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THE ROLE OF CARBONATES IN THE EVOLUTION OF EARLY MARTIAN OCEANS

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ABSTRACT. Central to the question of life on Mars is whether there has been liquid water on the martian surface and how the planet could have evolved from possible initial warm and wet conditions to the cold and dry present state. Virtually all models for this climatic evolution rely strongly on the removal of an initial thick carbon dioxide atmosphere by precipitation of carbonate minerals from surface waters that may have been quite similar to those of Hadean Eon Earth's oceans. In order for this to occur, a hydrologic cycle would be necessary in which chemical weathering of silicate rocks consumes CO_2 that precipitates as carbonates in an acidic martian ocean which probably had a very high alkalinity. The consumption of atmospheric CO_2 by this process would result in a gradual decrease of the atmospheric greenhouse influence and cooling of the climate.

Once the surface of Mars became cold enough so that freezing conditions prevailed, the hydrologic cycle would largely cease, and the uptake of CO_2 by silicate rock weathering would greatly diminish. The alkalinity of the freezing seawater would probably be sufficient to result in the removal of all calcium as calcium carbonate. Some magnesium and sodium would also likely be removed as carbonates as well. The removal of these cations as carbonates has a major influence on the final temperature at which liquid brines would be able to persist on the surface of Mars. During the period of freezing, the oceans would act as a source of CO_2 rather than a sink, further slowing the rate of climate change on Mars.

INTRODUCTION

General considerations.–A truly voluminous literature has grown up over about the last third of a century debating the extent to which conditions on early Mars may have been similar to those on Earth and the implications of this for life on Mars (McKay and others, 1992). The recent controversy over whether fossil evidence for life is present in a meteorite of presumed martian origin (Harvey and McSween, 1996; McKay and others, 1996; Kerr, 1997; Valley and others, 1997; Leshin and others, 1998), the observations from the Mars Rover of rocks and terrain on the surface of Mars indicative of floods (Rover Team, 1997), and evaluation of more refined observations of the martian valleys and channels from the Mars Global Surveyor indicating major flows of water (Malin and others, 1998) have invigorated both public and scientific interest in the question of whether life did or does exist on Mars.

Water on ancient Mars.–Central to the question of life on Mars and the objectives of this paper is whether or not liquid water ever existed in major quantities on the surface of Mars and, if so, under what climatic conditions. Numerous articles (Squyres, 1989; Baker and others, 1992) and even books (Carr, 1996) have been written on this subject and it is well beyond the scope of our paper to present a detailed review of this often controversial topic. However, we will summarize briefly the major aspects of current thought bearing on the question of liquid water on Mars and other relevant information on early martian geochemistry.

The primary evidence for liquid water on early Mars is the presence of valleys and channels whose formation by running water seems the most reasonable explanation for their existence (Masursky and others, 1977; Squyres, 1984). Most of the valleys appear to be older than the channels, and, because most occur in heavily cratered terrain, they appear to have formed mainly during a period roughly corresponding to the Hadean

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Eon on Earth. For example, Carr (1996) found that about 90 percent of the valleys were formed prior to the martian Noachian-Hesperian boundary with an estimated age of between 3.5 to 4.3 Ga. The valleys closely resemble terrestrial channels and can reach lengths in excess of 1000 km. The mechanism by which the large outflow channels were formed is more problematic and possibly they may even have formed at a time when surface conditions on Mars were similar to those currently present. (For an extensive review and discussion see, for example, Baker and others, 1992.) Discharge rates as high as $>10^9$ m^3 s^{-1}, more than 10,000 times the discharge rates of the largest terrestrial rivers, occurred and involved $\sim10^5$ km^3 of water flowing at speeds approaching 150 m s^{-1} (Smith and others, 1998). Estimates of the total amounts of water on Mars expressed in terms of an evenly thick layer spread over the surface range from about 0.1 to over 1 km, for the more recent studies (Carr, 1996, fig. 7-11). In comparison, the value for Earth is roughly 3 km; so the potential for martian oceans based on the amount of surficial planetary water available is substantial.

In addition to evidence for flowing water on the surface of Mars, there is also considerable evidence for the existence of large bodies of water in the northern hemisphere of Mars (for example, Oceanus Borealis, Baker and others, 1991). Although the best evidence is associated with ancient modest-sized lakes filling gigantic impact craters such as Hellas and Argyre, some estimates range up to much of the northern lowlands being covered with water at some point in time. These lowlands cover roughly 30 percent of the surface of Mars, and if surface water were concentrated in them it could have reached a depth of 100 to 2800 m (Schaeffer, 1990). Large scale erosional escarpments could most easily have been produced by a liquid ocean (Parker and others, 1989). However, the question of whether or not true terrestrial-type oceans once existed on Mars remains controversial (see Kargel and Strom, 1996, for recent review). The widespread presence of weathered surface rocks and soil (Huguenin, 1976; Sidorov and Zolotov, 1986; Burns, 1993; Romanek and others, 1994), as well as salts (Clark and Van Hart, 1981; Bell, McCord, and Owensby, 1990; Plumlee, Ridkey, and DeBRaal, 1992), support the presence of extensive surface waters over a fairly long period of time. Landforms resembling terrestrial glacial features are indicative that there were once glaciers requiring a hydrologic cycle on early Mars involving liquid water (Kargel and Strom, 1992).

Atmospheric CO_2 and carbonates on Mars.–The evolution of the chemistry of the martian atmosphere is of fundamental importance in understanding how the climate of Mars has changed and if conditions on early Mars were sufficiently warm for surface waters to have persisted over long spans of time. As on Earth and Venus, atmospheric carbon dioxide is believed to play a central role in controlling surface temperature (Pollack, 1979; Hoffert, and others, 1981; Pollack and others, 1987; McKay and Davis, 1991; Kasting 1991, 1997; Kasting and others, 1988; Zent, 1996), although other greenhouse gases such as methane and ammonia may also play a role (Sagan, 1977). The current P_{CO2} on Mars ranges from about 6 to 8 mbar, which is substantially greater than the ~0.36 mbar of P_{CO2} on Earth. However, outgassing models indicate that a much higher P_{CO2}, of at least 140 mbar and perhaps as much as 3000 mbar, existed on early Mars (see Kahn, 1985, for summary and discussion). Other estimates based on the assumption of a similar CO_2/H_2O for Earth and Mars and calculated amounts of surface water yield estimates of 2 to 10 bars (Carr, 1996).

Even though solar luminosity may have been close to 25 percent less in the early (~3.8 Ga) solar system (Gough, 1981), the high P_{CO_2} of the early martian atmosphere could have led to surface temperatures close to those of present day Earth. Pollack and others (1987) estimated that a P_{CO_2} of at least 5 bars would be necessary for liquid water on Mars under the conditions that existed during the time for which most evidence for liquid water exists. However, subsequent work, as discussed by Carr (1996), indicates that more sophisticated climate models are unable to reconcile a "warm and wet" Mars with current estimates of solar luminosity changes. This is largely the result of changes in planetary albedo associated with CO_2 condensation in the upper (20-40 km) atmosphere. In order to reach the needed temperatures for liquid water on the surface of Mars a solar luminosity of at least 0.9 that of the present value would be needed (Kasting, 1991). These apparently contradictory model results are currently one of the major conundrums in understanding the evolution of water and perhaps life on Mars.

On Mars, as on Earth, the atmosphere was the ultimate source of the carbon in sedimentary carbonates. For Earth, removal of atmospheric carbon dioxide prevented a runaway greenhouse, in which the oceans could have boiled, thus preserving liquid water. However, on Mars the removal of atmospheric carbon dioxide resulted in the current cold conditions under which liquid water cannot exist on the surface. The magnesium and calcium contained in the early carbonate mass was initially derived from the weathering of silicate minerals in the primordial igneous crust of the early Mars. An example reaction for the weathering of the calcium silicate component of the primordial igneous crust and the accumulation of the products of weathering as sedimentary carbonate and silica is:

$$CaSiO_3 + 2CO_2 + 3H_2O \Rightarrow Ca^{2+} + 2HCO_3^- + H_4SiO_4 \Rightarrow CaCO_3 + SiO_{2(s)} + CO_2 + 3H_2O \text{ (net reaction is simply } CaSiO_3 + CO_2 \Rightarrow CaCO_3 + SiO_2\text{).}$$

One of the carbons from the atmospheric CO_2 necessary for weathering of silicate accumulated in ocean sediments as calcium carbonate, depleting the reservoir of CO_2 in the primordial atmosphere, and leading to the build-up of the solid inorganic carbonate reservoir; the other was released back to the atmosphere as CO_2. The stable isotope studies of Romanek and others (1994) on the SNC martian meteorite ALH84001 are supportive of this process. They indicate that the carbonates in the meteorite may have formed on Mars in an open system where the source of CO_2 was the martian atmosphere and the temperature was in the range of 0° to 80°C.

On Earth, without recycling, it would only take under present-day conditions of calcium carbonate accumulation rates in the ocean less than 1 by to produce the total mass of the sedimentary inorganic carbonate reservoir from weathering of silicate minerals and the deposition of oceanic carbonates. The depletion of atmospheric CO_2 from perhaps as much as 30 bars to close to current levels is believed to have occurred on Earth in less than the first billion years (Morse and Mackenzie, 1998). Pollack and others (1987) estimated that about 1 bar of atmospheric CO_2 could be removed on early Mars in about 0.1 Ga by formation of carbonates in martian oceans. However, they also estimated that processes such as volcanic recycling of carbonate rocks might have preserved high atmospheric concentrations of CO_2 for on the order of a billion years. Schaefer (1993) has estimated a much slower removal rate, of about 0.5 Ga bar^{-1}, for atmospheric CO_2 removal.

Composition of martian seawater.–Terrestrial oceans of composition similar to the present ocean developed early in Earth history (see discussion of Morse and Mackenzie, 1998), it is therefore possible that aqueous bodies such as lakes and oceans that developed on Mars (McKay and Stoker, 1989; Schaefer, 1993; Carr, 1996) may have had a composition similar to Earth seawater. Evidence of martian minerals formed by aqueous precipitation mechanisms come from SNC meteorites; these minerals include smectite, illite, gypsum, halite, calcite, and hematite (Gooding, 1992). These minerals are hard to reconcile with soil salts suggesting formation by different mechanisms (Clark, 1993). Martian soils are not the simple weathering products of common martian igneous rocks; addition of mafic minerals and the reaction products of volcanic gases are necessary to account for the high Mg, Fe, SO_4, and Cl concentrations in soil salts (Clark and Van Hart, 1981; Clark, 1993; Banin and others, 1997; Rieder and others, 1997). These superficial deposits may or may not be related to earlier epochs of salt deposition due to ocean and lacustrine drying (Banin, and others, 1997).

Despite our limited direct knowledge of martian salt deposition, it is possible to examine, with an aqueous-phase chemical thermodynamic model, the potential roles of composition on martian seawater carbonate geochemistry and evaporation and freezing as drying mechanisms for martian brines, be they oceans or soil solutions. These theoretical simulations provide constraints on the mineralogy of martian salts and may be useful for elucidating processes that controlled the geochemical evolution of Mars.

Objectives of this paper.–Schaefer (1990) has suggested that shortly after planet formation Mars and Earth were probably very similar. Both had newly formed crusts, heavily bombarded by meteorites. Both were rich in water. And both likely had significant carbon dioxide atmospheres. It is therefore not unreasonable to use the early terrestrial oceans as a model for the early martian ocean.

Recently, Morse and Mackenzie (1998) presented a paper on the carbonate chemistry of the Earth's Hadean Eon (~4.3-3.8 Ga) ocean and the role it may have played in determining the major changes occurring in surface conditions on Earth during a time in which life is likely to have originated. We will take a largely parallel approach in this paper to the role that carbonate geochemistry may have played during about the same period of time on Mars, which is close to the estimated time span for liquid water on the martian surface. A major difference will be our discussion of the chemistry that probably occurred near the end of this time period when liquid water existed on Mars. At this time hypersaline brines, perhaps similar to those found in Antarctic lakes, may have been all that could survive during the increasingly deteriorating climatic conditions. McKay and Davis (1991) have estimated that the existence of such brines could have caused liquid water to be present on the martian surface for 0.7 ± 0.3 Ga. We will also place the results of this modeling effort of the oceanic carbonate system in a more general context of early martian global geochemical cycles.

APPROACH TO THE PROBLEM

Our general approach is to examine the impact of different conditions for ocean/atmosphere evolution on aqueous carbonate geochemistry using the Pitzer model for calculating activity coefficients in aqueous solutions. For temperatures greater than ~0°C, the program of He and Morse (1993) will be used. Their program is based on extensive experimental work on the carbonic acid system and has been tested for prediction of carbonate mineral solubility even in high ionic strength brines. The ability of the model to predict carbonic acid component activity coefficients has also been favorably tested against the most recent Pitzer models specifically "tuned" for seawater (Millero, personal communication, 1997).

The FREZCHEM model of Marion and Grant (1994) will be used for cold ($<0°C$) brines. Because of the highly specialized nature of this model we will provide a brief explanation of its major characteristics. FREZCHEM is a Fortran version of the Spencer-Møller-Weare (1990) model. This model is based on chemical thermodynamic principles and is parameterized for the Na-K-Mg-Ca-Cl-SO_4-H_2O system over the temperature range from 219 k to 298 K. A recent modification of FREZCHEM includes a Gibbs energy minimization algorithm for estimating the thermodynamically stable compositions (Mironenko and others, 1997). In addition, the sulfate chemistry in this model was recently reparameterized (Marion and Farren, in press). The FREZCHEM model calculates the reaction pathways for temperature change and evaporation of solutions. The temperature-change pathway calculates the chemical composition of a solution over a user-specified temperature range, which may include freezing of the solution. The evaporation pathway holds the temperature constant while removing water by evaporation. The Pitzer equations are used to calculate the activity of water and the activity coefficients for soluble ions. These equations allow calculation of activity coefficients at high ionic strengths in complex solutions (Plummer and others, 1988; Spencer, Møller, and Weare, 1990; Pitzer, 1991, 1995). This model explicitly considers ice formation and the precipitation-dissolution of 30 minerals (table 1). The Spencer-Møller-Weare and FREZCHEM models were validated by comparing model predictions to experimental measurements of solute concentrations and unfrozen water percentages during seawater freezing (Spencer, Møller, and Weare, 1990; Marion and Grant, 1994; Marion and Farren, in press) and freezing of Don Juan Pond in Antarctica (Marion, 1997).

In the past, FREZCHEM did not consider pH because none of the chloride and sulfate salts are pH dependent (table 1). In order to assess more accurately the roles of evaporation and freezing of brines containing carbonates, incorporation of carbonate chemistry into FREZCHEM necessitates that pH be explicitly considered.

In the pH range from 4.5 to 9.5, the following charge balance must exist for the cations and anions in solution:

$$[Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] = [HCO_3^-] + 2[CO_3^{2-}] + 2[SO_4^{2-}] + [Cl^-] \quad (1)$$

where brackets refer to concentrations. This equation ignores the insignificant contributions of $[H^+]$ and $[OH^-]$ to charge balance in this pH range. For a system in equilibrium with solid phase $CaCO_3$, this equation can be rewritten as:

$$\frac{2(K_{sp})(\gamma_{H^+})^2[H^+]^2}{(\gamma_{Ca^{2+}})K_HK_1K_2P_{Co_2}} \pm \Delta_i = \frac{K_HK_1K_2P_{Co_2}}{(\gamma_{H^+})[H^+](\gamma_{HCO_3^-})} + \frac{2K_HK_1K_2P_{Co_2}}{(\gamma_{H^+})^2[H^+]^2(\gamma_{CO_3^{2-}})} \quad (2)$$

where,

$$\Delta_i = [Na^+] + [K^+] + 2[Mg^{2+}] - [Cl^-] - 2[SO_4^{2-}]. \quad (3)$$

K_{sp} is the $CaCO_3$ solubility product, K_H is the Henry's Law constant, K_1 and K_2 are the first and second dissociation constants for carbonic acid, $[H^+]$ is the hydrogen concentration, P_{CO_2} is the partial pressure of CO_2, and the γ's are activity coefficients. Δ_i is the difference in non-carbonate species, which can be determined by the existing FREZCHEM model. Given the P_{CO_2}, activity coefficients, equilibrium constants, and Δ_i, eq (2) can be solved by successive approximations for the $[H^+]$, which is then used to

TABLE 1

Solid phases in the FREZCHEM model

1. H_2O(cr,I) (ice)
2. NaCl(cr) (halite)
3. $NaCl \cdot 2H_2O$(cr) (hydrohalite)
4. KCl(cr) (sylvite)
5. $MgCl_2 \cdot 6H_2O$(cr) (bischofite)
6. $MgCl_2 \cdot 8H_2O$(cr)
7. $MgCl_2 \cdot 12H_2O$(cr)
8. $CaCl_2 \cdot 6H_2O$(cr) (antarcticite)
9. $KMgCl_3 \cdot 6H_2O$(cr) (carnallite)
10. $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$(cr) (tachyhydrite)
11. Na_2SO_4(cr) (thenardite)
12. $Na_2SO_4 \cdot 10H_2O$(cr) (mirabilite)
13. K_2SO_4(cr) (arcanite)
14. $MgSO_4 \cdot 6H_2O$(cr) (hexahydrite)
15. $MgSO_4 \cdot 7H_2O$(cr) (epsomite)
16. $MgSO_4 \cdot 12H_2O$(cr)
17. $CaSO_4$(cr) (anhydrite)
18. $CaSO_4 \cdot 2H_2O$(cr) (gypsum)
19. $Na_2SO_4 \cdot 3K_2SO_4$(cr) (aphthitalite)
20. $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$(cr) (bloedite)
21. $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$(cr) (picromerite)
22. $CaCO_3$(cr) (calcite)
23. $CaCO_3 \cdot 6H_2O$(cr) (ikaite)
24. $MgCO_3$(cr) (magnesite)
25. $MgCO_3 \cdot 3H_2O$(cr) (nesquehonite)
26. $MgCO_3 \cdot 5H_2O$(cr) (lansfordite)
27. $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$(cr) (hydromagnesite)
28. $CaMg(CO_3)_2$ (dolomite)
29. $NaHCO_3$(cr) (nahcolite)
30. $Na_2CO_3 \cdot 10H_2O$(cr) (natron)
31. $NaHCO_3 \cdot Na_2CO_3. \cdot 2H_2 O$ (trona)

control $CaCO_3$ solubility (Marion and Schlesinger, 1994). For a system that is undersaturated with respect to $CaCO_3$, the $[Ca^{2+}]$ concentration can be included in the Δ_i term (eq 3). Then a modified eq 2 is solved for $[H^+]$ that is used to estimate $[HCO_3^-]$ and $[CO_3^{2-}]$ concentrations needed to balance the charges in the solution phase.

He and Morse (1993) have estimated Pitzer-equation parameters for calcite solubility in concentrated brines over the temperature range from 273 to 363 K. These parameters combined with temperature dependent equations for K_{sp}, K_H, K_1, and K_2 (Plummer and Busenberg, 1982; Plummer and others, 1988) supplemented with some Pitzer-equation parameters from Harvie, Møller, and Weare (1984) are sufficient to estimate calcite solubility in brines for the temperature range from 273 to 298 K. There are no systematic studies of carbonate chemistry at subzero (<0°C) temperatures that would allow a better parameterization at these low temperatures. In this paper, we simply extrapolated the above carbonate equilibrium equations and associated Pitzer parameters to temperatures below 273 K. The accuracy of these extrapolations is uncertain at present.

CARBONATE GEOCHEMISTRY OR EARLY MARTIAN SEAWATER

Pollack and others (1987) presented an estimated relationship between surface temperature and P_{CO_2} on Mars that we will use here. They show a difference of about 0.5 bar for the same temperature between a solar luminosity at the present value and 0.7 the current value. Based on the previous discussion we have taken a mid-range value for solar luminosity and, with considerable extrapolation, arrived at the relationship shown in figure 1 for a solar luminosity of 0.85 the current value. This results in an upper limit temperature of about 30°C at 10 bar P_{CO_2} and pure water or modern seawater freezing at about 0° to -4°C, respectively, at close to 5 bar P_{CO_2}. Later in this paper we will discuss the potential role of hypersaline brines on a cold Mars. Even such brines require on the order of 1 bar P_{CO_2} to remain liquid. Although this relationship between P_{CO_2} and temperature must be taken with considerable caution (Carr, 1996), it serves as a reasonable base for subsequent discussion. Our primary goal is to examine how possible evolutionary changes in the P_{CO_2} of the atmosphere and associated temperature changes, along with changes in the concentrations of major seawater constituents, may have influenced the chemistry of water on Mars.

Holland (1984) suggested that the composition of early terrestrial seawater was probably dominated by Na^+ and Cl^-, just as are modern seawater and most subsurface brines, and that K^+, Mg^{2+}, and Ca^{2+} were the other major cations present, being produced as weathering products. Therefore, if surface geochemical processes on early Mars were similar to those on Earth, the composition of early martian sea salt may not have differed dramatically from that in the present ocean of Earth. We caution the reader that this conclusion is controversial. Some authors contend that the early terrestrial ocean was similar to a soda lake in composition, rich in sodium and carbonate, and evolved into a sodium chloride, calcium-rich ocean in late Precambrian time (Kempe and Degens, 1985; Kempe, Kazmierczak, and Degens, 1989). In either the case of a sodium chloride or sodium carbonate early ocean, it is very likely that sulfate would have been absent because of the highly reducing conditions of the early atmosphere and ocean system. Also, as shall be discussed subsequently, seawater bicarbonate (HCO_3^-) concentration may have been substantially (about 10×) higher. What we certainly do not know is the absolute concentrations or ratios of the dissolved constituents in early martian waters. We will therefore explore the implications of compositional variations in major seawater components for the martian oceanic carbonate system.

As a starting point, we assume that the martian ocean had its near-surface waters relatively close to equilibrium or moderately supersaturated with calcite (the influences of major non-equilibrium conditions will be investigated later). Sumner (1997) recently

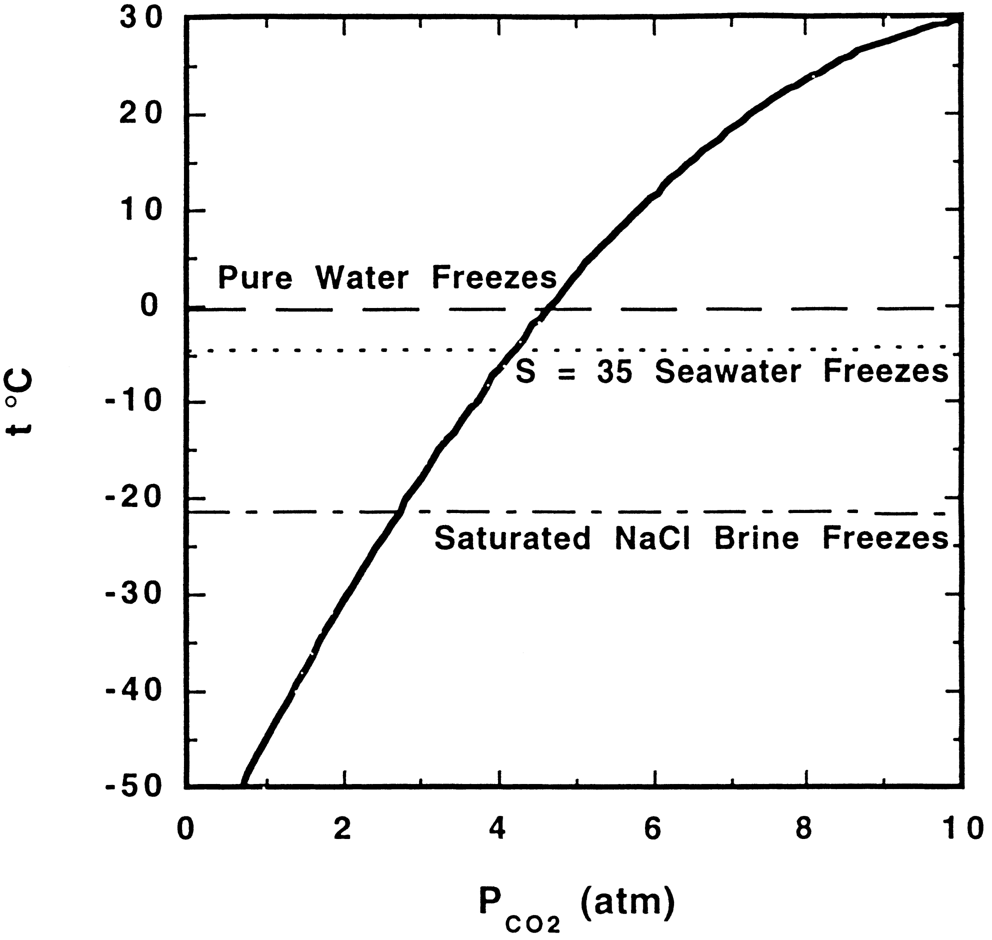

Fig. 1. Estimated relationship between surface temperature and atmospheric P_{CO_2} on ancient Mars extrapolated from Pollack and others (1987) for a solar luminosity of 0.85 the present value.

demonstrated that terrestrial Archean deep subtidal seawater was probably supersaturated with respect to calcite and that in situ calcite precipitation directly on the seafloor was an important feature and rock-forming process of Archean oceans. Grotzinger and Rothman (1996) and Grotzinger (1993) concluded that stromatolitic structures first evident in Archean rocks may be a result of inorganic precipitation of calcium carbonate from seawater and not directly related to biological activity. These conclusions plus the relatively short residence time of calcium and carbonate in at least the terrestrial ocean justify our assumption of an ocean at or slightly above saturation with respect to calcite on Mars as well as early Earth. Indeed, without biological calcium carbonate precipitating organisms, it is very likely that the ocean may have been oversaturated with respect to calcite throughout its extent.

Before proceeding with an examination of how several parameters of probable importance may have influenced martian ocean chemistry, the role of major changes in solution composition in controlling carbonate chemistry, at the mid-range estimated values of temperature and P_{CO_2} of 15°C and 6.7 bar (see fig. 1) are presented in table 2. Four solutions were chosen: (1) seawater with a salinity (S) of 35; (2) a NaCl solution with

TABLE 2

Carbonate chemistry for waters of different compositions at 15°C with a $P_{CO2} = 6.7$ bar and in equilibrium with calcite

Composition	pH	Alkalinity (molal)	DIC (molal)
Seawater (S = 35)	5.79	0.131	0.395
NaCl + 0.01 M Ca I = 0.7	5.77	0.125	0.385
Same as above also in equilib. wrt dolomite (Mg = 0.626)	5.83	0.138	0.402
Pure water (at equilib. wrt calcite Ca = 0.030 M)	5.53	0.060	0.575

the same ionic strength as solution (1) containing calcium at its seawater concentration; (3) solution (2) with magnesium added to a concentration in equilibrium with dolomite; and (4) pure water in which calcium carbonate has been allowed to dissolve to equilibrium under the given conditions. The range in pH is small (5.53-5.83) in the different solutions. Alkalinity and dissolved inorganic carbon (DIC) also show a small range of concentrations of 0.125 to 0.138 (~10 percent) and 0.385 to 0.402 (~4 percent) in the solutions of similar ionic strength. Alkalinity is about half as much, and DIC is close to 1.5 times higher in the pure water solution. It is therefore clear that even fairly major uncertainties in the composition of early martian waters do not lead to grossly unacceptable uncertainties in the carbonic acid system chemistry of these waters.

The influence of temperature between 0° and 30°C is not of first order importance to carbonate chemistry as shown by the relationships between temperature and the carbonic acid system parameters pH, DIC and alkalinity for seawater in figure 2. The calculations were made for seawater with a salinity of 35, 7 times supersaturated with respect to calcite (current terrestrial surface ocean water state) at a P_{CO_2} appropriate for a given temperature (~5-10 bars, see fig. 1). pH is close to 6, and the change in pH is only 0.06 over this temperature range. The change in alkalinity is small, but about a 50 percent change occurs in DIC. In subsequent calculations, a mid-range temperature of 15°C and P_{CO_2} of 6.7 bar will generally be used unless specified otherwise. Also, the influence of salinity under these conditions is relatively small, as shown in figure 3, for a range in salinity from 10 to 100 at 15°C. Therefore, an uncertainty of about ±15°C in temperature and close to an order of magnitude range in salinity will not lead to large uncertainties in the carbonic acid system chemistry.

Among the most important variables for the carbonate chemistry of martian seawater are the P_{CO_2} of the atmosphere and the concentration of calcium, because calcium concentration, at a given saturation state for calcite, directly influences the allowable carbonate ion activity. In figures 4 and 5, pH, alkalinity, and DIC have been plotted for seawater at 15°C and 7 times supersaturated with respect to calcite. At a normal seawater (S = 35) calcium concentration, the range in pH for a wide variation in P_{CO_2} (3-10 bar, fig. 4) is relatively small (~0.3), but both alkalinity and DIC exhibit fairly large changes of, respectively, 0.24 to 0.42 and 0.36 to 0.82 molal in concentration that are close to linearly proportional to atmospheric P_{CO_2}. For the same conditions, but at a fixed P_{CO_2} (6.7 bar) and variable calcium concentration (fig. 5), over a range relative to that in seawater of 0.1 to 10, there is distinctly different behavior above and below the concentration in normal seawater. At lower calcium concentrations pH, alkalinity, and DIC are quite sensitive to changes in concentration but at higher concentrations considerably less so. Morse and Mackenzie (1998), in discussing the carbonate chemistry of the terrestrial Hadean ocean, suggested that it is likely that high alkalinity ocean waters were likely to have lower calcium concentrations than current seawater. They suggested that this may have been a limiting factor in the development of calcifying organisms during the subsequent Precambrain Eon. Given the similarly high calculated alkalinity

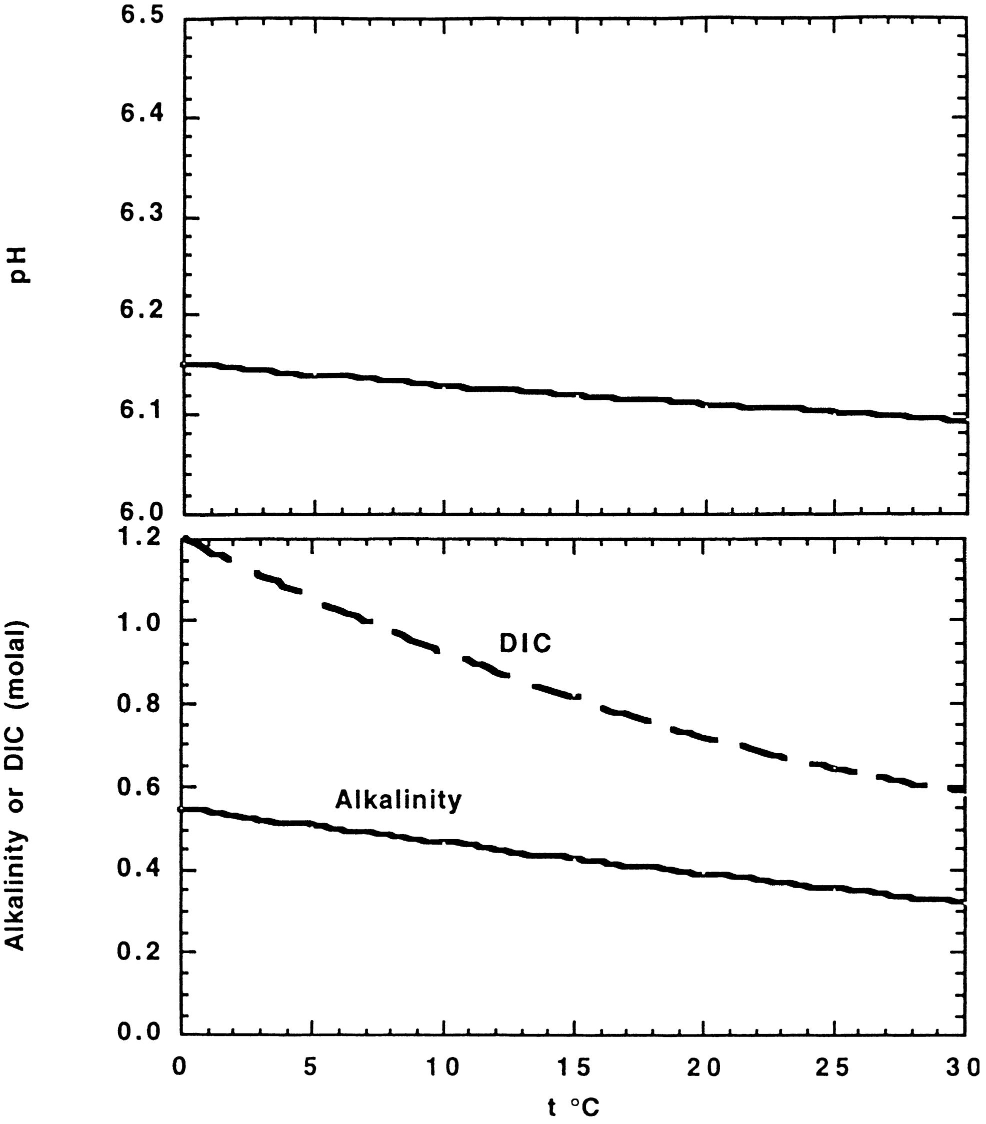

Fig. 2. pH, alkalinity, and DIC versus temperature for modern seawater of S = 35, 7 times supersaturated with respect to calcite and with a P_{CO_2} = 10 bar.

values for our martian ocean water, it is therefore possible that the calcium could have been less than in normal terrestrial seawater on Mars as well.

The final major variable to be considered is that of the saturation state of the martian seawater. In most of the previous calculations we have set it at what is probably a likely mid-range guess (7 times supersaturated which is what is found for most surface waters in Earth's present oceans) between the probable limits of equilibrium with respect to calcite and about 22 times supersaturated, where pseudo-homogeneous nucleation and precipitation of aragonite occurs from normal seawater (Morse and He, 1993). The major variable pH, alkalinity, and DIC have been plotted in figure 6 against the saturation state

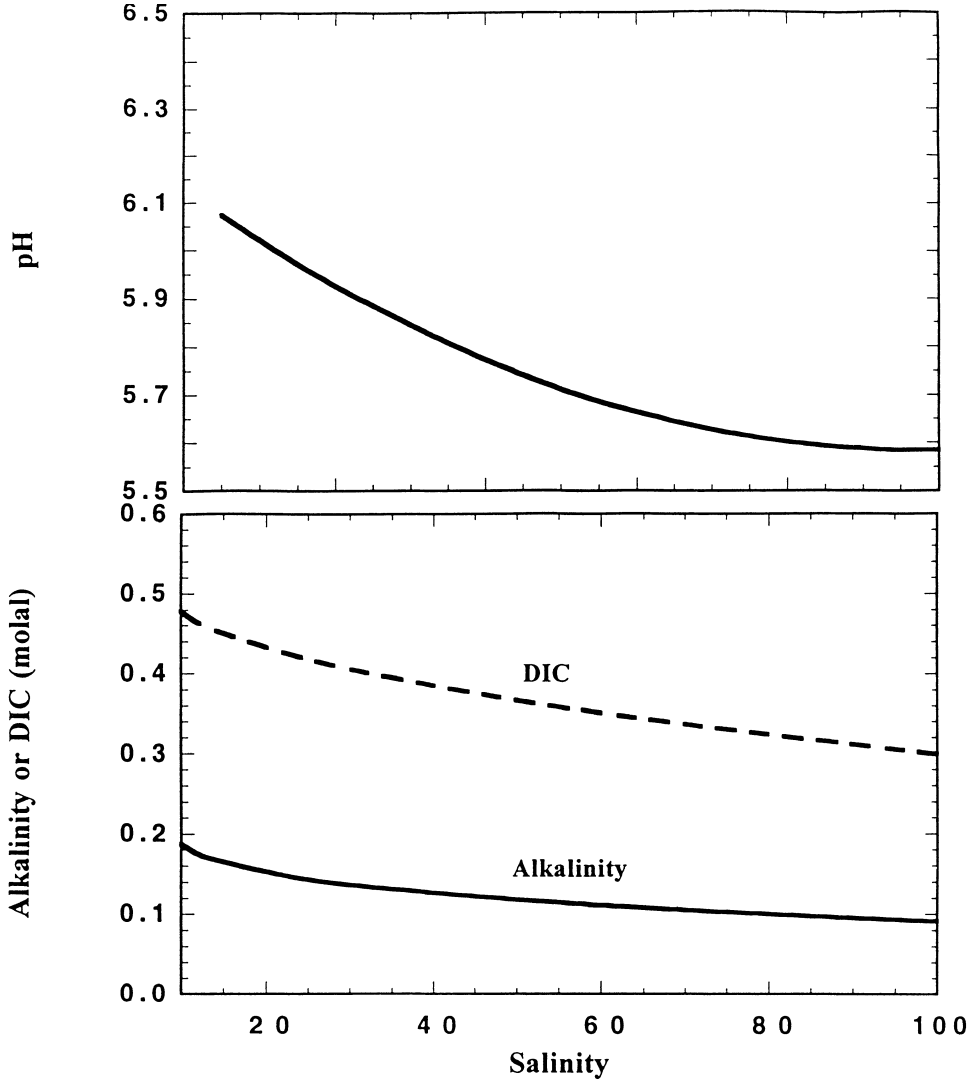

Fig. 3. pH, alkalinity, and DIC versus salinity for modern seawater 7 times supersaturated with respect to calcite and with a P_{CO_2} = 10 bar.

with respect to calcite for a P_{CO_2} = 10 bar and 30°C and for a P_{CO_2} = 4.7 bar and 0°C. For a given P_{CO_2}-temperature, the change in pH is about 0.4 over the saturation range, with approx a 0.2 offset for the two sets of conditions. There is close to a 0.4 molal change in alkalinity and DIC over the range in saturation states and less than ~0.1 offset between the two given P_{CO_2}-temperature sets. This saturation state is a relatively important variable in our calculations over a reasonable range of values. Although this examination of the probable influence of major parameters on the carbonate chemistry of a martain ocean points to some significant uncertainties, they are not overwhelmingly large. All results point to the pH of the waters being slightly acid and probably within a range of one pH unit of uncertainty (6.0 ± 0.5), and that alkalinity and DIC were probably within 0.3 ± 0.2 and 0.7 ± 0.3 molal, respectively.

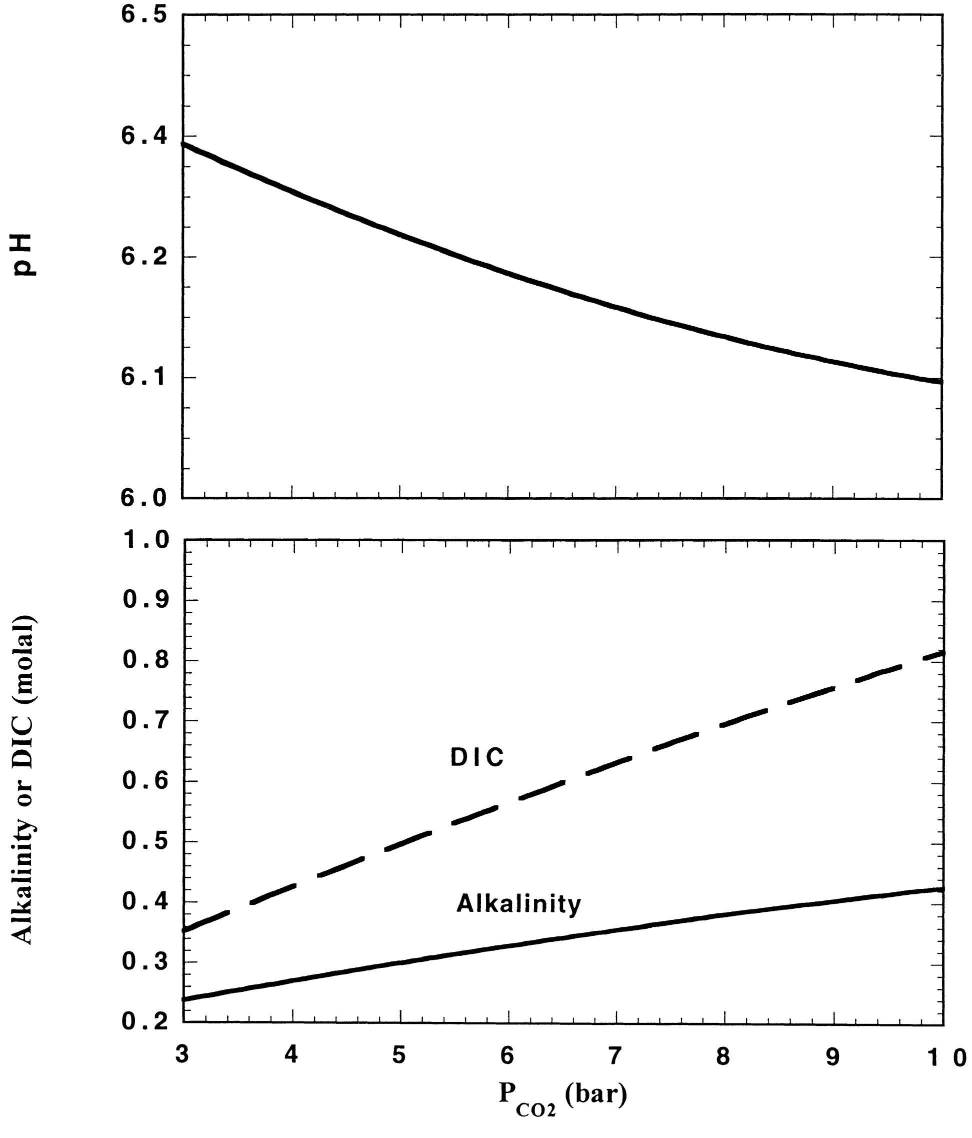

Fig. 4. pH, alkalinity, and DIC versus P_{CO_2} for modern seawater of S = 35, 7 times supersaturated with respect to calcite and 15°C.

Using the P_{CO_2}-temperature relationship in figure 1 and assuming an approximate rate of change of 1 bar P_{CO_2} per 0.1 Ga between 4.3 and 3.8 Ga (10-5 bars) curves for pH, alkalinity and DIC have been plotted for S = 35 seawater in equilibrium with calcite and 22 times supersaturated (fig. 7). An interesting observation is that the combined P_{CO_2}-temperature changes result in very little change in the carbonic acid system parameters with time. If we favor the equilibrium conditions we reach surface freezing conditions at a P_{CO_2} of about 5 bar and ocean water with an alkalinity of ~0.18 molal and pH of ~6. After this the processes start to change dramatically as the oceans freeze which is the topic of the next section in this paper.

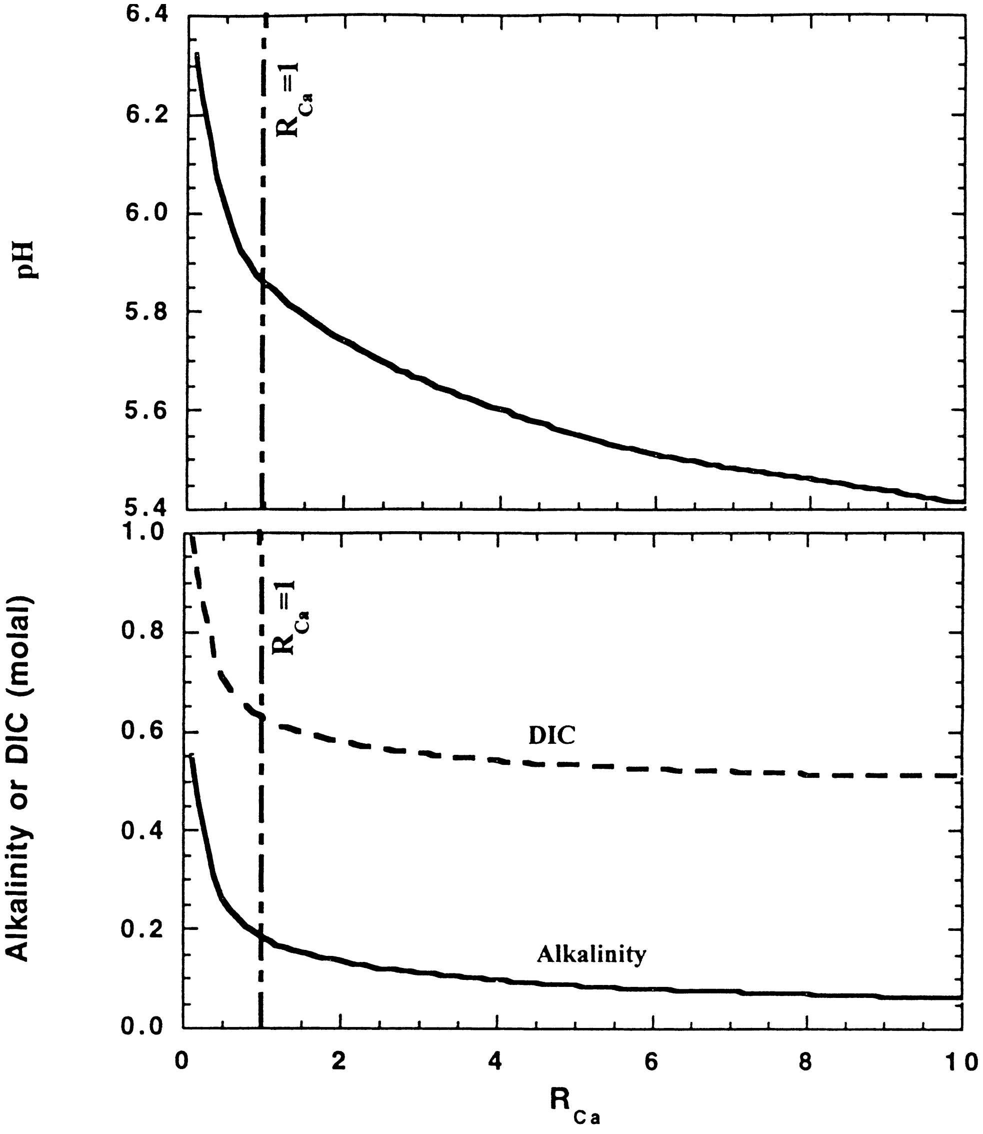

Fig. 5. pH, alkalinity, and DIC versus R_{Ca}(= Ca^{2+} concentration divided by that in S = 35 seawater).

CARBONATE GEOCHEMISTRY IN A FREEZING-BRINE MARTIAN OCEAN

Beginning of the end.–In the previous section we brought the evolution of the martian ocean-atmosphere system to the point at which the deposition of calcium carbonate had lowered the P_{CO_2} of the atmosphere to a level where climate had deteriorated so that freezing conditions for surface waters started to prevail. Under these increasingly harsh conditions, the only way in which liquid water could persist on the martian surface was for it to become increasingly saline (fig. 8). The two primary ways to do this are to either add considerably more salts to an existing volume of water or to reduce drastically the amount of liquid water available for a close to fixed or decreasing amount of salts. It seems likely that the later path was followed.

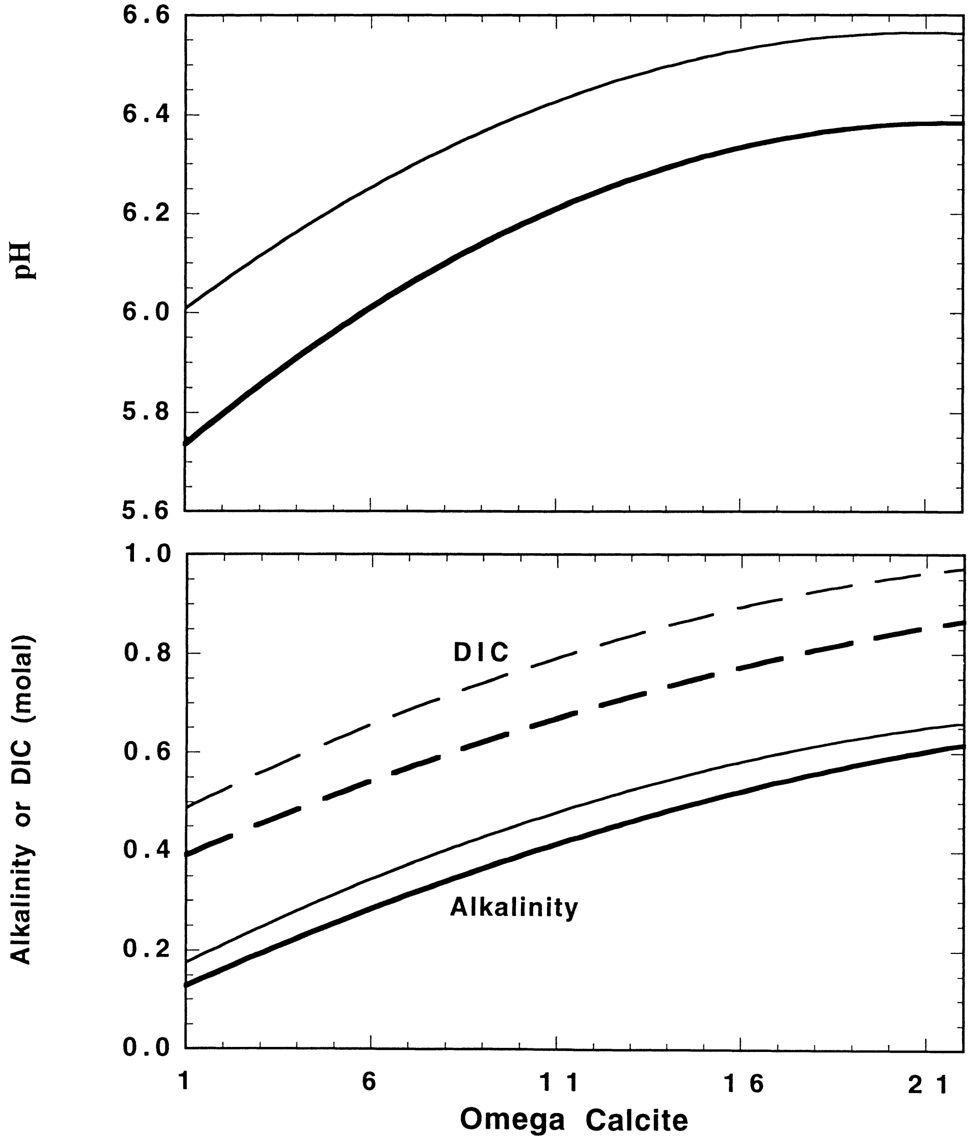

Fig. 6. pH, alkalinity, and DIC versus supersaturation state (omega) with respect to calcite for modern seawater of S = 35. Heavy lines for a P_{CO_2} = 10 bar and 30°C, and light lines for a P_{CO_2} = 4.7 bar and 0°C.

Water could dominantly be lost by two processes. The first is water evaporating from salty martian oceans could fall as freshwater precipitation (mainly snow and ice) that would not thaw and return to the oceans as runoff. Such water would be lost in a dispersed manner to the surface regolith. The second mechanism would be loss of water simply by freezing. Such freezing might well have proceeded as growing icecaps over the martian oceans analogous to what occurred in the northern Atlantic Ocean during glacial periods. Such an icecap would have the effect of insulating the underlying waters and stopping evaporative loss of water as well. This could substantially extend the period

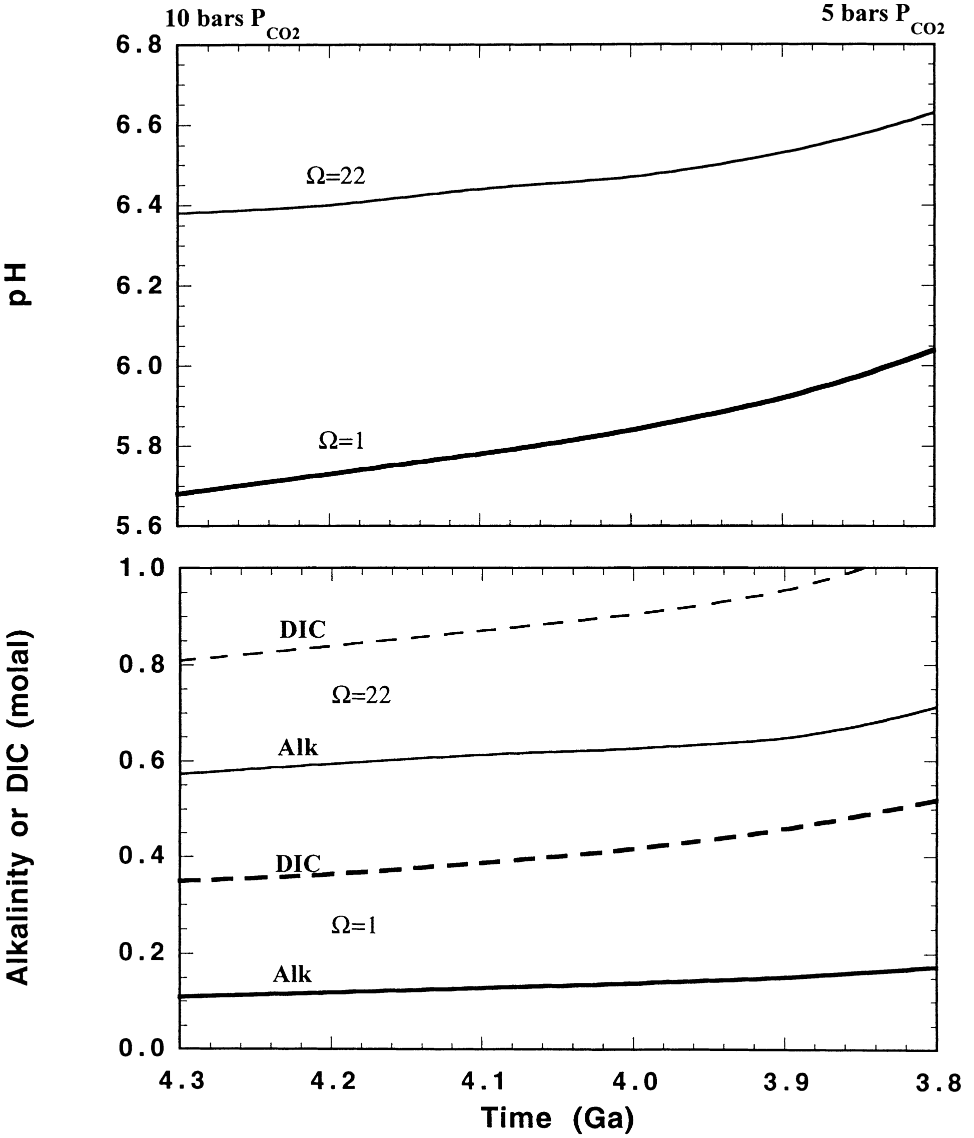

Fig. 7. pH, alkalinity, and DIC versus time. The time span considered is equivalent to the Hadean Econ on Earth. In the lower frame the dashed line is for DIC, and the solid line is for alkalinity. Heavy lines are for equilibrium with calcite, and light lines are for 22 times supersaturated with respect to calcite.

during which liquid water persisted on the martian surface (McKay and others, 1985; also see Carr, 1996, for discussion).

A major impact of these changing conditions would be that weathering on the martian surface would rapidly evolve to conditions approaching those in cold deserts on Earth and approximating those now occurring on present day Mars. In the absence of a hydrologic cycle to provide liquid water to drive the previously given silicate weathering reaction, the removal of atmospheric carbon dioxide via this mechanism which results in the precipitation of calcium carbonate could not occur. We are thus faced with a difficult

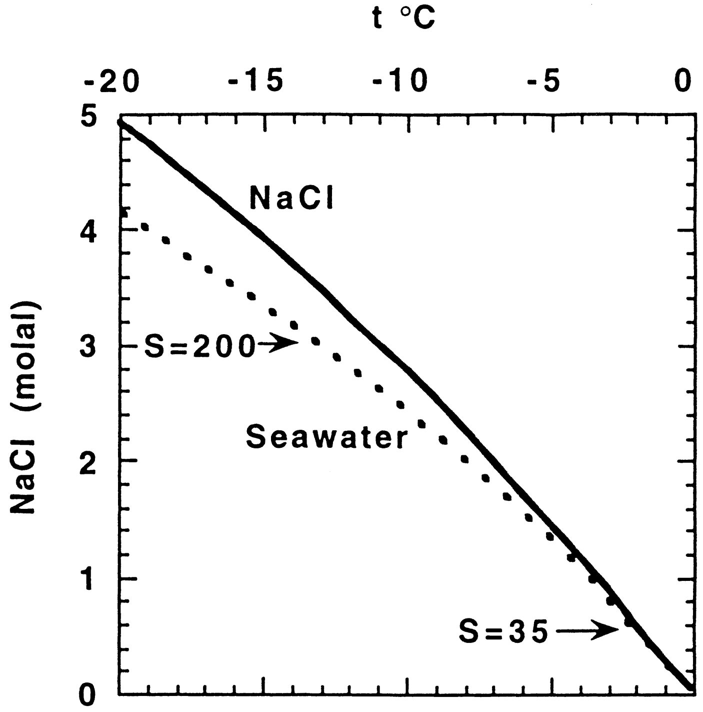

Fig. 8. The freezing temperature of a NaCl brine versus temperature (solid line) and seawater versus salinity (dashed line).

problem as freezing conditions begin to prevail on Mars. If calculations indicating that a P_{CO_2} of about 5 atmospheres, or roughly half of all superficial CO_2, remained in the atmosphere, how was it removed if not by weathering and carbonate deposition? A number of possibilities have been suggested including in CO_2-H_2O clathrates, carbon dioxide adsorption on minerals in the soil, sputtering, and, when conditions became sufficiently cold, in polar caps comprised of solid CO_2 (Carr, 1996). It is also possible that hypersaline brines could have formed similar to those in present-day Antarctica, which can persist in the liquid state to temperatures <-50°C (fig. 9). Hypersaline brines could serve as a sink for CO_2. However, it is difficult to obtain quantitative estimates of how important these sinks for CO_2 might have been as they evolved through time. What is likely is that the rate of removal of CO_2 from the atmosphere, and thus climate change, slowed considerably as the silicate weathering-oceanic $CaCO_3$ deposition process largely ground to a halt.

Mineral deposition during modern terrestrial seawater evaporation and freezing.–In order to understand processes occurring as the last of the martian oceans froze, we will examine the evolution of seawater brines by computer simulations. Before examining this process in our estimated martian seawater, we will first discuss the freezing process and the minerals it produces relative to the more familiar evaporative production of salts from terrestrial seawater. For simulations of terrestrial seawater evaporation at 25°C, glauberite ($Na_2Ca(SO_4)_2$), polyhalite ($K_2MgCa_2(SO_4)_4 \cdot 2H_2O$), and kieserite ($MgSO_4 \cdot H_2O$) solubility products (Plummer and others, 1988) were added to the database of minerals in the model (table 1), because these minerals precipitate during terrestrial seawater evaporation at 25°C (Eugster, Harvie, and Weare, 1980; Harvie, Møller, and Weare,

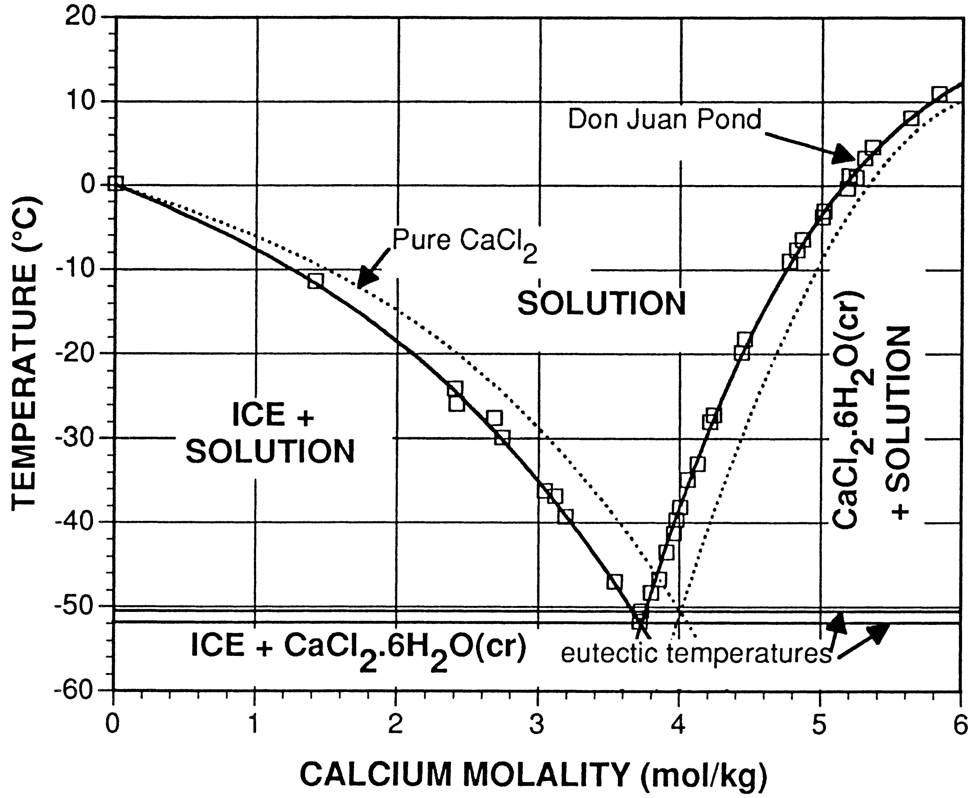

Fig. 9. A stability diagram for ice and antarcticite in a pure $CaCl_2$ solution and in Don Juan Pond (Marion, 1997).

1984). We removed dolomite and magnesite from the database of minerals (table 1) because these minerals do not precipitate during seawater evaporation or freezing.

Terrestrial seawater drying via evaporation and freezing are compared in figure 10. Seawater is supersaturated with respect to calcite at atmospheric P_{CO_2} and precipitates calcite early in both the evaporation and freezing processes (fig. 10) (Gitterman, 1937; Nelson and Thompson, 1954). Gypsum begins precipitating at a seawater concentration factor (SCF) for evaporation of 3.3× (fig. 10A), whereas mirabilite begins precipitating during freezing at a similar SCF of 3.0× (fig. 10B). At close to the same SCF of 10.3×, halite and glauberite begin precipitating during evaporation, and hydrohalite and gypsum begin precipitating during seawater freezing. The first K salt to precipitate during evaporation is polyhalite at a SCF of 34.0×, and during freezing, sylvite at a SCF of 39.8×. The first Mg salt to precipitate during evaporation is polyhalite at a SCF of 34.0×, and during freezing, $MgCl_2 \cdot 12H_2O$ at a SCF of 44.4, which occurs at the eutectic for seawater freezing (−36.2°C).

Although there are many similarities in evaporating and freezing of terrestrial seawater (fig. 10), these processes generally produce different suites of minerals. A few generalities can be made with respect to the minerals that precipitate during drying by evaporation or freezing. The minerals that precipitate during freezing are generally mixtures of simple salts such as $Na_2SO_4 \cdot 10H_2O$ and $CaSO_4 \cdot 2H_2O$ rather than complex salts such as $Na_2Ca(SO_4)_2$ or $KMgCl_3 \cdot 6H_2O$ that precipitate during evapora-

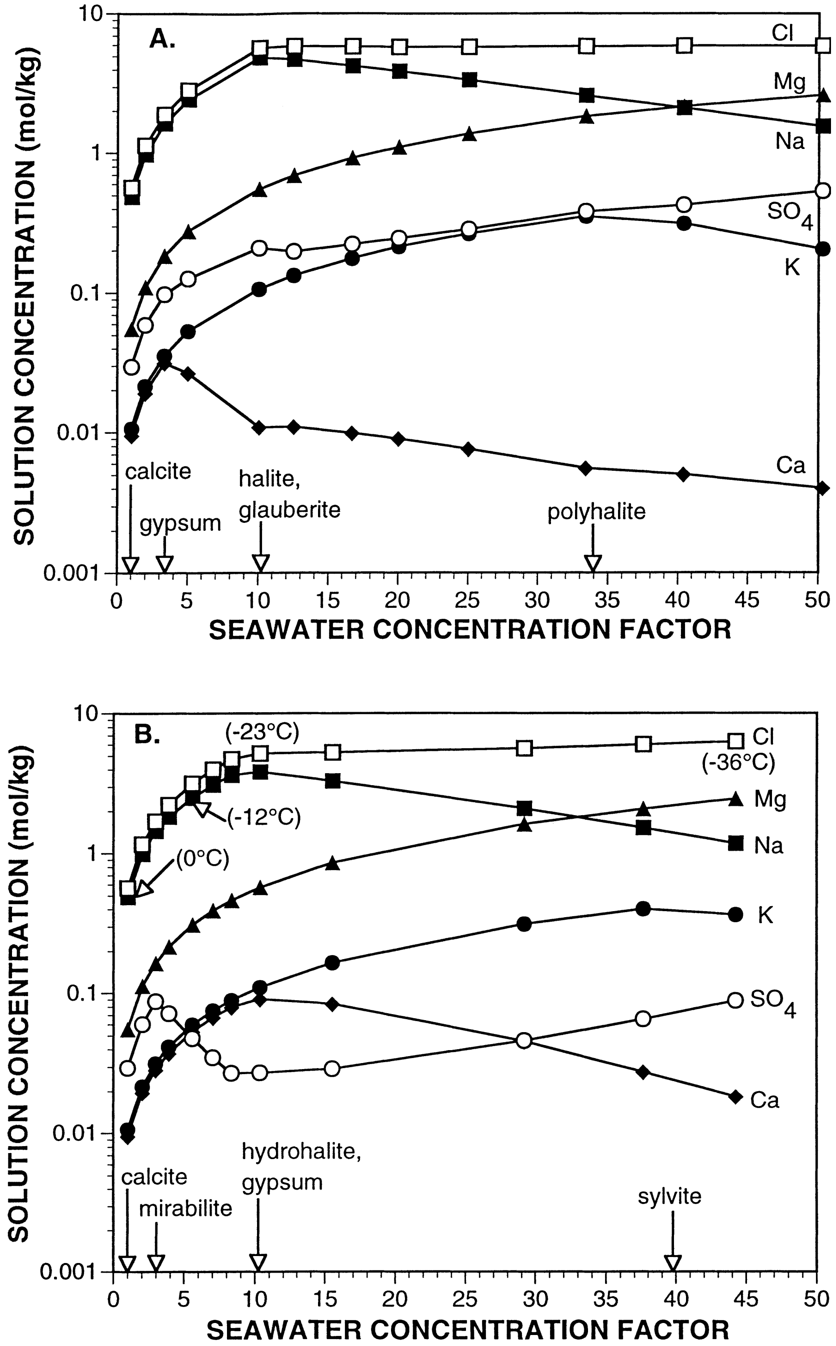

Fig. 10. The composition of terrestrial seawater and the minerals precipitated as a function of the concentration factor for evaporation at 25°C (A) and freezing (B).

tion at higher temperatures. Similar but more highly hydrated salts precipitate during freezing compared to evaporation (for example, $MgCl_2 \cdot 12H_2O$ versus $MgCl_2 \cdot 6H_2O$ or $NaCl \cdot 2H_2O$ versus NaCl). Differences of this nature might provide clues to the environmental conditions that prevailed during salt deposition from waters on Mars and thereby serve as a surrogate for early martian environments.

Seawater freezing on Mars.–A modified Hardie-Eugster diagram is useful for placing potential martian seawater evaporation/freezing into perspective. In many natural waters, calcite is the first mineral to precipitate (figs. 10, 11). If Ca > alkalinity, then calcite precipitation removes most of the alkalinity, and the evaporation/freezing pathway follows the left limb of figure 11. The next chemical divide along this limb occurs with respect to Ca-SO_4. If $SO_4 > Ca$, then gypsum/mirabilite precipitation removes Ca from the system leading to a predominantly Na-Mg-Cl-SO_4 system. Alternatively, where $Ca > SO_4$, a predominantly Na-Ca-Mg-Cl solution develops. Note that in terrestrial seawater freezing, both the latter pathways are possible depending on experimental protocols (Gitterman, 1937; Nelson and Thompson, 1954). The "Gitterman pathway" is the thermodynamically stable pathway for seawater freezing (fig. 10B) (Marion and Farren, in press; Marion, Farren, and Komrowski, in submission).

If alkalinity >"Ca + Mg," then alkali carbonate brines can develop during evaporation/freezing (fig. 11). These brines typically have high pHs in the range 9 to 10 (Hardie and Eugster, 1970; Drever, 1997). Important carbonate minerals that can precipitate along this limb are nesquehonite ($MgCO_3 \cdot 3H_2O$), lansfordite ($MgCO_3 \cdot 5H_2O$), nahcolite ($NaHCO_3$), thermonatrite ($Na_2CO_3 \cdot H_2O$), and trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) (Bukshtein, Valyashko, and Pel'sh, 1953; Hardie and Eugster, 1970; Ming and Franklin, 1985; Drever, 1997). In cold waters ikaite ($CaCO_3 \cdot 6H_2O$) may be the dominant calcium carbonate mineral (Marland, 1975; Bischoff, Fitzpatrick, and Rosenbauer, 1993;

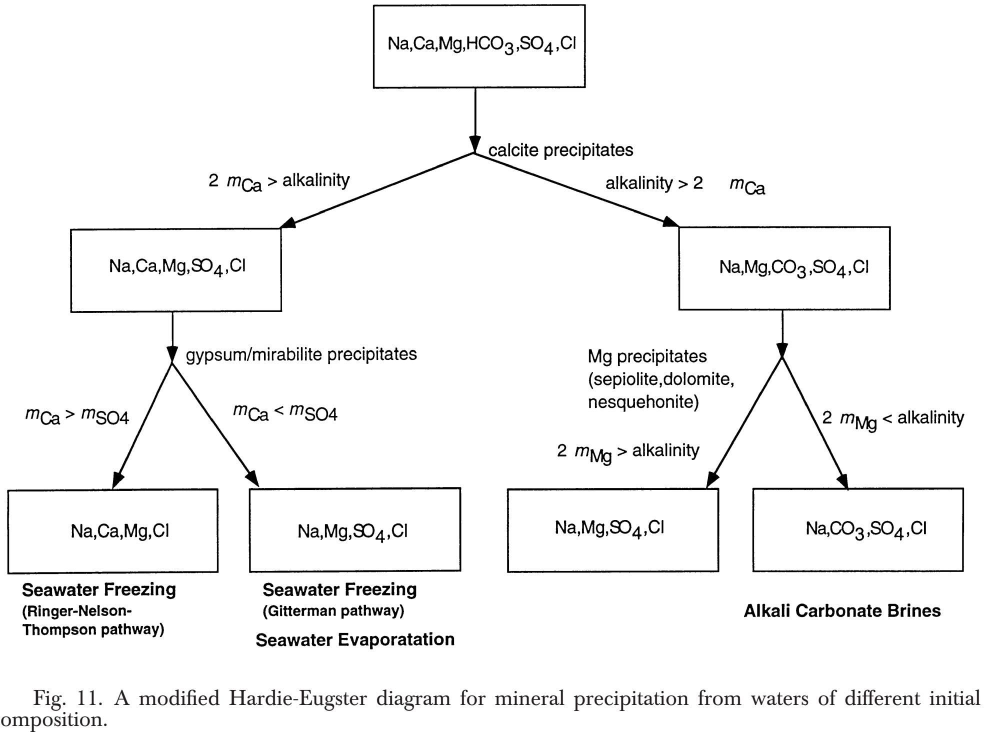

Fig. 11. A modified Hardie-Eugster diagram for mineral precipitation from waters of different initial composition.

Brecevic and Nielsen, 1993) and the formation of calcium carbonate monohydrate is also potentially possible (Kralj and Brecevic, 1995).

Although martian seawater evaporation/freezing might fall along any limb of figure 11, we made a few simplifying assumptions that facilitate understanding of the major processes likely to be followed during freezing-mineral formation. In our examination of the differences between the minerals produced via modern terrestrial seawater evaporation and freezing, carbonate minerals played a very minor role, whereas sulfate minerals were quantitatively second only to chloride minerals, reflecting the relative concentrations of these anions. However, on early Mars, as is probable during roughly the first 2 Ga on Earth (see Morse and Mackenzie, 1998, for recent discussion of this topic), sulfate may have been absent or at only minor concentrations in surface waters. This coupled with the very high alkalinities required to obtain even equilibrium, with respect to calcite, for high atmospheric P_{CO_2} values, means that Cl^- and HCO_3^- were likely to be the two important anions. This would result in chloride and carbonate minerals being the most important product of martian seawater evaporation/freezing.

The precipitation of carbonate minerals is greatly complicated by the relationship between temperature and P_{CO_2}. The general assumption we are using is that drops in temperature were dominantly associated with decreases in atmospheric P_{CO_2}. If large changes in P_{CO_2} occur at a constant temperature, then major decreases in seawater alkalinity must occur as well, if a close to constant saturation state with respect to a carbonate mineral is so be obtained.

For example, using sulfate-free $S = 35$ seawater in equilibrium with calcite at 0°C, at a $P_{CO_2} = 5$ atm the equilibrium alkalinity is about 160 meqv, but at a $P_{CO_2} = 0.1$ atm it is only about 22 meqv. The only way to accomplish this large change in alkalinity would be to precipitate carbonate minerals. A change of about 140 meqv in alkalinity requires the precipitation of roughly 70 mmol of calcite or magnesium carbonate mineral. This exceeds the combined concentrations of $Ca^{2+} + Mg^{2+}$ meaning that at some point sodium carbonate minerals must also form. Although carbonate minerals, such as calcite, tend to become more not less soluble with decreasing temperature, this effect would be more than offset by the increasing concentrations of ions caused by removal of water by freezing.

As an uncomplicated example, consider the previously described sulfate-free $S = 35$ seawater in equilibrium with calcite at 0°C and having a $P_{CO_2} = 5$ atm equilibrium. A temperature change to -20°C with the associated freezing of water, even at constant P_{CO_2} will result in precipitation of $\sim$80.8 percent of the calcium as calcite. If the initial seawater was 20 times supersaturated with respect to calcite (probably close to a maximum value, see previous discussion) and remained this supersaturated, none of the calcium would have precipitated at -20°C. However, ikaite begins precipitating at -27°C. If the P_{CO_2} dropped to about 2.7 atm (fig. 1) at -20°C, 89.6 and 8.7 percent of the calcium would precipitate at equilibrium and 20 times supersaturated, respectively. In the latter case, the precipitate is again ikaite. These calculations indicate that if our estimate of martian seawater composition is even remotely close to correct, that calcium was probably removed from the freezing ocean as calcium carbonate. This implies that martian seawater cannot have as low a eutectic temperature (<-50°C) as some terrestrial $CaCl_2$ brines (fig. 9).

More than ample alkalinity remains after the removal of calcium to result in the precipitation of all magnesium as a magnesium carbonate and some sodium as a sodium carbonate. We simulated martian seawater freezing to the eutectic at 0.1, 1.0, 2.7, and 5.0 atm P_{CO_2}. As was the case for terrestrial seawater simulations, these martian simulations were done without dolomite and magnesite in the minerals database. The eutectic composition and temperature are identical for 1.0, 2.7, and 5.0 atm P_{CO_2}. At these high P_{CO_2}s, the minerals that should theoretically precipitate are hydrohalite, sylvite,

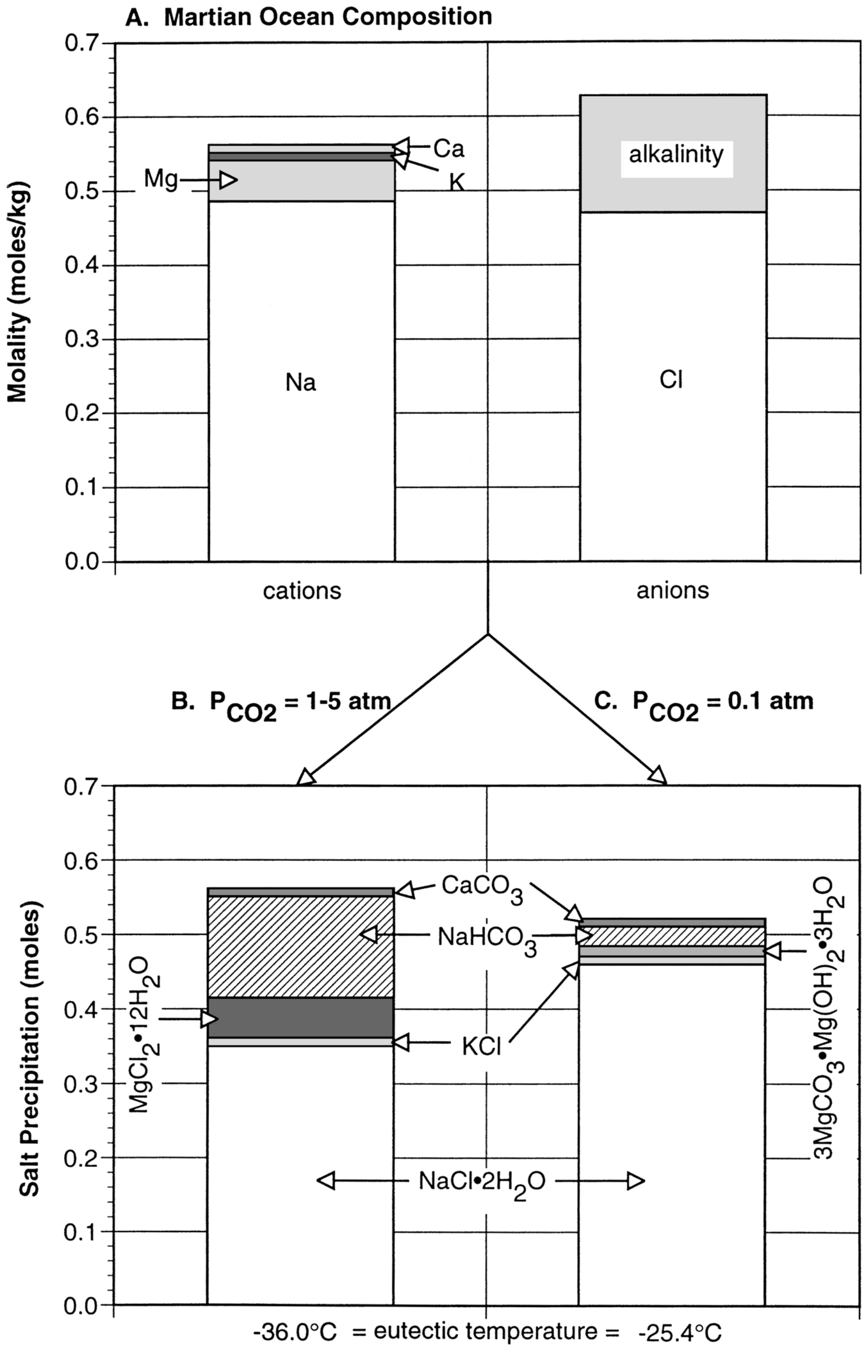

Fig. 12. The (A) hypothesized composition of an early martian ocean, and the composition of salts precipitating by freezing to the eutectic at (B) P_{CO_2} = 1 to 5 atm and (C) P_{CO_2} = 0.1 atm.

$MgCl_2 \cdot 12H_2O$, nahcolite, and calcite (fig. 12B). Along this pathway, the last mineral to precipitate during freezing is $MgCl_2 \cdot 12H_2O$ at -36.0°C, which is the eutectic temperature. In contrast, at a low P_{CO_2} of 0.1 atm, all the magnesium precipitates as hydromagnesite (fig. 12C). Along this pathway, the last salt to precipitate is KCl at -25.4°C, which is the eutectic temperature. In support of this scenario, there is spectroscopic evidence for the presence of hydrous magnesium carbonates on the martian surface (Calvin, King, and Clark, 1994). In interpreting these results, bear in mind that there is a strong correlation between P_{CO_2} and pH in this carbonate system. For the simulated P_{CO_2}s of 5.0, 2.7, 1.0, and 0.1 atm, the calculated pHs at -20°C are 5.78, 6.04, 6.47, and 7.45, respectively. The precipitation of minerals such as hydromagnesite, or hypothetically nesquehonite, natron, or trona (table 1), probably reflects precipitation at low P_{CO_2} and high pH.

The precipitation of carbonates would buffer atmospheric CO_2 by reactions such as

$$Ca^{2+} + 2HCO^{-} \Rightarrow CaCO_3 + H_2O + CO_2$$

that result in roughly half the CO_2 present in the martian oceans as alkalinity being converted to dissolved CO_2. Further dissolved CO_2 would be released as the volume of the oceans decreased and they became saltier.

SUMMARY

There is growing evidence that liquid water was present on the surface of Mars, for perhaps a time period approaching a billion years. Although more controversial, it is also very possible that during much of this time climatic conditions were sufficiently warm for an active hydrologic cycle to exist. Associated with such a hydrologic cycle would be chemical weathering in which CO_2 would be consumed. Just as on Earth, a major product of this weathering would be precipitation of calcium carbonate in an acidic martian ocean which likely had a very high alkalinity. The consumption of atmospheric CO_2 by this process would result in a gradual decrease of the atmospheric greenhouse influence and cooling of the climate.

Once the surface of Mars became cold enough so that freezing conditions prevailed, the hydrologic cycle would largely cease, and the update of CO_2 by silicate rock weathering would greatly diminish. The alkalinity of the freezing seawater would probably be sufficient to result in the removal of all calcium as calcium carbonate. Some magnesium and sodium would also likely be removed as carbonates as well. The removal of these cations as carbonates has a major influence on the final temperature at which liquid brines would be able to persist on the surface of Mars. During the period of freezing, the oceans would act as a source of CO_2 rather than a sink, further slowing the rate of climate change on Mars.

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