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Control of seawater composition by mixing of river waters and mid-ocean ridge hydrothermal brines

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Abstract—The two major input streams to seawater are Na-HCO_3-SO_4-rich river waters and Ca-Cl-rich mid-ocean ridge hydrothermal brines. A model is presented which accounts for the major element composition of modern seawater by mixing of river water with mid-ocean ridge hydrothermal brines and the precipitation of calcium carbonate. A steady-state composition for the major ionic species in seawater, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and HCO_3^-, can be obtained within the range of published volume fluxes for river water and mid-ocean ridge hydrothermal brines using reasonable estimates of river water and mid-ocean ridge hydrothermal brine compositions. A steady-state concentration of K^+ in modern seawater requires additional sinks for potassium.

The steady-state concentrations of the major ionic species in seawater are very sensitive to changes in the volume ratios of river water and mid-ocean ridge hydrothermal brines input to the oceans. It is likely that the ratio of these two major input streams to seawater has changed through geologic time, and that the major ion concentrations in seawater have changed. A smaller mid-ocean ridge hydrothermal brine flux results in lower concentrations of Ca^{2+} in seawater and higher concentrations of Na^+, Mg^{2+}, SO_4^{2-} and HCO_3^-. Larger mid-ocean ridge hydrothermal brine fluxes result in higher concentrations of Ca^{2+} in seawater and lower concentrations of Na^+, Mg^{2+}, SO_4^{2-} and HCO_3^-. The compositional variations in seawater that result from even modest changes of a few percent in the ratio of river water and mid-ocean ridge hydrothermal brines are significant because of the potential influence on chemical sediments produced from seawater. Smaller mid-ocean ridge hydrothermal brine volume fluxes are likely to favor aragonite precipitation rather than calcite and result in marine evaporites which contain magnesium sulphate minerals. Larger mid-ocean ridge hydrothermal brine volume fluxes favor calcite precipitation and result in marine evaporites containing potash salts (sylvite and carnallite) without magnesium sulphate minerals.

INTRODUCTION: THE PROBLEM OF THE CHEMICAL COMPOSITION OF SEAWATER

SINCE THE CLASSIC PAPER OF RUBEY (1951) on the problem of the history of seawater, a number of workers, using heterogeneous equilibrium models or mass balance methods, have attempted to account for the chemical composition of the present oceans (*e.g.*, SILLEN, 1961, 1967; GARRELS and THOMPSON, 1962; MACKENZIE and GARRELS, 1966; HELGESON and MACKENZIE, 1970; GARRELS and MACKENZIE, 1971; HOLLAND, 1972, 1984; LAFON and MACKENZIE, 1974; MAYNARD, 1976; DREVER, 1982). There is wide agreement among these workers that:

1) the basic salinity and chlorinity, and perhaps also the essential major ion composition of the oceans were, inherited from the primordial reaction between crustal igneous rocks and outgassed acid volatiles such as HCl and SO_2 at the time the oceans were formed (RUBEY, 1951; GARRELS and MACKENZIE, 1971; LAFON and MACKENZIE, 1974),

2) seawater has remained close to its present composition for the last 1–2 billion years (GARRELS and MACKENZIE, 1971; HOLLAND, 1972). Based on these assumptions, then, the principal question that a number of workers have addressed is how the chemistry of the oceans is buffered against the massive inflow of river waters which have compositions so widely different from that of modern seawater (Table 1).

SILLEN (1961, 1967) first suggested that seawater is in heterogeneous equilibrium with the silicate and carbonate sediments on the ocean bottom. In this approach, "reverse weathering" reactions such as detrital kaolinite forming authigenic illite-smectite were called on to control the ratios of the major cations at or near those of modern seawater (see also MACKENZIE and GARRELS, 1966; HELGESON and MACKENZIE, 1970). Recently, however, it has been argued that authigenic silicates are too sparsely distributed in the ocean, and that reactions involving detrital marine clays are too slow, to buffer seawater composition against the river input (DREVER, 1974, 1982; MAYNARD, 1976; HOLLAND, 1978).

This, together with the discovery of extensive hydrothermal alteration of seawater at mid-ocean ridges (see THOMPSON, 1983, for a summary), has given rise to steady-state models involving the balancing of sources and sinks (*e.g.*, MAYNARD, 1976; DREVER, 1982; HOLLAND, 1978). In these models the present day river water fluxes of ions are compared to the estimated rates of ion uptake from ocean waters by:

1) deposition of marine carbonates, cherts and evaporites,
2) storage of seawater in the pores of marine sediments,
3) low temperature interaction between seawater and ocean floor basalts,
4) high temperature interaction between seawater and basalt at mid-ocean ridges,
5) ion-exchange by marine clays,
6) precipitation of authigenic silicates and sulfides.

If the chemical composition of the oceans is to remain constant, then the input fluxes must remain in dynamic balance with the output fluxes throughout geologic time, that is, for each ion:

$$dA_i/dt = \sum f_{ir}\ (\text{inputs}) - \sum f_{ir}\ (\text{outputs}) = 0$$

where A_i is the concentration of ion i, t is time, and f_{ir} is the flux of ion i from reservoir r.

It is the view of HOLLAND (1978, p. 5) that "earth reservoirs are not at steady state" and that excursions in seawater composition through time are likely (see also GARRELS and MACKENZIE, 1971, p. 297) given that global tectonic cycles operate over time spans that are longer than the residence times of all the major ions in the oceans. In addition, climatic changes such as occurred during the major ice ages would have been capable of influencing the fluxes of those components with relatively short residence times. These components include bicarbonate-carbonate, silica, water and perhaps calcium. HOLLAND (1972, 1984) has attempted to determine the limits of these chemical excursions by inverse modelling using the mineralogy of marine evaporites deposited over the last 900 million years. He has concluded that while "the concentration of the major ions in seawater has not varied a great deal during the Phanerozoic . . . the imposed limits on excursions . . . are . . . fairly broad" (HOLLAND, 1984, p. 536). In particular, concentrations of Mg^{2+}, Ca^{2+} and SO_4^{2-} could have been two or three times larger or smaller than the present day ocean values. Such changes, coupled with variations in biologically-controlled or biologically-moderated components (oxygen, carbon dioxide, silica, phosphate, nitrate, trace elements, stable isotopes, etc.), may have considerable effects on the nature and composition of chemical and biochemical sedimentary deposits through geologic time.

With all this in mind we have explored the consequences of a simple model that assumes that the composition of seawater is mainly controlled now, and has been controlled through geologic time, by the mixing of river waters and mid-ocean ridge (M.O.R.) hydrothermal brines. Using this model we have attempted to predict the direction and pos-

Table 1. Major ion composition of seawater, mid-ocean ridge hydrothermal brines and average world river water in ppm

	1	2	3	4	5	6	7	8	9
Na^+	10800	9610	10444	11725	9932	11243	11794	6.3	5.15
K^+	407	1348	1382	1009	907	1896	1450	2.3	1.3
Ca^{2+}	413	1530	1812	805	625	1162	1663	15.	13.4
Mg^{2+}	1296	16	8	0	0	0	0	4.1	3.35
Cl^-	19010	19260	20745	20530	17338	21310	22586	7.8	5.75
SO_4^{2-}	2717	31	72	0	0	0	0	11.2	8.25
HCO_3^-	137	1926*	2650*	0	0	647	396	58.4	52.

1. Seawater, RILEY and CHESTER (1971).
2. Hydrothermal brine, Borehole #8, Reykjanes, Iceland, BJORNSSON *et al.* (1972).
3. Hydrothermal brine, Borehole #2, Reykjanes, Iceland, BJORNSSON *et al.* (1972).
4. Hydrothermal brine NGS, 21° North, VON DAMM *et al.* (1985a).
5. Hydrothermal brine OBS, 21° North, VON DAMM *et al.* (1985a).
6. Hydrothermal brine #1, Guaymas Basin, VON DAMM *et al.* (1985b).
7. Hydrothermal brine #3, Guaymas Basin, VON DAMM *et al.* (1985b).
8. Average world river water, LIVINGSTON (1963).
9. Natural average world river water, MEYBECK (1979).

* Reported as total CO_2.

sible magnitude of the changes in the major ion composition of seawater that would result from likely secular changes in the relative magnitudes of the fluxes of river water and M.O.R. hydrothermal brines. In turn, we have used the predicted seawater composition variations to determine the nature of variations likely to have occurred in the primary mineralogy of ancient marine carbonates and marine evaporites.

SEAWATER AS A MIXTURE OF RIVER WATER AND M.O.R. HYDROTHERMAL BRINES: A WORKING MODEL

We present in this paper a very simple model that explores how the chemical composition of seawater is influenced by the two major input streams of fluid to the oceans, that is, river waters and M.O.R. hydrothermal brines. To explain the evolution of brine compositions in non-marine saline lakes HARDIE and EUGSTER (1970) developed the idea of "chemical divides" in which early precipitation of the relatively insoluble minerals calcite and gypsum determined the ultimate chemical signature of the brines. The success of this simple concept in accounting for the composition of lacustrine brines, where mixing of several source waters is the norm, has encouraged us to apply it to the evolution of seawater.

The concept of chemical divides can be illustrated on a simple Ca-HCO_3-SO_4 ternary phase diagram (Fig. 1). Two chemical divides (one from $CaCO_3$ to SO_4 and one from $CaCO_3$ to $CaSO_4$) separate three fields (Na-HCO_3-SO_4, Cl-SO_4 and Ca-Cl waters) on the phase diagram. The body of the phase diagram is the primary stability field for calcite; the stability fields for gypsum and anhydrite are located along the Ca-SO_4 join. Waters within the body of the phase diagram precipitate $CaCO_3$ solid phases and the solution compositions evolve directly away from the $CaCO_3$ composition point. In this scheme modern seawater is a Cl-SO_4 type water (Fig. 1). The mole-equivalent concentration of Ca^{2+} in seawater is greater than the equivalents of HCO_3^-, but is less than the combined mole-equivalent concentration of HCO_3^- and SO_4^{2-}. Therefore, after the precipitation of calcite and gypsum, evolved seawater brines become enriched in both Cl^- and SO_4^{2-}, and depleted in Ca^{2+}.

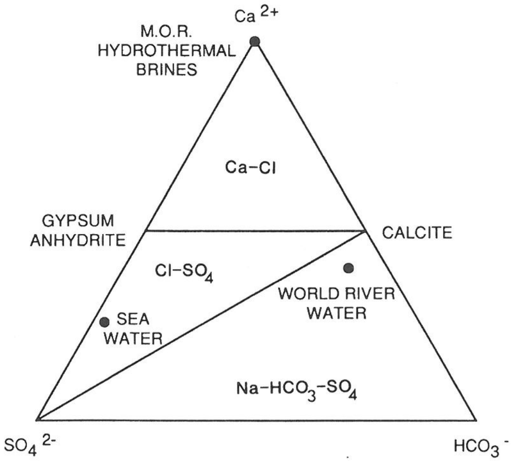

FIG. 1. Ternary Ca^{2+}-SO_4^{2-}-HCO_3^- phase diagram, in mole-equivalents. The body of the diagram is the primary stability field for calcite; gypsum and anhydrite stability fields are along the Ca^{2+}-SO_4^{2-} join. Lines from calcite to gypsum/anhydrite and from calcite to SO_4^{2-} are chemical divides for the system which separate Ca-Cl, Cl-SO_4 and Na-HCO_3-SO_4 type waters. Average world river water has a Na-HCO_3-SO_4 composition, modern seawater is a Cl-SO_4 water and M.O.R. hydrothermal brines have a Ca-Cl composition.

Evolved continental Cl-SO_4 brines, similar in composition to modern seawater, that have resulted from mixing of Na-HCO_3-SO_4 river waters and Ca-Cl spring waters, have been documented for the Great Salt Lake, Utah (SPENCER *et al.*, 1984, 1985) and several lakes on the Qarhan salt plain, Qaidam Basin, China (LOWENSTEIN *et al.*, 1989; SPENCER *et al.*, 1990). The compositions of these non-marine brines can be explained by our simple model. What is particularly relevant here is that the basic chemical signatures of the two major inflow waters to these non-marine basins are similar to the two major inflow waters to the oceans. In this sense the Great Salt Lake and Qaidam Basin mixed inflow systems are valuable analogues for the modern ocean system, and provide ample support for the basic concept behind our simple model.

In the chemical divide scheme, biological and chemical precipitation of calcium carbonate phases is the most important process in the early stages of brine evolution. Since seawater is a relatively dilute brine that falls into the calcium carbonate precipitation regime, we have restricted our modelling of seawater to simple mixing of Na-HCO_3-SO_4 river water and Ca-Cl M.O.R. hydrothermal brine combined with precipitation of calcium carbonate. We have not included more complex mechanisms such as cation exchange by river-borne clays, authigenic silicate mineral precipitation, or sulphate reduction by microbes, although their exclusion undoubtedly introduces some error (see estimations by MAYNARD, 1976, of the contributions of several processes to the chemical mass balance in the present day oceans). However, our experience in non-marine systems indicates that these reactions do not play more than minor roles in the chemical evolution of brines. We have not considered passive sinks such as evaporite precipitation and connate seawater storage that do not change the composition of seawater.

THE MIXING MODEL AND THE COMPOSITION OF THE MODERN OCEAN

The basic data needed to calculate the composition of seawater with this simple model are:

1) the chemical composition of average river water and M.O.R. hydrothermal brine,
2) the annual inflow volumes of river water and M.O.R. hydrothermal brine,
3) information on the anthropogenic input of solutes to the oceans.

River water composition

The average composition of modern rivers flowing into the oceans has been estimated by LIVINGSTON (1963) and MEYBECK (1979) (Table 1). This average world river water has a Na-HCO_3-SO_4 composition, as illustrated in Fig. 1. The concentration, in mole-equivalents, of HCO_3^- is greater than that of Ca^{2+} in this average world river water and therefore, on evaporation and precipitation of alkaline earth carbonates the resulting brines would be enriched in HCO_3^- and SO_4^{2-} and depleted in Ca^{2+}. With continued evaporative concentration these river water-derived brines will eventually precipitate $NaHCO_3$ and $NaSO_4$ salts and become alkaline brines (HARDIE and EUGSTER, 1970). Significant uncertainty in the river inflow composition is introduced by the uncertainties in the amounts of anthropogenic sources of solutes in modern river waters. MEYBECK (1979) estimates the anthropogenic input of sulphate to be 25% of the total river sulphate while HOLLAND (1978) suggests a higher value around 40%. For bicarbonate or carbon in modern river waters MEYBECK (1979, 1982) estimates 2 to 9% of the total is anthropogenic.

M.O.R. hydrothermal brine composition

For the M.O.R. hydrothermal brine input we have used the chemical analyses of BJORNSSON *et al.* (1972), EDMOND *et al.* (1979) and VON DAMM *et al.* (1985a,b) (Table 1). M.O.R. hydrothermal brines belong to the Ca-Cl composition type (Fig. 1). In these brines the mole-equivalent concentration of Ca^{2+} exceeds the combined mole-equivalent concentrations of HCO_3^- and SO_4^{2-} and therefore, on evaporation and precipitation of alkaline earth carbonates and calcium sulphate minerals, the residual brines will become depleted in HCO_3^- and SO_4^{2-} and enriched in Ca^{2+} and Cl^-.

Volume estimates

Volume estimates of river water inflow into the oceans today range from 3.0×10^{16} to 5.0×10^{16} litres per year (l/yr) (see HOLLAND, 1978, p. 65). LIVINGSTON (1963), for example, estimates 3.25×10^{16} l/yr while MEYBECK (1979) gives 3.74×10^{16} l/yr. The equation of PROBST and TARDY (1989, p. 276) yields runoff values from 3.90×10^{16} to 4.02×10^{16} l/yr. PROBST and TARDY (1989) suggest that anthropogenic sources have led to an increase in discharge with time. For the model calculations we have selected a value of 3.75×10^{16} l/yr for the total flux of river waters to the oceans. As a guide to the flux of M.O.R. hydrothermal brine we have used the estimates based on heat flow measurements (see, for example, HOLLAND, 1978). These values range from 6.0×10^{13} to $9. \times 10^{14}$ l/yr.

A constant composition modern ocean model

A constant composition modern ocean model requires that the net flux of each species be zero. In our model the net flux for each of the major ionic species in seawater is examined for various combinations of river water and M.O.R. hydrothermal brine volumes within the limits given above. We have made minor alterations in the composition of river inflow in order to simplify the model.

The starting point for our model calculation is the average world river water composition, for which we have used the estimate of MEYBECK (1979) (Table 2, line 1). The composition of this average river water is adjusted to zero chloride by subtracting ions in proportion to the composition of modern seawater (Table 2, line 2) on the assumption that the chloride in river waters is recycled from seawater as salt aerosols dissolved in rainwater. The chloride-adjusted composition of river water is used along with the estimate for the volume of inflow to arrive at an initial value of the total flux of solutes to the ocean from rivers.

The analysis of M.O.R. hydrothermal brine from borehole #8, Reykjanes, Iceland, given by BJORNSSON *et al.* (1972) (Table 1) is used to represent the composition of M.O.R. hydrothermal brines. The bicarbonate alkalinity is zero, by charge balance (Table 2, line 5). Seawater is assumed to be the original source water which interacted with oceanic basalts at greenschist facies temperatures to produce the hydrothermal brine (for details see THOMPSON,

Table 2. Composition of seawater inflows (meq/l)

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
				River			
1	0.224	0.036	0.669	0.275	0.162	0.172	0.852
2	0.085	0.033	0.663	0.244	0.0	0.155	0.852
3	0.083	0.032	0.644	0.237	0.0	0.126	0.852
4	0.089	−0.062	0.713	0.237	0.0	0.126	0.852
				M.O.R.			
5	418.0	37.3	76.3	1.3	532.3	0.6	0.0
6	430.2	38.4	78.5	1.3	547.9	0.7	0.0
7	469.7	10.3	20.6	106.6	547.9	56.6	2.2
8	−39.4	28.1	57.9	−105.3	0.0	−55.9	−2.2

1—natural river input (MEYBECK, 1978).
2—adjust for $Cl^- = 0$.
3—adjust for mass balance on SO_4^{2-}.
4—adjust for mass balance with constant M.O.R. hydrothermal flux.
5—M.O.R. hydrothermal brine.
6—M.O.R. hydrothermal brine at seawater Cl^-.
7—seawater.
8—net M.O.R. flux.

1983; HARDIE, 1983). Thus, all solutes are adjusted proportionately to modern seawater chlorinity (Table 2, line 6) and the difference between the adjusted composition and the average composition of modern seawater (from RILEY and CHESTER, 1971) as given in Table 2 (line 7) is used to estimate the net addition or subtraction of each solute from the M.O.R. hydrothermal brine system (Table 2, line 8).

The net flux of Cl^- is zero because we adjusted both of the inputs to be zero. The dissolved solute fluxes of all other river water components are positive. The fluxes of K^+ and Ca^{2+} from the M.O.R. hydrothermal brine source are positive, while those of Na^+, Mg^{2+}, SO_4^{2-} and HCO_3^- are negative. In order to maintain a constant composition ocean in our simple model, the net flux of Na^+, K^+, Mg^{2+} and SO_4^{2-} must be zero and the net flux of Ca^{2+} must equal that of HCO_3^-.

One test of whether this simple model can account for the composition of modern seawater is to calculate the residual net flux of each solute after mixing the adjusted compositions of river water and M.O.R. hydrothermal brine in proportion to their estimated volume inflow fluxes. The mixing of river water with M.O.R. hydrothermal brine leads to supersaturation with respect to calcite (and aragonite) and thus in the model calculations, appropriate amounts of Ca^{2+} and HCO_3^- must be subtracted. If after this the net solute fluxes are zero, or within the uncertainty of the input data, then the model is a viable one. Unfortunately, the range of estimates of the volume flux of M.O.R. hydrothermal brine is large enough that an unequivocal answer does not result from this approach. The range of mixtures calculated from the volume estimates are shown on the Ca-HCO_3-SO_4 ternary phase diagram (Fig. 2).

A test of the model that avoids the uncertainties

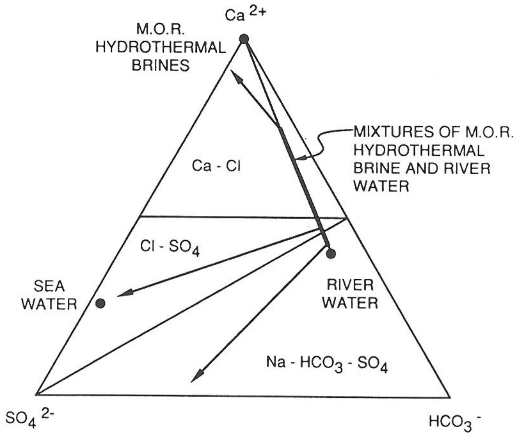

FIG. 2. Ternary phase diagram (see Fig. 1) showing the mixing line for M.O.R. hydrothermal brines and average world river water, heavy portion of the line is the range of mixtures obtained using published values of river water and M.O.R. hydrothermal volume fluxes to the oceans. Mixtures of M.O.R. hydrothermal brines and river waters are supersaturated with respect to calcite. Arrows indicate direction of brine evolution during calcium carbonate precipitation and range of compositions obtained from mixtures.

in the present day M.O.R. hydrothermal brine volume flux is to make this flux a dependent variable. In this approach, the volume flux of M.O.R. hydrothermal brine required to achieve a net zero flux for each major ion species is calculated. The calculated fluxes are compared with the published estimates of M.O.R. hydrothermal brine and with each other. This comparative approach will reveal whether or not our model is able to account for the composition of modern seawater within the range of uncertainty of the estimates of the volume flux for M.O.R. hydrothermal brine and whether or not a net zero flux for each ionic species can be obtained from the same M.O.R. hydrothermal brine volume flux.

With the initial estimates given in Table 2 (lines 2 and 8) the volume fluxes for M.O.R. hydrothermal brines required for net zero fluxes of the major ion species are given in Table 3. Zero net fluxes for Na^+, Mg^{2+} and SO_4^{2-} are obtained for very similar M.O.R. hydrothermal brine volume fluxes, indicating the ability of the mixing model to explain the proportions of these species in modern seawater. An improvement in the balance of these solutes can be obtained if more sulphate is attributed to anthropogenic sources, closer to HOLLAND'S (1978) estimate of close to 40% of the total river borne sulphate (as per Table 2, line 3). Larger M.O.R. hydrothermal brine inflow requires additional sources for these species, while a lesser inflow requires additional sinks.

The Ca^{2+} and K^+ fluxes for both the river and M.O.R. sources are positive. Excess Ca^{2+} is removed by "precipitating" an amount equal to the total mole-equivalent concentration of HCO_3^- to simulate biogenic uptake by organisms and chemical precipitation of $CaCO_3$. The M.O.R. hydrothermal brine volume flux required to balance the river-borne HCO_3^- is higher than the fluxes required for Na^{2+}, Mg^{2+} and SO_4^{2-} (Table 3), although an increase in river-borne Ca^{2+}, or decrease in HCO_3^- of less than 10% will yield volume fluxes for M.O.R. hydrothermal brines identical to those for Mg^{2+} and SO_4^{2-}. There is a net positive flux of K^+ that cannot be accounted for without introducing additional sinks such as the uptake of K^+ by terrestrial clays brought down to the sea by rivers or perhaps "reverse weathering" of oceanic basalts.

Overall, apart from the K^+ problem (see also MAYNARD, 1976), our model seems to be able to account for the present composition of seawater within the limits of the input data available in the literature. A river water composition with K^+ adjusted to a negative value to simulate exchange of Ca^{2+} on river clays for seawater K^+ as the clays enter the ocean which yields a net zero flux for all species using a M.O.R. hydrothermal brine flux of 8.45×10^{13} l/yr is given in Table 2, line 4. The model described allows for a constant composition ocean based on mixing of $Na-HCO_3-SO_4$ river waters and Ca-Cl M.O.R. hydrothermal brines, coupled with the precipitation of calcium carbonate and exchange of Ca^{2+} on river-borne clays for seawater K^+. Several reactions, such as sulphate reduction or Mg^{2+} uptake on clays, that other workers have suggested might have an influence on seawater composition have not been taken into account in our model. The acceptable balance achieved by our model suggests that these reactions do not play a major role in determining the composition of seawater, or that they have the same net effect as the processes underlying our model.

Table 3. M.O.R. hydrothermal brine volume fluxes required for zero net flux of species using river volume of 3.75×10^{16} l/yr and river water compositions from lines 2 and 3, Table 2, volumes in 10^{13} l/yr

	Line 2	Line 3
Na^+	8.09	7.90
Mg^{2+}	8.69	8.44
SO_4^{2-}	10.40	8.44
$Ca^{2+}-HCO_3^-$	11.60	12.98

VARIATIONS IN SEAWATER COMPOSITION IN RESPONSE TO SECULAR VARIATIONS IN RIVER WATER AND M.O.R. HYDROTHERMAL BRINE FLUXES

Variations in the fluxes of river water and M.O.R. hydrothermal brine are almost certain to have occurred back through geologic time as a function of variations in the rates of sea floor spreading, mountain building, continental accretion, global climate and so on. Therefore, if simple mixing of river waters and M.O.R. hydrothermal brines controls the composition of seawater, then it follows that any changes in the river water/M.O.R. hydrothermal brine flux ratios should result in changes in seawater major ion chemistry. If these changes in seawater composition are large enough they could affect the mineralogy of marine carbonates and marine evaporites. Such changes might explain, for example, the problem of "aragonite seas" *vs.* "calcite seas" (SANDBERG, 1983) or the restriction of $MgSO_4$-rich evaporites to the Permian and Neogene (HARDIE, 1990).

Our simple model is used to test the sensitivity of seawater composition to variations in the ratio of river water and M.O.R. hydrothermal brine fluxes. We use the composition of river water from line 4, Table 2, and hold the volume flux of river waters constant at 3.75×10^{16} l/yr. Steady-state seawater compositions are calculated assuming that the removal of Na^+, Mg^{2+} and SO_4^{2-} are proportional to the M.O.R. hydrothermal volume flux, and that the addition of K^+ and Ca^{2+} is controlled by charge balance. For instance, Mg^{2+} is removed nearly quantitatively from seawater at the mid-ocean ridge (compare lines 6 and 7, Table 2), so that if the M.O.R. hydrothermal flux were to double, then to balance the river input a seawater Mg^{2+} concentration one-half of the modern concentration is required. Our calculations indicate that steady-state concentration values for Mg^{2+} and SO_4^{2-} are approached rapidly (on the order of a few million to a few tens of millions of years), but that much longer times (several tens of millions of years) are required to reach steady-state values for Na^+ (because only a small proportion of Na^+ is removed from a given volume of seawater at the mid-ocean ridge). The sum of the change in K^+ and Ca^{2+} concentrations are calculated in order to balance the charge removed or gained in obtaining the new Na^+, Mg^{2+} and SO_4^{2-} steady-state concentrations. Distributions of K^+ and Ca^{2+} are calculated in proportion to the flux ratios for these species determined for the modern M.O.R. hydrothermal flux. Results of our calculations of steady-state seawater compositions for various river water/M.O.R. hydrothermal brine volume flux ratios are given in Table 4.

Modest changes in the ratio of river water inflow and M.O.R. hydrothermal brine inflow result in what we consider to be very significant changes in the major ion composition of seawater, significant because of the potential effect on chemical and biochemical sediments produced from these waters. A M.O.R. hydrothermal brine volume flux of between 95 and 96% of the modern flux results in a steady-state seawater composition along the Cl-SO_4 and Na-HCO_3-SO_4 chemical divide (see Figs. 1 and 2), a lesser M.O.R. hydrothermal brine volume flux leads to alkaline Na-HCO_3-SO_4 brines. An increase of 10% in the relative proportion of M.O.R. hydrothermal brine results in a steady-state seawater composition along the Cl-SO_4 and Ca-Cl chemical divide. Higher relative proportions of M.O.R. hydrothermal brine inflow result in Ca-Cl brines. Our calculations indicate that a 25% increase in the M.O.R. hydrothermal brine influx yields a seawater composition with Ca^{2+} rather than Mg^{2+} as the third most abundant ionic species in seawater (Table 4).

Table 4. Steady-state composition of major ions in seawater (meq/l) as a function of M.O.R. hydrothermal brine flux

Flux*	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
0.95	495	2.0	0.5	112	548	59.6	3.0
0.96	490	3.7	4.8	111	548	59.0	2.7
1.00	470	10.2	20.3	106	548	56.6	2.2
1.05	448	17.6	36.2	101	548	53.9	0.6
1.10	427	24.3	51.8	97	548	51.4	0.4
1.25	376	41.2	91.4	85	548	45.3	0.3

* Ratio of M.O.R. hydrothermal brine flux relative to modern.

SOME IMPLICATIONS FOR CHANGES IN CHEMICAL SEDIMENTS THROUGH TIME

Calcium carbonate precipitation

Although calcite is the more stable polymorph of calcium carbonate at earth surface conditions, aragonite, rather than calcite, is the dominant form in the present ocean. The dominant polymorph precipitated from seawater may have changed through the Phanerozoic (see SANDBERG, 1983). FUCHTBAUER and HARDIE (1980) precipitated either calcite (with varying Mg) or aragonite or both from Na^+-Mg^{2+}-Ca^{2+}-CO_3^{2-} solutions depending on the Mg^{2+}/Ca^{2+} in solution. For solutions with Mg^{2+}/Ca^{2+} less than two (mole ratio) only calcites formed, and for low ionic strength solutions with Mg^{2+}/Ca^{2+} greater than five only aragonite formed, both formed from solutions of intermediate ratios. Comparison of our model ratios with the values found by FUCHTBAUER and HARDIE (1980) to control the polymorph of calcium carbonate precipitated indicates that aragonite is favored to precipitate from seawater with a relatively low M.O.R. hydrothermal brine volume flux (high Mg^{2+}/Ca^{2+}). Calcite precipitation is favored from seawater with relatively higher M.O.R. hydrothermal brine volume fluxes (low Mg^{2+}/Ca^{2+}). It may be possible to use the presence of "aragonite seas" as indicators of low M.O.R. hydrothermal brine volume flux and "calcite seas" as indicators of high M.O.R. hydrothermal brine volume flux.

Composition of evaporites through time

Evaporation paths and equilibrium mineral precipitation sequences are calculated using the thermochemical model of HARVIE *et al.* (1984). Mineral precipitation sequences for the seawater compositions presented in Table 4 are given in Table 5. The mineral precipitation sequences vary significantly. Waters with a Cl-SO_4 composition (including modern seawater) all end their crystallization with a final

Table 5. Equilibrium mineral precipitation sequences for seawater compositions in Table 4

0.96	1.00	1.05	1.10	1.25
C	C	C	C	C
C + G	C + G	C + G	C + G	C + G
C + A	C + A	C + A	C + A	C + A
C + A + GL	C + A + H	C + A + H	C + A + H	C + A + H
C + GL	C + A + H + GL	C + A + H + P	C + A + H + S	C + A + H + S
C + GL + H	C + A + H	C + A + H + P + S	C + A + H + S + CR	C + A + H + S + CR
C + GL + H + A	C + A + H + P	C + A + H + P + S + CR	C + A + H + CR	C + A + H + CR
C + H + A	C + A + H + P + E	C + A + H + P + CR	C + A + H + CR + B	C + A + H + CR + AT
C + H + A + P	C + A + H + P + HX	C + A + H + P + CR + K	C + A + H + CR + B + T	C + A + H + CR + AT + T
C + H + P	C + A + H + P + K	C + A + H + CR + K		
C + H + P + E	C + A + H + P + K + CR	C + A + H + CR + K + B		
C + H + P + HX	C + A + H + K + CR			
C + H + P + K	C + A + H + K + CR + B			
C + H + P + K + KA				
C + H + K + KA + A				
C + H + K + A + CR				
C + H + K + A + CR + B				

A	anhydrite
CR	carnallite
H	halite
P	polyhalite
AT	antarcticite
E	epsomite
HX	hexahydrite
S	sylvite
B	bischofite
GL	glauberite
KA	kainite
T	tachyhydrite
C	calcite
G	gypsum
K	kiesertie

invariant assemblage of calcite-anhydrite-halite-kieserite-carnallite-bischofite. The paths taken in order to reach this assemblage vary; glauberite appears earlier from waters with a lower M.O.R. hydrothermal brine input (lower Ca^{2+} and higher SO_4^{2-}). The mineral kainite also appears in these sequences, but not in the sequence for modern seawater.

Slight increases in the M.O.R. hydrothermal brine input to seawater result in the disappearance of glauberite as a replacement of anhydrite and the precipitation of magnesium sulphate-bearing phases (polyhalite, epsomite, hexahydrite and kieserite) at later stages in the evaporation sequence. Progressive increase in the proportion of M.O.R. hydrothermal brine to the mixture (between 1.00 and 1.05 times our estimated modern flux) results in carnallite precipitation prior to magnesium sulphate phases (epsomite, hexahydrite and kieserite), and eventually to sylvite precipitation prior to carnallite. Still higher input of M.O.R. hydrothermal brines results in Ca-Cl type waters, which do not precipitate $MgSO_4$-bearing phases (flux ratios greater than 1.10, Tables 4 and 5). All Ca-Cl brines follow similar mineral precipitation sequences during evaporation and vary significantly from that of modern seawater. The final invariant assemblages include calcite-anhydrite-halite-carnallite-tachyhydrite, with either bischofite or antarcticite.

Ancient evaporites have been used to evaluate changes in the composition of surface waters, including seawater, through time (for example see: HOLSER, 1983; HARDIE, 1984; HOLLAND, 1984; DAS *et al.,* 1990). Evaporites have the potential to give a great deal of information about the composition of ancient surface waters, however, there are problems in using evaporites to estimate seawater composition. The most important problem is the determination of the purely marine origin of a given evaporite (HARDIE, 1984). Our models show that relatively minor changes in the input of Ca-Cl brines greatly influence the composition and mineral precipitation sequence of evaporating seawater. Mixtures of Ca-Cl hydrothermal brines with river waters can produce brine compositions and mineral precipitation sequences similar to or very different from those of modern seawater. This is demonstrated for the entirely non-marine evaporites of the Qaidam Basin, China, reported by LOWENSTEIN *et al.* (1989) and SPENCER *et al.* (1990). The same types of changes we expect for seawater as a result of changes in M.O.R. hydrothermal brine volume fluxes can be produced on a local or regional scale by mixtures of Ca-Cl brines and river waters with or without a marine component. Reading the composition of ancient seawater from ancient evaporites is not straightforward and is unlikely to yield unique solutions. Examples of Permian evaporites are used to illustrate the problems.

HARVIE *et al.* (1980) compare the evaporation sequence predicted from modern seawater with that of the Permian Stassfurt Series of the German Zechstein II. They find a remarkable agreement in the mineral assemblages, precipitation sequence and even in the relative proportions of various minerals. This sequence of minerals includes glauberite as a replacement of gypsum or anhydrite, as well as polyhalite as a replacement of gypsum or anhydrite at relatively early stages in the evaporation sequence. These minerals are not found in our evaporation sequences with increased M.O.R. hydrothermal input. Further, glauberite is reported from the Permian Salado Formation, and polyhalite is reported to replace glauberite, gypsum and anhydrite (LOWENSTEIN, 1983). Magnesium sulphate salts are also present in the Salado Formation (JONES, 1972; LOWENSTEIN, 1983). The presence of these "key minerals," which indicate compositional ratios for the major elements close to that of modern seawater, appear to give strong evidence for a similar composition of Permian and modern seawater.

However, glauberite and polyhalite have not been reported from a number of other Permian evaporites, including those found stratigraphically above and below, and time equivalents of the Stassfurt Series of the German Zechstein II (see HARDIE, 1990). Many of these deposits lack these "key minerals" which form at relatively early stages during the evaporation of seawater, yet contain potassium chloride salts (sylvite or carnallite), which are found much later in evaporation sequences. The mineral assemblages for these Permian evaporites are similar to those formed during the evaporation of our calculated seawater compositions with a relatively high M.O.R. hydrothermal brine input, compositions which vary greatly from that of modern seawater.

If we assume that the Stassfurt Series of the Zechstein II and the Salado Formation evaporites resulted from the evaporation of Permian seawater, then Permian seawater must have been similar in composition to modern seawater. The M.O.R. hydrothermal brine volume flux during the Permian would have been similar, possibly slightly lower, than the modern flux. Mineral sequences found in the other Permian evaporites may have resulted from local or regional input of Ca-Cl brines which altered the evaporation sequence. However, if the Permian evaporites which lack the "key minerals" glauberite and polyhalite and contain potassium chloride salts, such as sylvite and carnallite, but do not contain $MgSO_4$ minerals, are the result of the evaporation of Permian seawater, then Permian seawater must have been compositionally very different from modern seawater. The minerals indicate a higher M.O.R. hydrothermal brine volume flux. In this case the Stassfurt series of the Zechstein II and the Salado Formation evaporites may have received a significant input of river water. The work reported by LOWENSTEIN *et al.* (1989) and SPENCER *et al.* (1990) on modern salt deposits of the Qaidam Basin, China, demonstrates that alteration of evaporation sequences by changes in the relative input of river water and Ca-Cl brines does occur.

CONCLUSIONS

The major ion composition of modern seawater can be explained by mixing of river water and M.O.R. hydrothermal brine. A steady-state composition for the major ions in seawater can be obtained by removal of river-borne Na^+, Mg^{2+} and SO_4^{2-} during seawater circulation through mid-ocean ridges, without significant additional sources or sinks. The mole-equivalent concentration of bicarbonate input by river waters to the oceans is in excess of Ca^{2+}. Additional Ca^{2+} added to the oceans at mid-ocean ridges is precipitated along with river-borne Ca^{2+} and HCO_3^- as calcium carbonate. Additional sinks for K^+ are required, as the dissolved potassium fluxes from river waters and from M.O.R. hydrothermal brines are positive.

The major element composition of seawater is very sensitive to changes in the M.O.R. hydrothermal brine volume flux. This flux is likely to have changed during geologic time. Therefore, we expect that the major element composition of seawater has also changed through time. The compositional variations in seawater that result from even modest changes of a few percent in the ratio of river water and mid-ocean ridge hydrothermal brines are significant because of the potential influence on chemical sediments produced from seawater. Smaller mid-ocean ridge hydrothermal brine fluxes result in lower concentrations of Ca^{2+} in seawater and higher concentrations of Na^+, Mg^{2+}, SO_4^{2-} and HCO_3^-. These compositional variations are likely to favor aragonite precipitation rather than calcite as the dominant marine carbonate mineral, and result in marine evaporites which contain magnesium sulphate minerals. Larger mid-ocean ridge hydrothermal brine volume fluxes result in higher concentrations of Ca^{2+} in seawater and lower concentrations of Na^+, Mg^{2+}, SO_4^{2-} and HCO_3^-. These compositional variations favor calcite as the dominant marine carbonate mineral. Marine evaporites formed from such calcium-rich waters contain potash salts (sylvite and carnallite) without magnesium sulphate minerals.

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