

Secular variation in seawater chemistry: An explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 m.y.

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ABSTRACT

Secular changes in the mineralogies of marine nonskeletal limestones and potash evaporites occur in phase on a 100–200 m.y. time scale such that periods of “aragonite seas” are synchronized with MgSO_4 evaporites and periods of “calcite seas” with KCl evaporites. It is proposed that these coupled changes are the result of secular variation in seawater chemistry controlled primarily by fluctuations in the mid-ocean ridge hydrothermal brine flux, which in turn have been driven by fluctuations in the rate of ocean crust production. Quantitative predictions based on this hypothesis yield secular variation in limestone and potash evaporite mineralogies that closely match the observed variation over the past 600 m.y., providing strong support for the thesis that seawater chemistry, rather than remaining constant, has oscillated significantly over geologic time.

INTRODUCTION

Marine nonskeletal limestones and potash evaporites (salt deposits characterized by potassium chloride and/or potassium sulfate minerals) display well-defined secular oscillations in their mineralogies on a 100–200 m.y. scale over the Phanerozoic Eon that have yet to be satisfactorily explained.

In marine limestones these mineralogical oscillations are well known as alternating periods of so-called “aragonite seas” and “calcite seas” (Sandberg, 1975, 1983, 1985a, 1985b; Mackenzie and Pigott, 1981). Changes in the Mg/Ca ratio of seawater (e.g., Sandberg, 1975; Wilkinson, 1979) and changes in atmospheric $p\text{CO}_2$ (e.g., Mackenzie and Pigott, 1981; Sandberg, 1983, 1985a, 1985b; Wilkinson and Given, 1986) have been suggested as the most likely causes of the “calcite sea”–“aragonite sea” oscillations, but the problem remains unresolved.

In evaporites the secular variation takes the form of periods when potash deposits are characterized by MgSO_4 salts, such as polyhalite ($2\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{H}_2\text{O}$) and kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), as found in the latest Precambrian (Vendian), Mississippian, Pennsylvanian, Permian, Miocene, and Quaternary (Fig. 1), alternating with periods when potash deposits are characterized by KCl salts, such as sylvite (KCl), in the absence of MgSO_4 salts (Hardie, 1990, 1991), as found in the Cambrian through Mississippian, and Jurassic through the Paleogene. These secular oscillations in potash

evaporite composition, not widely recognized, have not been explained.

It is significant that these secular changes in marine limestones and potash evaporites occur in phase, such that periods of “aragonite seas” are synchronized with MgSO_4 evaporites (Fig. 1) and periods of “calcite seas” are synchronized with KCl evaporites, suggesting a common cause. Clearly, changes in nonconservative components such as CO_2

cannot account for the mineralogical changes in evaporites. These mineralogical changes would require secular changes in the major ion chemistry of seawater, particularly Mg, Ca, and SO_4 . In this paper I argue for secular variation in the major ion composition of global seawater as the explanation for the synchronized secular oscillations in the mineralogies of marine nonskeletal limestones and potash evaporites. At the core of the explanation is the hypothesis that this secular variation in seawater chemistry is controlled primarily by secular changes in the mid-ocean ridge hydrothermal brine flux, which in turn has been driven by secular changes in the rate of ocean crust production.

QUANTITATIVE PREDICTION OF SECULAR VARIATION IN SEAWATER CHEMISTRY

Spencer and Hardie (1990) showed that the composition of modern seawater can be accounted for by steady-state mixing of the two major contributors to ocean chemistry, river water (RW) and mid-ocean ridge (MOR) hydrothermal brines, coupled with precipitation of solid CaCO_3 and SiO_2 phases. They presented a simple quantitative model for calculation of the chemistry of ancient seawater based on the MOR/RW flux ratio. The most significant prediction of the model is that relatively small changes in the MOR flux, as little as 10% of the modern value, can lead to changes in the Mg/Ca, Na/K, and Cl/ SO_4 mole ratios of seawater

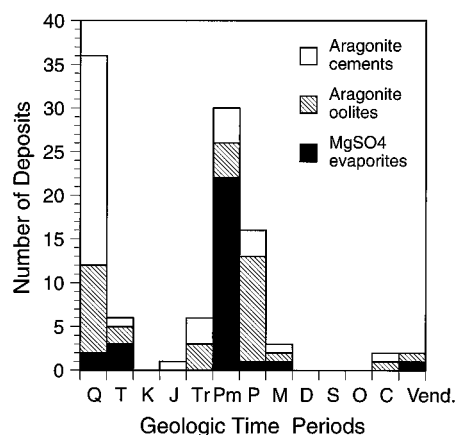


Figure 1. Secular variation in marine aragonite ooids, early marine aragonite cements, and MgSO_4 -bearing potash evaporites. Limestone histogram is based on data compiled by Sandberg (1983, 1985a, 1985b) with additional Vendian ooid data from Singh (1987). Evaporite data are based on 62 potash deposits (Zharkov, 1984; Hardie, 1990), of which 32 are KCl type and 30 are MgSO_4 bearing (latter are plotted here).

that would drastically alter the primary mineralogy of marine evaporites and limestones.

Seawater-basalt interaction at greenschist and amphibolite facies temperatures generates the hot calcium chloride hydrothermal brines that well up at mid-ocean ridges in today's ocean basins. The conversion of oceanic basalt to spilitic greenstone or amphibolite involves the net transfer of Na+Mg+SO₄ from seawater to rock and Ca+K from rock to seawater. The resulting MOR hydrothermal brine thus becomes enriched in CaCl₂-KCl and impoverished in MgSO₄ compared to the parent seawater. The flux of this MgSO₄-depleted MOR brine is a function of the volume of seawater convectively circulated at the ridges, which in turn is a function of the heat flux associated with ocean crust production at the ridges.

Ocean crust production rate, as measured from maps of ocean floor age by area, has varied considerably over the past 150 m.y.: maximum production was in the Middle Cretaceous (ca. 80–120 Ma) at almost twice the modern rate (Hays and Pitman, 1973; Larson, 1991; Larson and Olson, 1991; Richards and Engebretson, 1992). Because of ocean floor recycling in subduction zones, it is necessary to find a suitable proxy that will allow the estimation of crust production rates to be extended back in geologic time beyond the Late Jurassic. Gaffin (1987) used the Exxon first-order global sea-level curve (Vail et al., 1977) to calculate the changes in "seafloor generation rate" over the Phanerozoic on the assumption that long-term eustatic changes are mainly due to secular changes in ridge volume. Gaffin's (1987) calculated curve of sea-floor production over the past 150 m.y. shows a rise in generation rate from the Late Jurassic culminating with a maximum in mid-Cretaceous time (120–100 Ma), followed by a progressive decrease through the Tertiary to the present-day value (see Fig. 2). This same trend is displayed by (1) ocean crust production estimated by other workers (e.g., Larson, 1991), (2) relative sea-level changes determined by Hallam (1977) from the record of continental flooding, (3) sea-surface paleotemperatures determined from oxygen isotopes (Savin, 1977), and (4) atmospheric CO₂ predicted by Lasaga et al. (1985). The coherence of these variables provides support for Fischer's (1982, p. 101) suggestion that secular variation in climate ("icehouse"–"greenhouse" cycles), first-order global sea-level, mean ocean temperatures, and oceanic aeration, are linked to "volcanicity and plate motions." In this regard, Gaffin's curve is a plausible representation of the secular variation in ocean crust production. A less-di-

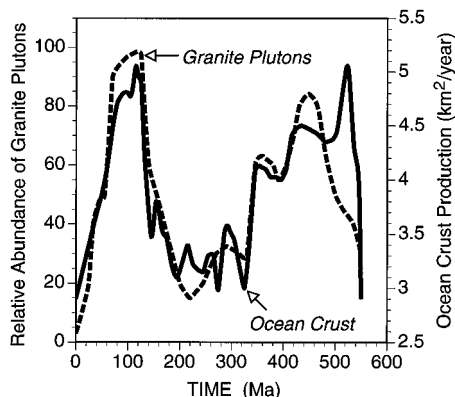


Figure 2. Comparison of secular variation in ocean crust production rate calculated by Gaffin (1987) with secular variation in relative abundance of granite plutons determined by Engel and Engel (1964) for Phanerozoic time.

rect proxy, but one that could be used to estimate ocean crust production rates during the Precambrian as far back as the beginning of the Proterozoic, is the secular variation in granite pluton emplacement within the North American continent over the past 2.5 b.y. compiled by Engel (1963) and Engel and Engel (1964) (see also Fisher, 1981). A genetic connection between pluton abundance and oceanic basalt production follows from the fact that because granite plutons and oceanic basalts constitute the outputs of crust-forming processes operating at opposite ends of a moving plate, increased rates of ocean crust production at ocean-ocean divergent boundaries should be coupled with increased rates of orogeny and associated granite plutonism at ocean-continent convergent boundaries (Hamilton, 1969; Larson and Pitman, 1972). Figure 2 shows that the timing of the main maxima and minima in granite pluton emplacement as presented by Engel and Engel (1964) is in exceedingly good agreement with Gaffin's ocean crust curve over the past 500 m.y. (the two curves diverge only in the Cambrian).

The relation between the rate of ocean crust production and the MOR flux is likely to be nonlinear, considering the complexity of the physical, chemical, and hydrological processes involved in the production of MOR brines. However, as a first approximation MOR flux at any given time during the Phanerozoic will be taken to scale linearly with crust production (but not necessarily at a one-to-one ratio). This allows secular variation in MOR/RW flux ratio to be calculated, in terms relative to the modern MOR/RW flux ratio, from Gaffin's ocean crust production curve or Engel and Engel's granite pluton curve. From the resulting MOR/RW flux ratios, the major ion chem-

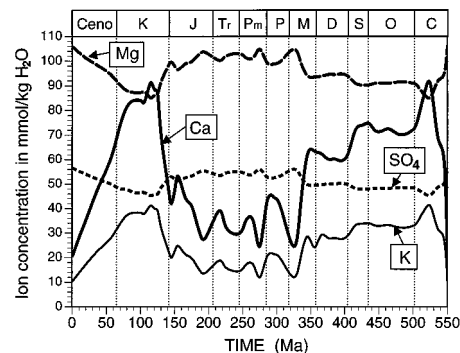


Figure 3. Secular variation in major ion chemical composition of seawater during Phanerozoic predicted assuming MOR/RW (mid-ocean ridge/river water) = 1.25.

istry for any given time period can be calculated by means of the Spencer-Hardie mixing model. The calculation procedure is as follows. A second-order polynomial equation is fitted to the following data points: (1) MOR/RW = 0 when crust production = 0, (2) MOR/RW = 1.00 when crust production = 2.9 km²/yr (the modern value; Gaffin, 1987), and (3) MOR/RW = y_{\max} when crust production = 5.05 km²/yr (Cretaceous value when crust production was a maximum; Gaffin, 1987). The quantitative relation between ocean crust production and MOR flux is unknown, so the value of y_{\max} is arbitrarily chosen, say $y_{\max} = 1.25$ (flux ratio 25% higher than the modern ratio). From a series of such polynomial equations using different values of y_{\max} between 1.00 and 1.75, a set of curves for the secular variation in MOR/RW flux ratio scaled to Gaffin's ocean crust curve is computed. From this set of curves, secular variation in the Na, K, Mg, Ca, SO₄, and Cl concentrations of ancient seawater are calculated by using the Spencer-Hardie mixing model. A typical set of ion concentrations (normalized to modern seawater chloride concentration) is shown in Figure 3, calculated for $y_{\max} = 1.25$. In Figures 3 through 6 the Decade of North American Geology geologic time scale (Palmer, 1983) is used. As Figure 3 shows, a relatively small increase in MOR/RW flux ratio (25% in the Cretaceous compared to today's value) produces significant increases in Ca (from 20 to 90 meq/L) and K (from 10 to 40 meq/L), moderate decreases in Mg (from 106 to 85 meq/L) and SO₄ (from 57 to 45 meq/L), and a dramatic decrease in Mg/Ca mole ratio (5.2 to about 1). No data are available for secular variation in the fluxes of the major ions in riverwater. Thus, in calculating the composition of ancient seawater from the predicted MOR/RW ratio, any changes from modern seawater chemistry were attributed to the

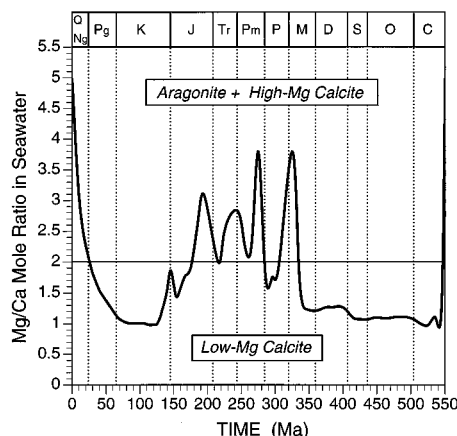


Figure 4. Prediction of secular variation in mineralogy of nonskeletal marine carbonates during Phanerozoic from Mg/Ca vs. time plot assuming MOR/RW (mid-ocean ridge/river water) = 1.25.

net effect of changes in MOR hydrothermal brine flux. Tardy et al. (1989) estimated the variation in global continental runoff over the past 570 m.y. Their average runoff curve shows oscillations that mimic the crust production oscillations shown in Figure 2 (cf. Tardy et al., 1989, Fig. 11), a sympathetic relation that dampens the influence of

changes in RW volume flux on MOR/RW ratio. Preliminary calculations of MOR/RW made from Tardy et al.'s (1989) runoff estimates, corrected using Holland's (1978, p. 89–92) data on the relation between runoff and total dissolved solids, yield timing of oscillations in the MOR/RW ratio that are in good agreement with those made using the Spencer-Hardie model (except the Cambrian-Ordovician for which the Tardy et al. (1989)–based calculations give considerably lower MOR/RW values).

TESTS OF THE HYPOTHESIS

The secular variation in the major ion chemistry of seawater over the past 600 m.y. determined by using the hypothesis presented here was tested by comparing the results with the observed secular variation in the mineralogies of marine nonskeletal limestones and potash evaporites.

Marine Nonskeletal Limestones

Füchtbauer and Hardie (1976, 1980) carried out an experimental study of the precipitation of alkaline earth carbonate minerals induced by adding Na_2CO_3 to aqueous solutions of MgCl_2 - CaCl_2 at surface temperatures (4–50°C), 1 atm total pressure, and

atmospheric $p\text{CO}_2$. They found that, for a given temperature and ionic strength, the Mg/Ca mole ratio of the aqueous solution determined whether low-Mg calcite alone, a mixture of high-Mg calcite and aragonite, or aragonite alone precipitated. These experimental results are in close accord with the behavior of nonskeletal calcite, Mg-calcite, and aragonite precipitating in modern active marine and saline lake environments (Hardie, 1987, Fig. 3). Thus, these results can be used with some confidence to predict carbonate mineral precipitation behavior at 25 °C and 1 atm pressure in ancient seawaters with compositions different from that of today's oceans, as follows: (1) low-magnesian calcite will precipitate from seawaters with Mg/Ca mole ratios less than about 2; (2) high-magnesian calcite + aragonite at Mg/Ca mole ratios between about 2 and 5.3; and (3) aragonite at Mg/Ca mole ratios above about 5.3.

The Mg/Ca secular variation curve computed from Gaffin's ocean crust curve and assuming that $y_{\text{max}} = 1.25$ (Fig. 4) predicts that (1) "aragonite seas" occurred during the following periods: Holocene through Miocene (0–25 Ma), Middle Jurassic through Early Permian (175–285 Ma), Middle Pennsylvanian through Late Mississippian (305–335 Ma), Early Cambrian to late Precambrian (545–600+ Ma); (2) "calcite seas" occurred during the following periods: Oligocene through Middle Jurassic (25–175 Ma), Late Pennsylvanian (285–305 Ma), and Early Mississippian through Middle Cambrian (335–545 Ma). For comparison, Sandberg (1983, 1985a, 1985b), on the basis of the mineralogy of marine ooids and cements, located his three "aragonite-facilitating" periods as Holocene to early or middle Cenozoic, Early Jurassic to Late Mississippian, and Early Cambrian to late Precambrian. The agreement between the observed and the predicted periods of "aragonite seas" and "calcite seas" is extremely good, as illustrated in Figure 5 (columns on left side). Whereas the $y_{\text{max}} = 1.25$ value used here provided a good overall fit to the observed data, all flux ratios within the range 1.15 to 1.30 yielded periods of "aragonite seas" and "calcite seas" that differ by no more than 10 m.y. from those listed above for 1.25.

Further support for the hypothesis comes from extension of the prediction of secular variation in calcite vs. aragonite into the Precambrian by using Engel and Engel's (1964) granite pluton curve. Figure 5 demonstrates that the granite pluton curve for the Phanerozoic can predict the secular variation in the mineralogy of marine ooids and cements as accurately as Gaffin's ocean crust

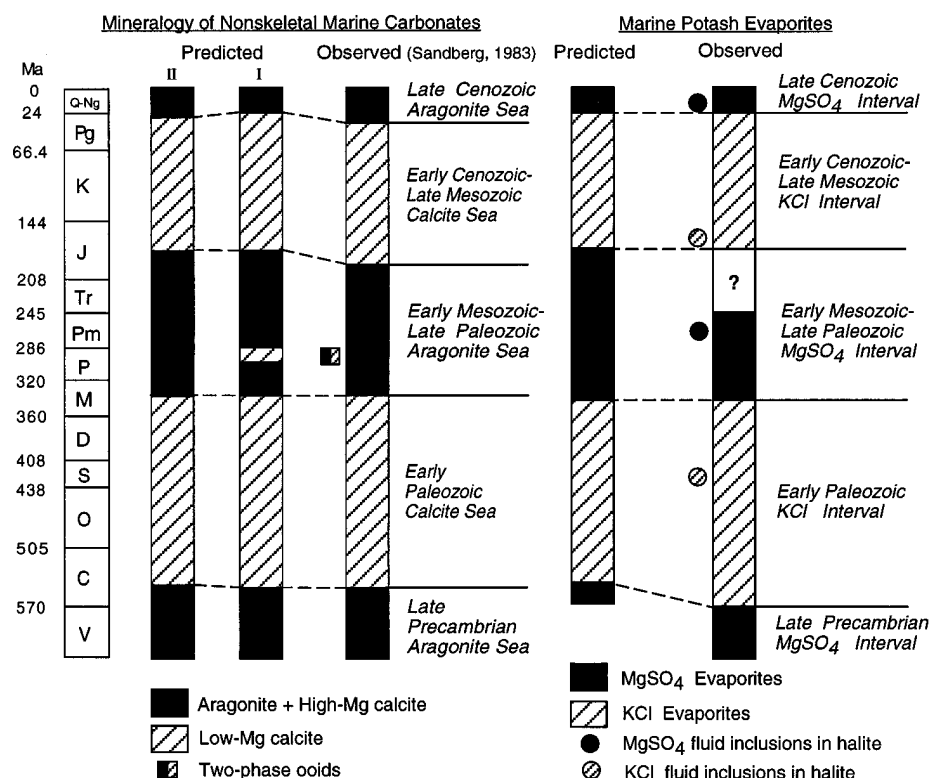


Figure 5. Comparison of predicted and observed periods of "calcite seas" vs. "aragonite seas" (three columns on left) and "MgSO₄ potash evaporite intervals" vs. "KCl potash evaporite intervals" (two columns on right) during Phanerozoic assuming MOR/RW (mid-ocean ridge/river water) = 1.25. Column I is based on ocean crust and column II is based on granite plutons (see Fig. 2). Fluid-inclusion data on ancient halite deposits are from Lazar and Holland (1988), Stein and Krumhansl (1988), Das et al. (1990), Horita et al. (1991), Ayora et al. (1994), and Land et al. (1995).

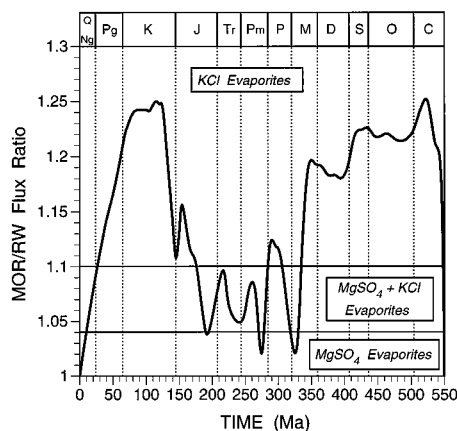


Figure 6. Prediction of secular variation in potash evaporite types over past 550 m.y. from MOR/RW (mid-ocean ridge/river water) flux ratio vs. time plot assuming MOR/RW = 1.25.

production curve (compare columns I and II). Thus, if the granite pluton curve is used as a proxy for Precambrian ocean crust production, it is possible to predict periods of “calcite seas” and “aragonite seas” back to the beginning of the Proterozoic, as follows: (1) “calcite seas” occurred at 950 to 1100 Ma, 1325 to 1375 Ma, 1700 to 1850 Ma, and 2500 to 2600 Ma, and (2) “aragonite seas” occurred at 500 to 950 Ma, 1100 to 1325 Ma, 1375 to 1700 Ma, and 1850 to 2500 Ma. The very limited data available on the primary mineralogy of early marine cements in Proterozoic marine limestones are in accord with these predictions: cements interpreted to have been aragonite originally are reported from carbonates in Norway dated at 700 Ma, in Montana (United States) dated at 1200 Ma, and in the Wopmay orogen of Canada dated at 1900 Ma (Sandberg, 1985a, 1985b).

Potash Evaporites

The computer program of Harvie and Weare (1980) that quantitatively simulates evaporative concentration of aqueous ionic solutions at 25 °C and 1 atm total pressure was used to compute the mineral successions of potash evaporites that would result from evaporation of seawaters of different compositions predicted from MOR/RW flux ratios by the present hypothesis.

From a series of such evaporation simulations, it was determined that there are well-defined critical divides that separate the “stability” fields of the basic types of potash deposit, as follows: (1) for MOR/RW flux ratios <1.04, seawater compositions are such that evaporative concentration would yield potash evaporites of the *MgSO₄* type characterized by polyhalite ($2\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{H}_2\text{O}$) \pm kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) \pm carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) in the *absence*

of sylvite (KCl); (2) MOR/RW flux ratios between 1.04 and 1.10 would yield potash evaporites of the *MgSO₄ + KCl* type characterized by polyhalite \pm kieserite \pm carnallite in the *presence* of sylvite; (3) MOR/RW flux ratios >1.10 would yield potash evaporites of the *KCl* type characterized by sylvite \pm carnallite \pm CaCl_2 minerals (tachyhydrite or antarcticite) in the *absence* of *MgSO₄* minerals. In Figure 6, a plot of secular variation in MOR/RW for $y_{\text{max}} = 1.25$ (the same value used above to predict aragonite-calcite oscillations), these critical values are shown as field boundary lines that allow determination of the time periods when each of the three potash types, *MgSO₄*, *MgSO₄ + KCl*, and *KCl*, should be the characteristic deposit. The secular variation in the types of potash evaporite deposited during the Phanerozoic predicted from Figure 6 are as follows: (1) the *KCl* type dominates during two long periods, Oligocene to Middle Jurassic (25–180 Ma) and Middle Mississippian through Middle Cambrian (335–545 Ma), and a third brief period in the Late Pennsylvanian (285–305 Ma); (2) the *MgSO₄* type dominates during four relatively short periods, the first from the Holocene through late Miocene (0–10 Ma), the second in the middle Permian (265–275 Ma), the third in the Late Mississippian (315–330 Ma), and the fourth from Early Cambrian into the Vendian (550–600+ Ma); (3) the transitional variety, the *MgSO₄ + KCl* type, occurs in the middle to early Miocene (10–25 Ma), Early Jurassic to middle Permian (180–265 Ma), in the Early Permian (275–285 Ma), in the Early Pennsylvanian (305–315 Ma), in the Late Mississippian (330–335 Ma), and in the Early Cambrian (545–550 Ma).

The stratigraphic record of potash evaporites against which the above predictions must be tested is complicated by uncertainty about the origin of several of the known *KCl* potash deposits, i.e., whether they are marine or nonmarine (Hardie, 1990, 1991). This question particularly concerns those *KCl* type deposits that accumulated in continental rift zones that were precursors to the opening of new oceans, e.g., the potash evaporites of the Triassic Meseta basins of Morocco or the Cretaceous of the Sergipe basin, Brazil, and the Gabon basin, west Africa (Hardie, 1990). These deposits were not used in the testing. To further simplify the testing, potash evaporites were divided into two broad groups, *MgSO₄*-bearing and *KCl*. The observed and predicted secular variation in these two groups of potash evaporites are compared in Figure 5 (right). The agreement between the two sets of data, observed and predicted, is very close

and suggests that the hypothesis of secular variation in the chemistry of seawater offers a viable explanation for the puzzling temporal distribution of *MgSO₄*-bearing marine evaporites. The limited data available on the major ion chemistry of fluid inclusions in Phanerozoic halite deposits (Lazar and Holland, 1988; Stein and Krumhansl, 1988; Das et al., 1990; Horita et al., 1991; Ayora et al., 1994; Land et al., 1995) are in accord with these predictions (Fig. 5, right). However, in those analyses that yielded brines with compositions different from that of modern seawater bitterns, the authors called on secondary chemical modification of the brines or the evaporites to explain the apparent anomalies. Without doubt, uncertainty must remain about the validity of these analyses as representative of pristine ancient seawater bitterns because, with the exception of the work of Ayora et al. (1994), they were done on very large inclusions in clear halite (recrystallized?) and not on the small inclusions within primary chevron bands.

The hypothesis offers a solution to the long-standing problem of the “anomalous” *KCl* composition of those *MgSO₄*-poor potash evaporites that appear to be of marine origin, in particular the Silurian Salina salt of the Michigan basin, the Devonian Prairie Evaporite of Canada, the Middle Jurassic Louann Salt of the U.S. Gulf Coast, and perhaps also the highly unusual CaCl_2 -rich Late Cretaceous Maha Sarakham Formation of Thailand.

COMPARISON OF PRESENT PREDICTIONS WITH THOSE OF OTHER WORKERS

On the basis of mass-balance calculations using box models, Lasaga et al. (1985) and Wilkinson and Algeo (1989) estimated the secular variation in seawater Mg/Ca ratio. These estimates are significantly different from each other and from those of this study. Lasaga et al. (1985) predicted an overall increase in Mg/Ca mole ratio from the present-day value of 5.2 to 7.3 in the Cretaceous. Wilkinson and Algeo (1989) used an approach similar to that of Lasaga et al. (1985), but added contemporaneous dolomitization of marine carbonate sediments by seawater as a major sink for Mg. Their model yields Mg/Ca mole ratios that change little from today’s value until the Late Cretaceous, when they drop steeply to near unity in the Early Cretaceous, and stay below 2.5 into the Early Permian. Neither of these two predicted Mg/Ca trends are in accord with secular variation in “aragonite seas” and “calcite seas” as determined by Sandberg (1983) or *MgSO₄* and *KCl* evaporite variation summarized in Figure 5. There

is, however, one most significant point on which all three models agree: the major ion chemistry of seawater has changed significantly back through geologic time. This point of agreement transcends the existing disagreements on the details of the changes and should provide us with an important stimulus to expand our efforts to unravel the apparently eventful chemical history of seawater.

CONCLUSIONS

The quantitative aspects of the hypothesis offered here are at best only approximations based on several simple assumptions, but the success in predicting the coupled first-order oscillations in nonskeletal limestone and potash evaporite mineralogies suggests that the basic tenets of the hypothesis are correct. It is proposed that ocean chemistry, rather than remaining constant, has oscillated significantly over at least the past 600 m.y., with major inflection points occurring in Middle Cenozoic, Middle Jurassic, Middle Mississippian, and Early Cambrian time (Figs. 3–6).

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