solution principally by mineral precipitation, commonly involving carbonate minerals. Carbonate species are depleted through mineral precipitation, degassing, and selective dissolution of efflorescent crusts.

The fractionation between Na and K is pronounced in the inflow waters of all but one of the closed basins, with Na being enriched over K in solution up to 100-fold. We believe that K is screened out by sorption and exchange processes on active surfaces related either to volcanic glasses and gels or to clay minerals. This screening is most effective at Lake Magadi, less so at Lake Abert, Devils, and Great Salt Lakes, even less so at Deep Springs Lake, and it does not operate at Basque Lake. In lake brines, K is usually conserved in solution, and it is eventually enriched over Na through the precipitation of Na-rich saline minerals.

Silica is lost from solution at Lake Magadi even more extensively than is K, presumably through the formation of opaline cements and crusts. In the intermediately saline and more perennial Oregon and North Dakota lakes, diatoms are also important for extracting silica from solution. Surface sorption and bacterial reduction appear to be the principal processes for sulfate fractionation from closed basin saline waters. In more concentrated brines, sulfate often accumulates until saturation with respect to sodium sulfate minerals is reached.

Of the solute fractionation mechanisms operative in closed basins only mineral precipitation has been tested by computer simulation. The others are more difficult to assess, and their importance differs from basin to basin depending in part upon circulation patterns, availability of reactive surfaces, solids:solution ratios, and residence time for the solutions.

INTRODUCTION

During the chemical evolution of natural waters in an evaporative setting a series of solute fractionations manifest themselves which simplify the end product. Of the eight or so most abundant initial solutes (SiO_2, Na, K, Ca, Mg, HCO_3, Cl, SO_4), some are removed preferentially from solution, while others increase in relative abundance. Consequently, final brines are dominated by two, three, or at most four species.

Overall effects of solute fractionation during brine evolution are illustrated in figure 1, where the compositions of a wide variety of inflow

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** U.S. Geological Survey, Reston, Virginia 22092 waters are compared with closed basin brines. The dominant anion is bicarbonate in the inflow, whereas the cations are variable. In contrast, sodium is the dominant cation in nearly all the brines, whereas the anions are variable. What is responsible for this characteristic evolution? Obviously not a single process but a multitude of mineral-water interactions.

The general principles of continental brine evolution have been discussed by Jones (1966), Garrels and MacKenzie (1967), and Hardie and Eugster (1970), while case studies have been presented by Jones (1965), Lerman (1967), Hardie (1968), Eugster (1970), Phillips and VanDenburgh (1971), Maglione (ms), VanDenburgh (1975), Jones, Eugster, and Rettig (1977) and others. Brine evolution can be analyzed most completely in hydrologically closed basins, where dilute inflow waters can be compared with the most concentrated brines. In order to follow the

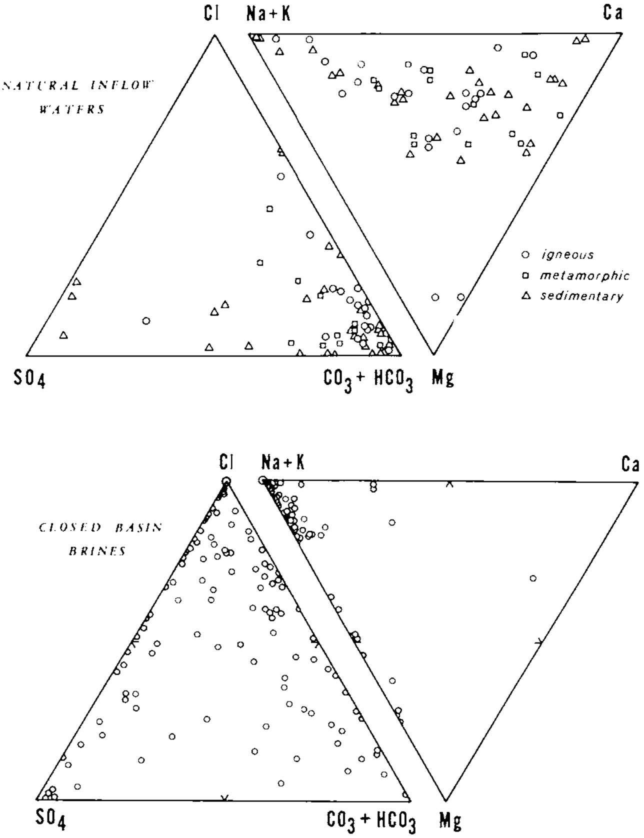

Fig. 1. Trilinear diagrams contrasting the major ion composition of inflow waters grouped by drainage basin lithology (top) with that of continental closed basin brines (bottom). Data from sources quoted by Hardie and Eugster (1970).

solute fractionation trends, the composition of the inflow waters must be reasonably homogeneous.

Some of the processes of enrichment and depletion are well documented, whereas others must be inferred, and their effectiveness differs from basin to basin. It is the purpose of this paper to evaluate these processes by comparing published data from a variety of closed basins. Our interpretations have been influenced particularly by the studies of such processes at Lake Magadi, Kenya.

BRINE EVOLUTION AND FRACTIONATION MECHANISMS

In the past, closed basin brine evolution has been considered primarily in terms of mineral precipitation. Garrels and McKenzie (1967) presented a quantitative scheme for the evolution of a single closed basin water composition, based solely on mineral precipitation. Na and K were considered together, and sepiolite was used to remove magnesium. Hardie and Eugster (1970) adapted this scheme to the computer and calculated the fate of many inflow waters, while Al-Droubi (1976) extended the more comprehensive evaporite concentration model of Fritz (1975) to Lake Chad water. Eugster and Hardie (1978) have suggested that sepiolite be replaced by carbonates as the predominant Mg-phases in sediments of closed basins.

In fact, mineral precipitation is only one of several solute fractionation mechanisms. Other significant solute fractionations are associated with selective dissolution of efflorescent crusts and sediment coatings, with exchange and sorption reactions on active surfaces, with degassing, and with redox reactions.

MINERAL PRECIPITATION

Precipitation of a mineral phase has a profound effect on the subsequent evolution of solution compositions. This is illustrated in the evolutionary scheme of Eugster and Hardie (1978), reproduced in figure 2. In this scheme, inflow waters are placed in three categories depending on their $Ca+Mg/HCO_3$ ratios (paths I, II, and III), and their evaporative development differs distinctly, the removal of solids providing the critical branching points. The importance of these branching points can be understood best by considering an example, such as the precipitation of calcite, which normally is the first mineral to precipitate upon evaporative concentration. During its equilibrium precipitation two conditions must be fulfilled simultaneously:

1. The ion activity product, $a_{Ca^{2+}} \cdot a_{CO_3{}^{2-}}$ must remain constant.
2. Ca^{2+} and $CO_3{}^{2-}$ are removed from solution in equal molar proportion.

Condition 1 specifies that the concentrations of Ca and CO_3 must vary antithetically, whereas condition 2 requires that the Ca/CO_3 molar ratio will change, unless it was precisely 1 at the outset. The net effect is that waters of path I will become enriched in HCO_3 and depleted in Ca through calcite precipitation, and the opposite holds true for waters of path III. Waters of path II have an initial ratio close to 1 and can go in either direction, depending upon their initial ratio. In the process, they need to precipitate a large amount of alkaline earth carbonates before either Ca^{++} or HCO_3^- are exhausted, and the waters can leave the central rectangle of figure 2. Consequently, calcite precipitation represents a critical branching point. Waters in which bicarbonate is dominant over calcium initially will become enriched in HCO_3^- and depleted in Ca^{2+} and vice versa. During the precipitation of calcite or low magnesian calcite, the Mg/Ca ratio in the residual solution increases, causing a concomitant increase in Mg/Ca in the solid phase. Eventually, especially for waters of path II, low-Mg calcite is replaced by high-Mg calcite or protodolomite or perhaps even magnesite, depending on the degree of Mg enrichment in the solution. This, in turn, is dependent on the silica concentration and the possible formation of Mg-silicate.

Another important branching point is the precipitation of gypsum, $CaCO_4 \cdot 2H_2O$, which causes waters to become enriched either in Ca or in SO_4 depending upon the initial Ca/SO_4 ratio, because gypsum precipitation is governed by two conditions analogous to those for calcite precipitation.

Precipitation of alkaline earths occurs early in the evolution of closed basin waters. Nevertheless, it is sufficient to account for the most common brine types. In other words, the eventual compositional fate of a particular water during evaporative concentration is already sealed

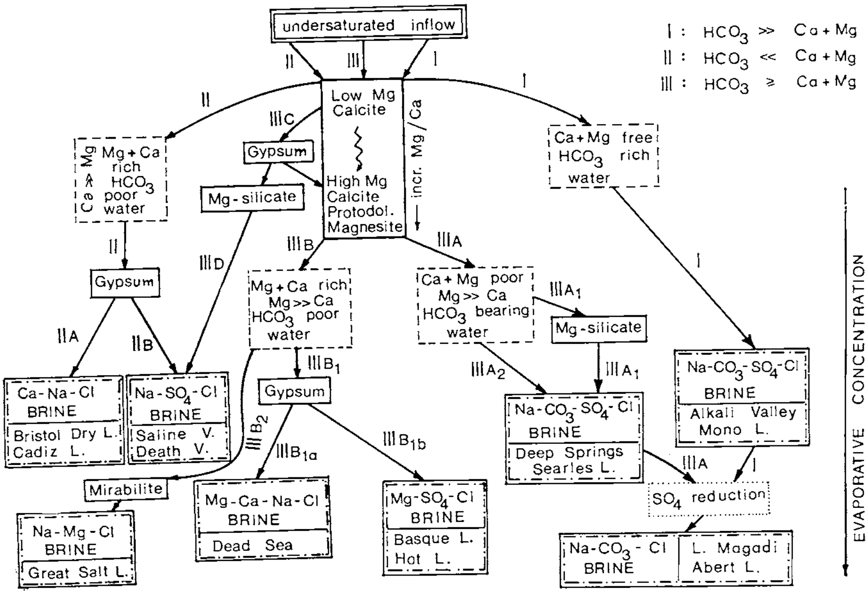

Fig. 2. Flow diagram for the geochemical evolution of closed basin brines from Eugster and Hardie (1978). The position of Mg–silicate precipitate in the scheme should be considered problematic.

at the dilute inflow stage. However, in order to account for the detailed behavior of all major solutes, other fractionation mechanisms must also be considered.

FRACTIONATION MECHANISMS OTHER THAN MINERAL PRECIPITATION

The solute load of closed basin waters can be increased by the formation and partial dissolution of efflorescent crusts and subsurface sediment coatings. The importance of this process has been stressed by Smith and Drever (1976), Jones, Eugster, and Rettig (1977), and Eugster and Hardie (1978). Efflorescent crusts are present in all arid basins with sufficient inflow. They form by capillary evaporation of groundwater, wherever subsurface fluids are close enough to the surface or, to a lesser extent, by evaporation of ephemeral surface waters. They are the result of complete desiccation and hence contain solutes in the same proportion as the water from which they are derived (Hardie, 1968). Upon later contact with dilute runoff, however, a pronounced fractionation occurs, because the most soluble constituents dissolve first, whereas the least soluble parts of the crusts, such as silica and alkaline earth carbonates, remain behind. The runoff either evaporates again, forming more soluble efflorescences in a lower part of the basin, or it mixes with existing groundwater, adding solute load. This is probably the mechanism by which saline groundwaters of closed basins pick up most of their solutes.

Along with the formation of efflorescent crusts, capillary evaporation will also produce similar crusts and coatings within the soil zone. Drever and Smith (1978) have produced such coatings in laboratory experiments and have tested their differential solubilities. The effects were similar to those predicted for efflorescent crusts. Hence we must include differential dissolution of such soil coatings among the important solute fractionation mechanisms.

Ion exchange and sorption processes have long been recognized as being important to the chemistry of dilute waters (as in reviews by Gorham, 1961; Hem, 1970). In particular, differential uptake and exchange of major cations on clays seems to be responsible for preferential solute loss from solution. For instance, a K^+ loss has been specifically documented for the alkaline closed basins of Oregon (Jones and others, 1969; Phillips and VanDenburgh, 1971) and Kenya (Eugster, 1970; Jones, Eugster, and Rettig, 1977). Wood (1978) has demonstrated sorption of sulfate by Holocene continental and lacustrine sediments in the vadose zone of the high plains of west Texas. Surface exchange and sorption processes have been deemed critically important for the less abundant solutes, as well (Jenne, 1968, 1977; Turekian, 1977).

Another mechanism for differential solute loss is degassing resulting from equilibration with the atmosphere, increase in temperature, decrease in solubility with salinity, or organic activity such as photosynthesis. Numerous examples may be given for the precipitation of Ca–Mg carbonate resulting from CO_2 loss (for example, see references in Graf, 1960, or Jones and Bowser, 1978). CO_2 degassing by the reaction

$$2HCO_3^- = CO_3^{2-} + CO_2 + H_2O \qquad (1)$$

is essential to explain the rise in pH accompanying evaporative concentration of alkaline brines and is enhanced by the decrease in solubility of CO_2 with increase in salinity. The reaction has been cited by Nesbitt (ms) for Basque Lake, British Columbia, and Jones, Eugster, and Rettig (1977) for Lake Magadi, Kenya. Bacterial reduction can lead to sulfate loss through degassing of H_2S, precipitation of native sulfur, or formation of iron sulfides.

Redox processes affect mainly sulfate among the major solutes found in natural waters and brines. However, oxidation of ferrous iron or ammonia may significantly influence the pH, on which, in turn, other solute fractionation mechanisms depend.

Mineral precipitation is normally initiated either by evaporation or by degassing, but mixing of waters can also lead to supersaturation (Runnels, 1969; Wigley and Plummer, 1976). Alkaline earth carbonate precipitation, in particular, can be caused by mixing alkaline brines with dilute inflow (Eugster and Maglione, in press).

GENERAL SOLUTE BEHAVIOR

Depending upon the extent of fractionation during brine evolution and the effectiveness of the individual fractionation processes, solutes may behave in a variety of patterns. Using our experience from Lake Magadi, Kenya (Eugster, 1970; Jones, Eugster, and Rettig, 1977) we can predict five basic types of behavior, all of which have been illustrated in figure 3. Type I represents a solute that remains in solution throughout the concentration process: a perfectly conserved species. This does not mean that this solute is not involved in the formation of efflorescent crusts, but simply that it will be redissolved quantitatively by subsequent runoff. Na and Cl are good examples. Conservative constituents are used to indicate concentration factors and thus monitor increases in concentration.

IIa and b are solutes, one a cation and the other an anion, which combine in the precipitation of a mineral phase. At the point of satura-

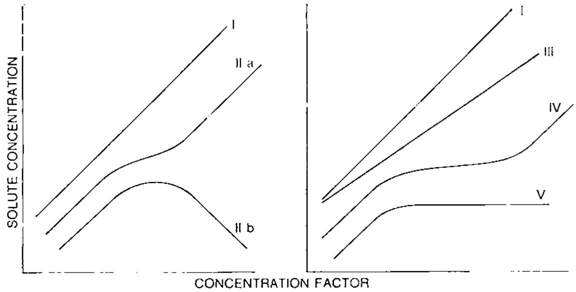

Fig. 3. Schematic plots of individual solute content versus the degree of overall solution concentrations, illustrating the characteristic effect of specific mechanisms on changes in chemical composition. Basic types described by roman numerals are explained in the text.

tion, the branching point, solute b is rapidly depleted. Solute a increases, but less rapidly than a conservative constituent, and after precipitation is virtually completed, its slope of concentration increases again. Typical examples would be Ca^{2+} and $CO_3{}^{2-}$ as discussed earlier.

A type III solute is removed from solution gradually by a variety or combination of mechanisms, such as mineral precipitation, sorption, or degassing. This is the case for $HCO_3 + CO_3$ at Magadi. The removal mechanisms operate over the full range of evaporative concentration, so that an essentially linear relationship results, but with a slope less than that for conservative solutes. A removal mechanism which is not strongly concentration dependent, but is effective only over the middle part of the concentration range, produces a sigmoid curve such as curve IV in figure 3. Examples of such mechanisms are ion exchange, surface adsorption, and biogenic reduction. K and SO_4 commonly follow this trend. Finally, an uncharged solute such as SiO_2, when it reaches saturation with respect to the corresponding solid phase, simply remains constant (curve V). These are the basic types of solute behavior we have encountered up to now, though others, particularly among the minor constituents, are of course possible.

CONSERVATIVE ELEMENTS

Of the eight principal solutes that dominate the chemistry of natural waters, chloride is usually conserved over the widest concentration range, because anion exchange is minor and Cl^- remains in solution until halite saturation. An exceptional situation would be the freezing out of hydrohalite, $NaCl \cdot 2H_2O$, suspected for Great Salt Lake during winter months. Up to halite saturation chloride is a reliable measure of degree of evaporative concentration, but beyond that other solutes must be used, such as Mg, K, or minor constituents such as Br, depending on the particular brine composition. Problems with normalizing against chloride in estuarine or coastal waters have been discussed by Hanor (1977).

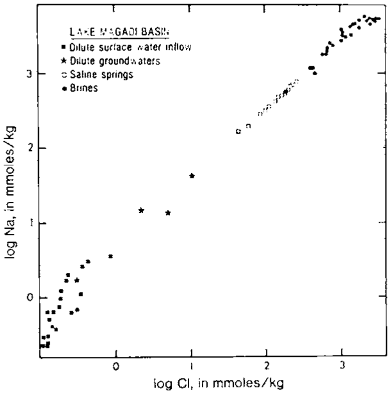

Fig. 4. Plot of sodium versus chloride concentration for waters from the Lake Magadi basin, Kenya.

The usefulness of plotting solutes against chloride has been well documented for the Magadi basin, Kenya (Jones, Eugster, and Rettig, 1977), which has particularly homogeneous inflow compositions. Figure 4 shows a test of the relative conservation of Na and Cl. Inflow waters (full squares, data from Jones, Eugster, and Rettig, 1977, table 1a) show some scatter reflecting local variance in solute sources. The few dilute groundwater samples (stars) have similar Na/Cl ratios. A surprising constancy of Na/Cl is shown by the hot springs (open squares) and by the lake brines (dots), except for the highest concentrations, where sodium depletion indicates trona ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$) precipitation. The line defined by the data of figure 4 has a slope near unity, as it should for two conservative elements plotted on the same scale. Similar behavior was found for F, Br, and B in the Magadi basin.

A more sensitive test of the relative behavior of Na and Cl is a plot of molar Na/Cl ratio versus Cl concentration (see fig. 5). For the Lake Magadi basin this plot consists of two segments. For the dilute surface inflow waters the Na/Cl ratio increases rapidly with increasing chloride content and is given by $\log Na/Cl = 0.99 + 2.57 \log Cl$, with a correlation coefficient of 0.87. We interpret this segment as indicating sodium sources from rock weathering in addition to sodium directly associated with chloride. For higher concentrations Na/Cl remains constant except for the saturated brines, as noted above.

CARBONATE–BICARBONATE AND Ca–Mg REMOVAL

Using chloride as a reference, we can now compare the behavior of the other solutes. $HCO_3 + CO_3$ concentration versus chloride for Magadi is shown in figure 6. As mentioned earlier, CO_2 species are removed gradually over the whole concentration range. The initial removal corresponds with depletion of alkaline earths and precipitation of carbonates. In fact, the trend of points in the lower part of figure 6 is similar to curve IIa in figure 3. But at the higher concentrations, from the saline

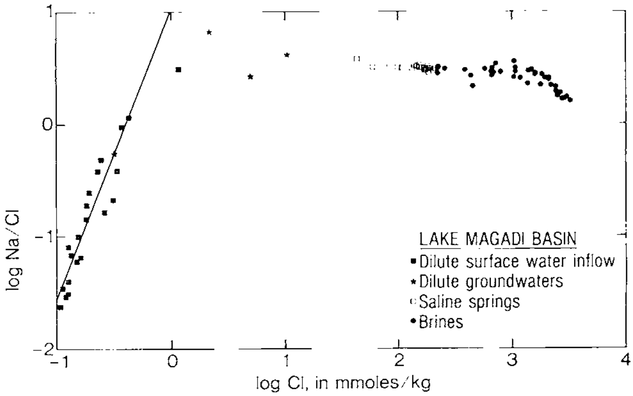

Fig. 5. Plot of the molar ratio of sodium to chloride versus chloride concentration for waters of the Lake Magadi basin, Kenya.

hot springs to the lake brines, departure from a slope of one indicates that carbonate-bicarbonate removal continues. The principal mechanisms for CO_2 loss, degassing and mineral precipitation, can be differentiated by comparing a plot of carbonate alkalinity with one for total carbonate. Carbonate alkalinity ($HCO_3^- + 2CO_3^{2-}$) is unaffected by CO_2 degassing (see eq 1), while total carbonate ($HCO_3^- + CO_3^{2-}$) decreases for both degassing and mineral precipitation. Such a plot, normalized to chloride, is shown in figure 7. The loss of total carbonate with increasing Cl is clearly evident. On the other hand, the hot springs have essentially constant carbonate alkalinity, indicating that degassing is responsible for most of their carbonate loss (see also Jones, Eugster, and Rettig, 1977, table 2). Precipitation of alkaline earth carbonates is important for the more dilute waters, and trona precipitation for the brines. Formation and subsequent dissolution of efflorescent crusts containing thermonatrite ($NaCO_3 \cdot H_2O$) is another important process for CO_2 loss.

To check on the alkaline earth carbonate precipitation, (Ca + Mg) concentrations are plotted in figure 8. The points show the typical behavior of curve IIb of figure 3. Initially, (Ca + Mg) increase in concentration along with Cl, but then there is a very rapid drop exemplified by the dilute groundwaters. After a 100-fold concentration in Cl they have been removed nearly quantitatively, and in waters more concentrated than the hot springs they are below detection limit.

The behavior of calcium and magnesium in the Great Salt Lake system is shown by figures 9 and 10 based on the data of Hahl and Mitchell (1963), Hahl and Langford (1964), Hahl (1968), and unpublished data. Besides major river inflow (Bear, Weber, and Jordan Rivers), also included are the large inflow spring systems, as well as a selection of North and South arm brine from Hahl and Handy (1969), Whelan (1973), and Whelan and Petersen (1975). As figure 9 shows, Ca is lost from solution gradually over the whole concentration range, as in curve III, figure 3. The loss is associated with a variety of processes. Interest-

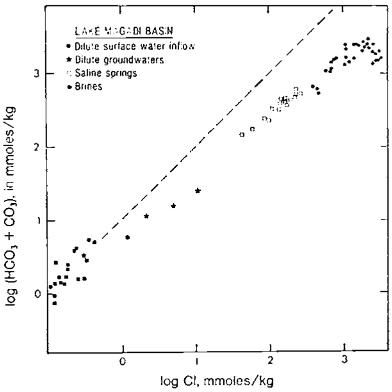

Fig. 6. Plot of bicarbonate plus carbonate versus chloride concentration for waters of the Lake Magadi basin, Kenya.

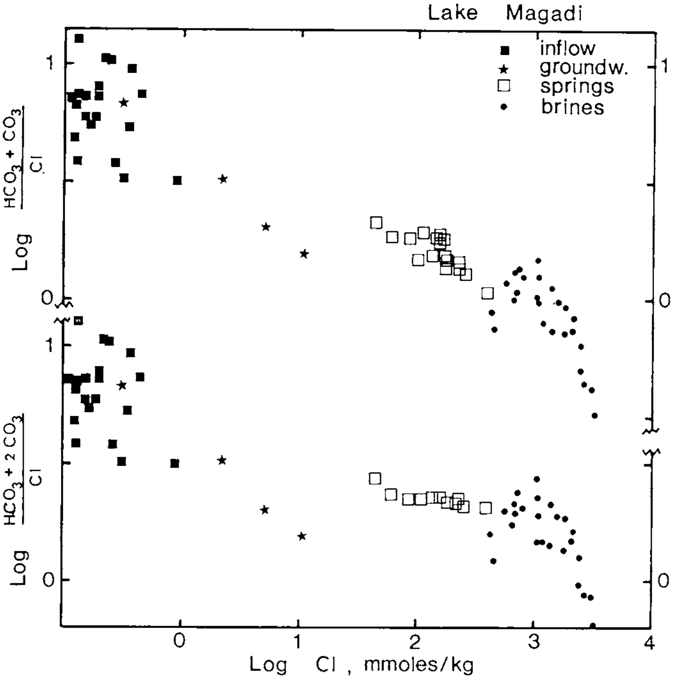

Fig. 7. Plot of total carbonate ($HCO_3^- + CO_3^{2-}$) divided by chloride (top) and carbonate alkalinity ($HCO_3^- + 2CO_3^{2-}$) divided by chloride (bottom) versus chloride concentration for waters of the Lake Magadi basin, Kenya. Note the break in scale between the two plots.

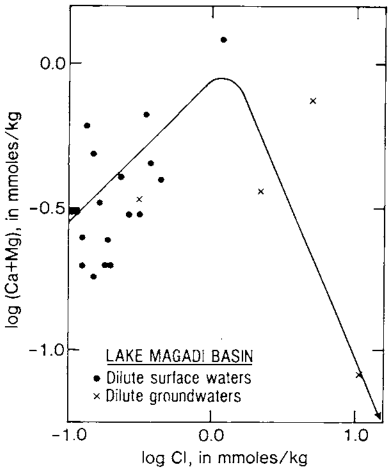

Fig. 8. Plot of calcium plus magnesium versus chloride concentration for dilute waters of the Lake Magadi basin, Kenya.

ingly enough, as shown in figure 10, Mg is lost only during the first half of the concentration range and subsequently behaves as a conservative constituent. A satisfactory accounting of this fractionation awaits further study of lake sediment and pore fluids, which is in progress.

SODIUM–POTASSIUM FRACTIONATION

The behavior of K during evaporative concentration in the Magadi basin is shown in figure 11. It follows a type IV trend, indicating initial conservation in solution (inflow stage), followed by differential loss from solution over an extended range (groundwater stage) and finally conservation in concentrated waters (hot springs and surface brines). The loss of K from solution has been associated with uptake on active surfaces (Jones, Eugster, and Rettig, 1977). Since clay minerals are very rare at Magadi, these surfaces must be related either to the aluminosilicate gels reported by Eugster and Jones (1968) and Surdam and Eugster (1976) or the abundant volcanic glass. The conservation of potassium between hot springs and the most concentrated brines is surprisingly

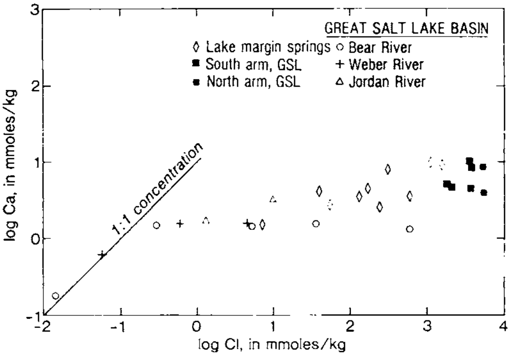

Fig. 9. Plot of calcium versus chloride concentration for representative samples of waters from the Great Salt Lake basin of Utah. The line of unit slope expected from simple evaporative concentration is shown for reference.

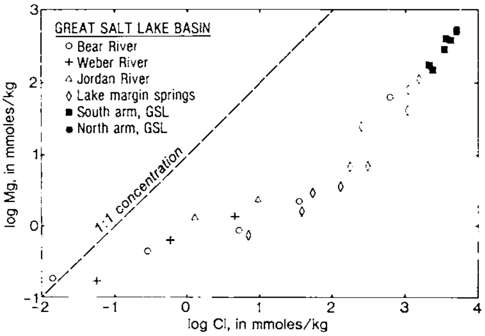

Fig. 10. Plot of magnesium versus chloride concentration for representative samples of waters from the Great Salt Lake basin of Utah. The line of unit slope expected from simple evaporative concentration is shown for reference.

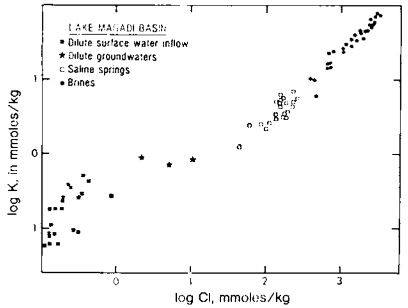

Fig. 11. Plot of potassium versus chloride concentration for waters of the Lake Magadi basin, Kenya.

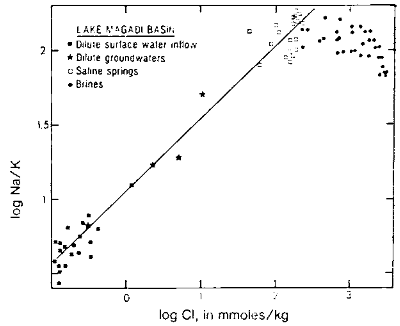

Fig. 12. Plot of the molar Na/K ratio versus chloride concentration for waters of the Lake Magadi basin, Kenya.

complete. This could be due to three factors: lack of contact with active surfaces during circulation (such as suggested for Lake Abert, Oreg., by Jones, Eugster, and Rettig, 1969), saturation of exchange or sorption sites with potassium, and rejection of K from the trona and halite lattices. Under these conditions, K in fact is conserved more completely than Cl. This late-stage enrichment of K is also typical for marine evaporites and for similar reasons. In other words, K removal by solute sorption and cation exchange is most effective during relatively dilute subsurface circulation, the groundwater stage, where Ca is the major cation to be displaced.

The fractionation between sodium and potassium is best shown by plotting atomic ratios of Na/K against Cl (fig. 12). The correlation from inflow to saline hot springs is surprisingly good and can be expressed by $Na/K = 10.96\ Cl^{0.49}$. During this concentration, the Na/K ratio changes from as low as 2.7 to as high as 175, whereas Cl increases 1000 fold. This represents a very efficient and consistent fractionation of Na in favor of K. It cannot be related to a simple Na–K exchange reaction, because Na does not increase in solution correspondingly with respect to chloride (see fig. 4), and hence other cations must be involved. Nesbitt (ms) has suggested that the precipitation of a potassium silicate may be responsible for much of the K depletion, but as we shall see, SiO_2 and K loss from solution are not strongly coupled.

As we have observed earlier, there is no K loss from solution between hot springs and lake brines, and hence the Na/K ratio remains constant while Cl is enriched 10-fold. In the most concentrated brines, those precipitating trona, a distinct Na loss from solution is indicated by the drop in the Na/K ratios. We now can compare the Na/K fractionation at Magadi with that observed in other basins. Figure 13 was drawn from data of Phillips and VanDenburgh (1971) for the Abert, Summer, and Goose Lake basins. Even though these basins are hydrologically separated, their volcanic bedrock geology and their waters are sufficiently similar to warrant plotting them on the same figure. Strong

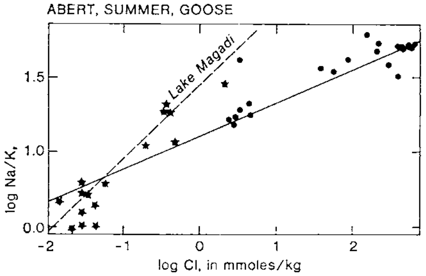

Fig. 13. Plot of the molar Na/K ratio versus chloride concentration for waters of the Lake Abert, Summer, and Goose Lake brines, south-central Oregon. For symbols see fig. 20.

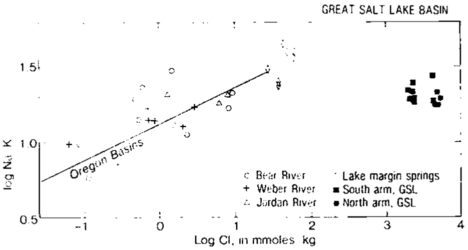

Fig. 14. Plot of the molar Na/K ratio versus chloride concentration for representative samples of waters from the Great Salt Lake area. Utah.

Na/K fractionation is evident, as at Magadi, but over the same concentration range Na/K increases only about half as fast, from 3 to 60. As figure 13 shows, the Na/K fractionation in the dilute waters may be viewed as very similar to the Magadi trend, while the more concentrated solutions clearly have lost less potassium than the corresponding Magadi brines. This is presumably because larger open water bodies are involved in the Oregon basins with less input from subsurface circulation. The fractionation is governed by Na/K = 13.2 $Cl^{0.24}$. The most concentrated brines are those of Lake Abert, but even these are not yet close to saturation with respect to trona. If they were, a marked enrichment of potassium could result.

The bedrocks in the Oregon basins are mainly andesitic and basaltic in nature and should be almost as effective for K removal as the trachytes at Magadi. Also, Abert, Summer, and Goose lakes have extensive marginal mud flats containing unconsolidated clays (Jones and others, 1969). However, as the presence of perennial lakes shows, there is much more water present here, and the higher solution to solid surface ratio may make the sorption and preferential uptake mechanisms less efficient. Also, chemical weathering is less intense in these more northerly areas than at Magadi, and this may be related to less effective fractionation.

The major inflow sources to Great Salt Lake, the Bear, Weber, and Jordan rivers, follow a trend very similar to that of the Oregon lakes (see fig. 14), but from the most concentrated inflow to the lake brines there has been some Na depletion, perhaps associated with halite or mirabilite ($Na_2SO_4 \cdot 10H_2O$) precipitation in the lake. Halite precipitation occurred during the low stands of 1933-34 and 1959-1963, and a halite crust is present now at the bottom of the north arm. Mirabilite has precipitated frequently during the winter months, and it accumulates as crystal mush on the west shore. At present most of the mirabilite apparently redissolves during the spring and summer, but some has been incorporated into the sediments in the past, presumably under colder climatic conditions, as exemplified by the bed of mirabilite found 7 m below the surface near Promontory Point (Eardley, 1962).

The catchment area for the Great Salt Lake inflow is very large and complex, and more detailed analysis is necessary to clarify the K removal mechanisms.

A trend very similar to that of the Great Salt Lake area but with a lower initial Na/K ratio in the inflow is shown by the Devils Lake basin of North Dakota (see fig. 15), as extracted from data of Swenson and Colby (1955) and Mitten, Scott, and Rosene (1968). Apparently the Na-enrichment mechanisms in the dilute waters of the Devils Lake system are just as effective as they are in the Oregon lakes, although Pleistocene glacial deposits are involved here rather than volcanics.

Potassium enrichment in the most concentrated brines has been observed at Deep Springs Lake, Calif., according to the data of Jones (1965) (see fig. 16). Hydrochemically, the Deep Springs Valley is more complex than either the Lake Abert or Magadi system, and the wide scatter of points is certainly due to the presence of several inflow types, including even a small amount of groundwater which has been in contact with leucite-bearing lavas. In spite of the lack of correlation exhibited in figure 16, two points can be made. As shown by the Lake Abert trend superimposed upon the diagram, Na enrichment is never greater and in general less at Deep Springs than it is in the Oregon basins, and the most concentrated brines have a Na/K ratio that is not significantly larger than that of the most dilute inflow. Saline Valley, Calif. (Hardie, 1968), is more complex, and the scatter of data is still greater.

Deep Springs Valley is similar to the Magadi basin in that it does not have a perennial body of open water. Efflorescent crusts are important for solute recycling, but they are not as extensive as at Magadi. The biggest differences lie in the host rocks and in the size of the basin. Deep Springs contains a substantial section of alluvial basin fill sediments derived from igneous, metamorphic, and sedimentary rocks and very little volcanics. Removal of K from solution must be on clay surfaces, and these may be less efficient than volcanic glasses and gels. On the other hand, circulation paths at Deep Springs, which is a comparatively small basin, may be much shorter than they are at Magadi and

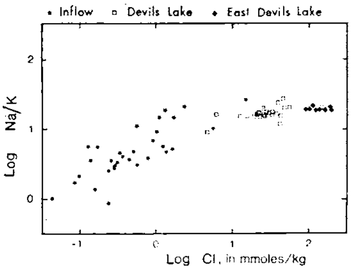

Fig 15. Plot of the molar Na/K ratio versus chloride concentration for waters from the Devils Lake basin N. Dak.

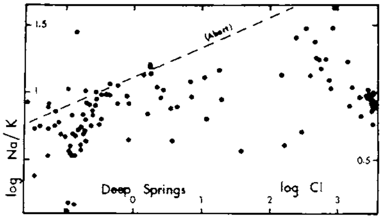

Fig. 16. Plot of the molar Na/K ratio versus chloride concentration for waters from the Deep Springs Valley, Calif.

hence the residence time of the groundwaters would be much shorter, decreasing the opportunities for exchange reactions.

The final case, no preferential loss of K from solution, is exhibited in the Basque lakes described by Nesbitt (ms) (see fig. 17). Very few data points are available, but over a 10-fold increase in concentration, little change in Na/K occurs, suggesting that K is conserved in solution. In the most concentrated brines K-enrichment takes place by the precipitation of Na-sulfates such as thenardite, mirabilite, or bloedite. Spotted Lake, outside the Basque Lake drainage system and more dilute, seems to belong to the same trend.

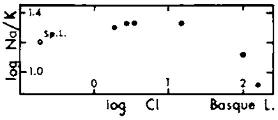

Fig. 17. Plot of the molar Na/K ratio versus chloride concentration for waters from the Basque Lake area, British Columbia.

The Basque lakes are a special case in the solute fractionation spectrum. The area of each lake is very small (less than 8000 m^2), and increases in solutes occur mainly through evapotranspiration from a single thin aquifer containing Mazama Ridge andesitic tuffs. No K fractionation occurs either because the exchange capacity of the tuffs has long since been exhausted or throughflow is too rapid. Alkaline earth and carbonate removal is still effected through precipitation of Mg–calcite and protodolomite (Nesbitt, ms).

In summary, overall Na/K fractionation is most pronounced in the Lake Magadi basin, where abundant reactive surfaces are available and where solute transport is largely subsurface. Shallow subsurface circulation is usually associated with soil coatings and efflorescent surface crusts which aid in the fractionation process. Since clays are absent at Magadi, volcanic surfaces seem to be at least as effective for preferential sorption of K as clays or perhaps even more so. In the Oregon and North Dakota basins the overall Na enrichment in solution is less extreme. Both basins have open water bodies, and the ratio of solution to reactive surfaces is probably lower than it is at Lake Magadi. Weathering rates are lower also. While the Devils Lake sediments contain abundant clays, the active surfaces in the Oregon basins are dominated by volcanic material. It is not clear why the Deep Springs basin is less effective in removing K from solution than the Oregon and North Dakota basins. Detrital material and clay surfaces are abundant, but the size of the basin may have something to do with it. The Deep Springs basin is rather small, and hence the time for contact between solutions and active surfaces may be restricted. Finally, the Basque Lakes represent a situation either of saturation of the active surfaces or, perhaps more likely, of very rapid flowthrough. Late stage K enrichment through precipitation of Na-rich minerals is apparent in every basin in which the appropriate concentrations are reached.

SILICA REMOVAL

Silica can be removed by a variety of processes and hence its behavior differs from basin to basin. In the Lake Magadi basin it appears to be a typical example of a solubility-controlled solute (curve V in fig. 3). Whereas the silica content of the inflow varies randomly (see fig. 18), it never reaches levels greater than 1 mmol/kg (60 ppm), and this level also holds for groundwater and the most dilute hot springs. The silica content effectively remains constant while Cl increases 1000-fold. Such consistent fractionation suggests a solid phase as a silica buffer. It cannot be amorphous silica, because then the plateau would have to be higher (log SiO_2 = 0.26 mmols/kg). The level of 50 to 60 ppm SiO_2 is dictated most probably by the solubility of volcanic glass which is present in great abundance. Meanwhile, a large amount of silica must be sorbed or precipitated during the concentration process to conform to this level, and this precipitation is presumably in the form of opaline cement coatings and crusts associated with efflorescences.

The hot springs at Lake Magadi have a pH between 9 and 10. Under such alkaline conditions, species other than H_4SiO_4, such as $H_3SiO_4^-$ and $H_2SiO_4^{2-}$, become important, and the solubility of amorphous silica increases rapidly (see for instance Stumm and Morgan, 1970). Consequently, over the concentration range from hot springs to lake brines, silica acts essentially as a conservative element, and its concentration increases as pH and Cl rise. At no stage does the silica content consistently exceed the solubility of amorphous silica for that particular pH level (see Jones, Rettig, and Eugster, 1967). As shown by Eugster and Chou (1973), diatoms are not important at Magadi for the silica budget.

The coupling between potassium and silica removal from solution can be tested by considering the SiO_2/K ratio of the material removed. Figure 19 shows SiO_2/K of the waters of Magadi against Cl. The correlation is surprisingly good and can be expressed by $SiO_2/K = 1.90Cl^{-0.30}$. The SiO_2/K ratio of the precipitate can be calculated by combining this relation with that for Na/K versus Cl quoted earlier. The results for a

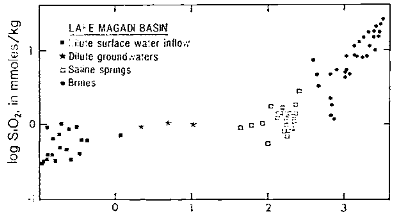

Fig. 18. Plot of silica versus chloride concentration for waters of the Lake Magadi basin, Kenya.

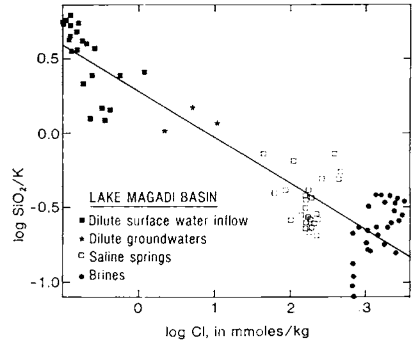

Fig. 19. Plot of molar SiO_2/K ratio versus chloride concentration for waters from the Lake Magadi basin, Kenya.

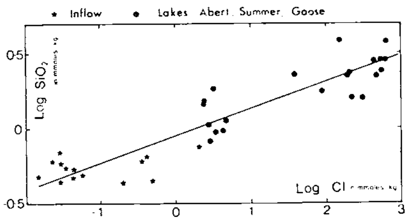

Fig. 20. Plot of silica versus chloride concentration for waters from the Lake Abert, Summer, and Goose Lake basins, southcentral Oreg.

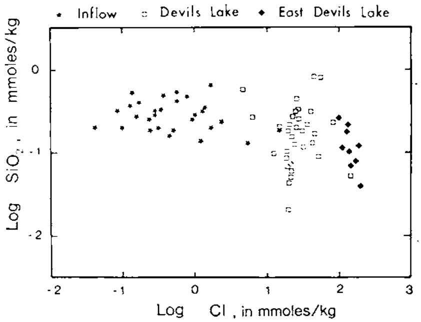

Fig. 21. Plot of silica versus cloride concentration for waters from the Devils Lake basin, N. Dak.

single step of 1000-fold concentration as well as for three successive steps of 10-fold concentration are given in table 1. Although the overall ratio of 3.96 is close to that of a tetrasilicic layered silicate, the initial ratios are too high, and the final ratios too low. Hence the removal of the two ions apparently is not very strongly coupled, and other mechanisms must be responsible for the very rapid initial loss of SiO_2 and the more sustained loss of K from solution. Presumably, the former is represented by opaline cements and crusts, while the latter is a more gradual sorption and exchange process.

TABLE 1

Atomic SiO_2/K ratios of material removed from solution during evaporative concentration (based on Cl)

Concentration, times	1-10	10-100	100-1000	1-1000
Average SiO_2/K	4.80	2.36	1.16	3.96

In the Oregon lakes SiO_2 behaves differently (see fig. 20). Silica increases gradually during the concentration process but with a slope of much less than one. This corresponds to curve III (fig. 3) and indicates multiple processes. In the open lake, diatoms are an important agent for silica removal from solution (Phillips and Vandenburgh, 1971), while in the mud flats cement, coatings, and crusts presumably are the sinks for silica. The final silica enrichment in the Oregon lakes is not as pronounced as it is at Magadi, because the necessary pH levels are not reached in the most concentrated brines.

At Devils Lake, N. Dak., silica exhibits a still different solute behavior (fig. 21). Silica content of the inflow is low (<20 ppm), and it does not increase during evaporative concentration. In the open lake waters, on the other hand, silica values can be distinctly lower, and values as low as 1.2 ppm have been reported (Mitten, Scott, and Rosene, 1968, table 4). Such effective removal is most likely associated with organic utilization, for example by diatoms.

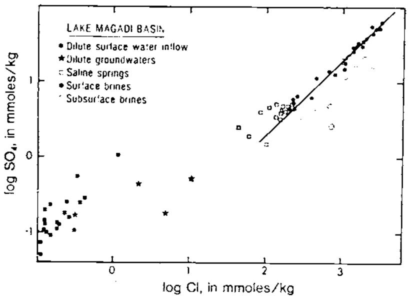

Fig. 22. Plot of sulfate versus chloride concentration for waters from the Lake Magadi basin, Kenya.

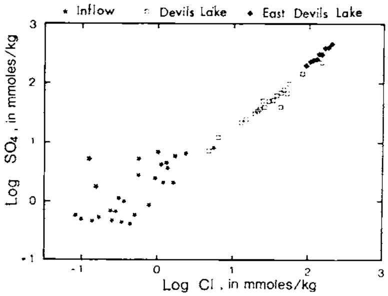

Fig. 23. Plot of sulfate versus chloride concentration for waters from the Devils Lake basin, N. Dak.

SULFATE FRACTIONATION AND CHLORIDE ENRICHMENT

In many closed basins, sulfate is removed from solution by mineral precipitation, principally gypsum and mirabilite. This is indicated in figure 2 for paths II, IIIB, and IIIC. In those basins, in which gypsum saturation cannot be reached because calcium has been lost through carbonate precipitation (paths I and IIIA, fig. 2), sulfate may be involved in other fractionation mechanisms. An example is shown in figure 22, for the Magadi basin, where sulfate has a similar concentration behavior to that of potassium; there is initial conservation with evaporative concentration during the inflow stage, followed by gradual loss from solution in the groundwater stage, and finally conservation in surface waters, from saline hot springs to lake brines. Subsurface brines collected from drill holes, on the other hand, are clearly depleted in sulfate. Bacterial sulfate reduction has been invoked by Jones, Eugster, and Rettig (1977) for the sulfate loss from more concentrated waters at Lake Magadi. Evidence for subsurface reduction is found in the black, H_2S-rich muds interbedded with the trona layers.

Loss of sulfate from solution by bacterial reduction is well documented for sedimentary environments (see, for instance, Goldhaber and others, 1977). For closed basin settings, such losses have been discussed by Phillips and VanDenburgh (1971) for the Oregon basins, and by Jones (1966) for the Western Great Basin in general. Products are in the form of either H_2S or iron sulfides. Sulfate reduction has also been invoked by Neev and Emery (1967) to account for the disappearance of gypsum from the laminated bottom sediments of the Dead Sea.

Loss of sulfate by sorption on surfaces is well known from the soil literature (see for instance Aylmore, Karin, and Quirk, 1967; Bornemisze and Llanos, 1967; Swoboda and Thomas, 1965), and it has been demonstrated experimentally (Drever and Smith, 1978; Wood, 1978). Such processes could also be active in the groundwaters of Lake Magadi and responsible for some of the sulfate losses from solutions.

Figure 23 illustrates an example of a closed basin system where little sulfate removal takes place. The Devils Lake chain shows essentially complete conservation of sulfate in solution. There is, however, a slight de-

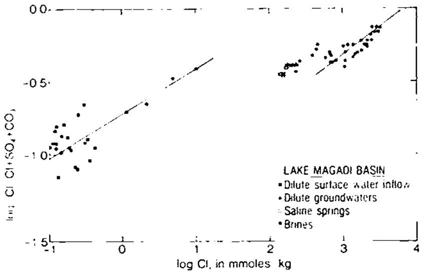

Fig. 24. Plot of the molar ratio of chloride to total anions for waters of the Lake Magadi basin, Kenya.

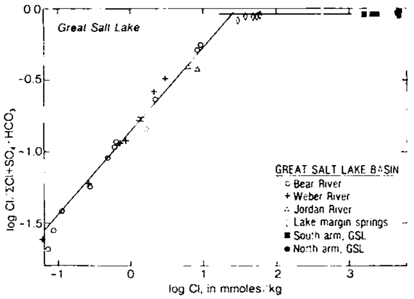

Fig. 25. Plot of the molar ratio of chloride to total anions for representative samples of water from the Great Salt Lake area, Utah.

crease of SO_4 between average inflow and the most dilute lake waters, presumably related to sorption processes on the glacial clays. In the lakes sulfate reduction is not important perhaps because of the shallow depths and the effective wind mixing. In nearby more concentrated Eastern Stump Lake, some sulfate is removed from solution by reduction in bottom sediments, but more by sodium sulfate precipitation (Mitten, Scott, and Rosene, 1968).

In most closed basin waters, Cl, $HCO_3 + CO_3$, and SO_4 are the only important anions. Hence removal of carbonate and sulfate from solution inevitably leads to chloride enrichment. This is shown clearly in figures 24 and 25, where Cl/Σ anions is plotted for the Magadi basin and for Great Salt Lake, two contrasting examples, one with relatively low and the other with relatively high proportions of chloride. In figure 24, the initial chloride enrichment must be due to alkaline earth carbonate precipitation, but the enrichment continues through the groundwater stage, as a result of sulfate loss from solution. The hot springs show little chloride enrichment, and what there is must be due to CO_2 degassing; however, the carbonate loss from concentrated brines through trona precipitation is expressed very clearly. For Great Salt Lake (fig. 25) chloride enrichment is more extensive during the inflow stage, perhaps because the initial Ca + Mg contents are higher, exceeding the equivalent concentrations of CO_2 species. But over the concentration range from springs to lake brine no further chloride enrichment is noted. Bicarbonate has been drastically reduced, and open lake surface waters are not subject to sulfate reduction.

SUMMARY

By using data from some of the better known closed basins such as Magadi, Lake Abert, Great Salt Lake, Deep Springs Lake, Devils Lake, and others, it has been possible to delineate the behavior of the most abundant solutes during the hydrochemical evolution from dilute inflow water to concentrated brines. Evaporative concentration leads to increased solute load by two related processes: (1) direct evaporation from surficial water bodies or from shallow groundwater by capillary draw and (2) formation of efflorescent crusts and soil coatings by desiccation of surface or capillary waters and subsequent partial dissolution of such crusts by rain or dilute runoff. Both processes are responsible for chemical fractionation of the waters, the first by mineral precipitation, and the second because only the most soluble constituents of the crusts are returned to the solution. Other important solute losses may be associated with sorption or exchange reactions on active surfaces (for example, K and SO_4), degassing (for example, CO_2), and bacterial reduction (for example, SO_4). Solutes that are unaffected by such processes — conservative solutes — can be used to monitor the concentration effects. Depending upon the particular removal mechanisms involved and their relative importance, each solute follows a different evolutionary path, and paths for the same solute may differ from basin to basin. In order to delineate the different behavior patterns we have restricted ourselves to basins with relatively homogeneous inflow, so that mixing of inflow waters of different geochemical parentage need not be considered. If sufficient data are available, such mixing effects can be included in the analyses (see, for instance, the case of Lake Natron in Eugster, 1970).

Fractionation processes depend strongly on circulation patterns. If paths are restricted largely to the surface, efflorescent crusts and sorption and exchange reactions will be subordinate, and fractionation occurs either through direct mineral precipitation, degassing, or oxidation. If, on the other hand, subsurface circulation becomes important, as in most desert environments, efflorescent crusts and soil coatings will be ubiquitous. There will be ample opportunity for sorption and exchange reactions between waters and fine-grained sediments, the amount and activity of the available surfaces governing the extent of such reactions. Bacterial reduction is also associated with subsurface circulation, because anaerobic conditions are readily maintained.

It has not yet been possible to model quantitatively the evolution of brine by considering all these fractionation processes. Computer tests, such as those of Hardie and Eugster (1970), Al-Droubi (1976), and others, rely on mineral precipitation as the only fractionation mechanism, and hence they are crude guides at best. On the other hand, from a study of many natural settings we now have a reasonable understanding of the major solutes. Their behavior can be used to delineate the important processes for a particular basin, and thus they aid in unravelling its hydrochemical history.

We can now state that the hydrochemical transformations from dilute waters to concentrated brines depicted in figure 1 are the results of the complex interplay of a variety of fractionation processes. The cationic evolution toward sodium dominance is caused mainly by precipitation of alkaline earth carbonate, gypsum, and Mg-silicates, whereas the anionic evolution away from bicarbonate dominance is related to precipitation of carbonates and sulfates coupled with degassing, sorption, and bacterial reduction of sulfates.

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