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A chemical model for evaporites on early Mars: Possible sedimentary tracers of the early climate and implications for exploration

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Abstract. Martian geomorphology seems to indicate extensive hydrological activity during the Noachian era. Liquid water at the surface would require a large greenhouse effect that is widely hypothesized to have been caused by a high partial pressure of atmospheric carbon dioxide, P_{CO_2}. A sedimentation model driven by sequential evaporation is used to calculate the evaporite mineral sequence in a closed basin lake subject to high P_{CO_2}. The initial fluid is derived from weathered igneous rock similar to Martian meteorite basalts. Siderite ($FeCO_3$) is always the first major carbonate to precipitate. Thus siderite is predicted to be an important facies component in ancient Martian sediments along with silica, which is also an early precipitate. These would form varves in lakes that undergo cycles of evaporation and water recharge. After silica and siderite, the sequence is magnesian calcite, nearly pure hydromagnesite, and gypsum, followed by highly soluble salts like NaCl. The presence of siderite sediments generally requires an atmospheric P_{CO_2} level in excess of ~ 0.1 bar, otherwise iron silicates (such as greenalite) would form. This may be used in exploration as an observational test on the past atmospheric composition of Mars, subject to consideration of the depositional environment. At P_{CO_2} of approximately several bar, gypsum precipitation could occur before calcite upon evaporation if the initial SO_4^{2-}:Ca^{2+} ratio is high and there is no water recharge. The predicted carbonate sequence upon evaporation is generally consistent with recent hypotheses suggesting traces of evaporite carbonates in some Martian meteorites. Several mechanisms destroy or obscure carbonates at the Martian surface. Consequently, in situ analysis of the interior of ejecta from recent impact craters lying within sedimentary basins may offer the most practical approach to future exploration of ancient carbonate sediments.

1. Introduction

Currently, the mean atmospheric pressure (~ 6 mbar) is too low and the mean temperature (~ 215 K) is too cold to support liquid water on the Martian surface. However, valley networks and high erosion rates on ancient geologic units provide compelling evidence for an early epoch of hydrological activity [e.g., *Carr*, 1996]. The formation of valley networks by fluvial processes almost certainly required local surface temperatures above the freezing point of water. Also, crater erosion rates in the Noachian may have been caused by precipitation [*Craddock and Maxwell*, 1993]. This "warm, wet early Mars" explanation of surface geology demands a denser atmosphere to provide sufficient greenhouse warming. This has to offset sunlight that was some 20-30% less intense 4 Gyr ago. Consequently, a dense atmosphere with CO_2 as the predominant constituent has been hypothesized (e.g., reviewed by *Haberle* [1998]). Other possible greenhouse gases, such as NH_3, CH_4, or SO_2, are short-lived because of rapid photodissociation and chemical reactions, whereas CO_2 could feasibly have been sustained against weathering loss by volcanism [*Pollack et al.*, 1987] or low-velocity impacts [*Carr*, 1989]. Photochemically labile gases could persist if protected by a high-altitude organic haze [*Sagan and Chyba*, 1997], but the amount of CH_4 needed would imply a biological source of unlikely magnitude [*Kasting*, 1997]. *Kasting* [1991] noted that CO_2 condensation would occur in a thicker CO_2 atmosphere and limit the P_{CO_2} level. However, since CO_2 ice particles are highly reflective in the infrared, CO_2 clouds cause greenhouse warming by scattering infrared radiation back to the surface [*Forget and Pierrehumbert*, 1997]. The CO_2 cloud model sets a minimum level of $P_{CO_2} \sim 0.7$ bar required for liquid water on the surface within the context of a one-dimensional model, though it is somewhat

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sensitive to assumed cloud parameters. Another possibility is that a sufficient background level of SO_2 prevents condensation through UV absorption and allows for a thick CO_2 atmosphere [*Yung et al.*, 1997], although maintaining sufficient levels of SO_2 in the presence of liquid water has been questioned [*Murphy and Bass*, 1998].

However, little has been said about how one can verify by measurement the supposed high level of past P_{CO_2}. Observational studies of the present-day climate on Mars would allow us to refine parameters for climate models, but the links between the very ancient climate and present climate are direct in only a few instances: For example, by measuring the effects of CO_2 clouds in the current climate we might better understand the past. But how can we establish observational limits on the ancient atmospheric composition and test the hypothesis of an early thick CO_2 atmosphere?

If early Mars had been "warm and wet" for millions of years, geochemical processes should have left definitive isotopic and mineralogical evidence. Moreover, post-Noachian rates of erosion are $\sim 10^3$ times less than those predating them [*Arvidson et al.*, 1979; *Carr*, 1992], so that the ancient surface of Mars should be well preserved compared to the Earth's. Geochemical evidence of a past climate conducive to liquid water should be locked up in sediments and evaporites like on Earth [e.g., *Holland*, 1984; *Krupp et al.*, 1994]. Discussion in the literature relates to the possible isotopic tracers of Martian climate evolution [*Jakosky and Jones*, 1997] or the mineralogical stability conditions on present-day Mars [*Gooding*, 1978; *Clark and Van Hart*, 1981], but this paper focuses on possible mineralogical indicators of an earlier warm, wet era. During this period, there may have been substantial rain on Mars [*Craddock et al.*, 1997]; here we assume significant aqueous weathering whether the water originated from glacial melt, precipitation, or upwelling groundwater. Even in a perennially cold climate, if running water exists, weathering rates in local spatial maxima can be comparable to terrestrial temperate or tropical regions according to Antarctic studies [*Lyons et al.*, 1998].

The assumption of aqueous activity on Mars earlier in its history is supported by observations that may be grouped chronologically: (1) evidence for a supposed period of sustained warmer and wetter conditions in the Noachian era and (2) evidence for episodic water throughout the rest of Martian history. For the early period the evidence consists of the aforementioned valley networks and heavily eroded craters; there are also geological features that have been interpreted as crater lakes, playas, and sedimentary layers [*Forsythe and Zimbelman*, 1995; *Grin and Cabrol*, 1997; *Edgett and Parker*, 1997]. Minority opinion speculates that mass wasting may have been the predominant process in eroding the valley networks [*Carr*, 1995], and recent evidence suggests erosion from a groundwater source [*Malin and Carr*, 1999], so perhaps the highly eroded craters provide the most unambiguous support for wetter, warmer conditions on early Mars. Such conditions should have produced sediments. Many valley networks terminate in closed sedimentary basins which have depths of several kilometers [*Goldspiel and Squyres*, 1991]. In addition, analogs to terrestrial evaporites may exist in ancient crater basins [*Forsythe and Zimbelman*, 1995]. Hydrological analysis of closed drainage basins suggests evaporation and water recharge [*Forsythe and Blackwelder*, 1998]. It therefore seems extremely likely that geochemical evidence of the early Martian environment awaits our discovery, locked up in ancient sediments. In all cases where water debouched at the ends of valley networks or onto plains, it must eventually have precipitated some quantity of sediments in the terminal phases by solute concentration through evaporation or freezing.

Evidence for episodic water later in Martian history includes outflow channels cut by enormous floods and possible large terminal lakes estimated to have covered from 1 to 30% of the planet's surface [*Carr*, 1996]. Geomorphic evidence for the latter includes mottled plains, shorelines, terraced slopes, and layered sediments [*Baker et al.*, 1991; *Costard*, 1988; *Parker et al.*, 1989, 1993; *Scott et al.*, 1991]. It is plausible that subsequent to such flooding events, lakes may have become ice-covered and persisted for hundreds of millions of years [*McKay and Davis*, 1991]. The ice cover would have been ablated away by the wind to leave sediments [e.g., *McKay and Nedell*, 1988].

This paper considers the case of mineral deposits formed in sedimentary basins on Mars. A thermodynamic model is used to investigate the early primary precipitates in basin water that evolves from freshwater to a brine. Apart from intrinsic interest, it is important to consider the nature of such minerals for the future Mars exploration program. The interpretation of sedimentary minerals and determination of the past climate (particularly, whether it was conducive to life) are high priorities. Indeed, consensus scientific opinion strongly recommends targeting future landers and rovers at sedimentary environments [see *Gulick*, 1998, and references therein; and *Brack et al.*, 1998]. Furthermore, it has recently been suggested that some Martian meteorites may contain evaporite salts [*Bridges and Grady*, 1998; *Warren*, 1998; *McSween and Harvey*, 1998a, b; *Scott*, 1999]. It is therefore important and timely to begin to model the possible chemistry of such evaporite deposits. Previously, some short comments on this problem have been presented [*DeBraal et al.*, 1993; *Catling*, 1998; *Murphy and Bass*, 1998]. This is the first extended paper to discuss the detailed computation of the mineral chemistry of evaporite sediments on Mars and their possible implications.

2. Aqueous Weathering on Early Mars

2.1. Geochemical Influences of the Early Atmosphere

In principle, sediments on early Mars will be related to the past geochemical nature of the planet and its past atmosphere (see Figure 1). Assuming sedimentation on early Mars took place in an atmospheric environment with high P_{CO_2}, this would decrease the pH of aqueous environments at the surface and change the type of sediments that may form in them (see section 4). Clearly, the chemistry of the atmosphere can influence possible aqueous chemistry, but apart from the general opinion based on models that there were higher levels of CO_2 in the early Martian atmosphere, little else has been theorized about its bulk chemistry. However, the early atmospheric composition would depend upon the geochemistry of the mantle because atmospheric gases would have originated from volcanic degassing with some unknown fractional input from impacts by water-rich asteroids and comets. In the case of comets, they likely caused impact erosion of the Martian atmosphere rather than net addition of volatiles [*Zahnle*, 1998]. Whether volcanic gases were reduced or oxidized depends on the mantle redox state and its water content. Estimates of the latter from igneous Martian meteorites [*McSween*, 1994] vary between water-rich melt inclusions [*McSween and Harvey*, 1993] and very dry bulk rock [*Wänke and Dreibus*, 1994]. If the water-rich inclusions are representative (which is certainly consistent with the evidence of Mars as a water-rich planet), then we would expect much reduced volcanic gas to have been produced on early Mars because equilibria would have shifted toward the reduced gas form. For example,

$$SO_2 + H_2O = H_2S + \tfrac{3}{2}O_2 \qquad (1)$$

is shifted toward the right for reasonable values of the mantle oxygen fugacity at higher levels of water content. Apparently, this was the case on early Earth. Thermodynamic stability analysis for sedimentary Archean minerals formed in equilibrium with the atmosphere possibly indicate that the H_2S concentration was many orders of magnitude higher in the Archean atmosphere than its trace contemporary value [*Krupp et al.*, 1994]. Consequently, if early Mars is analogous, important redox couples of gases emanating from volcanoes (Figure 1), such as CH_4/CO_2 and H_2/H_2O, would have been relatively shifted toward the reduced form compared to conditions today on Earth. In any case, active volcanism on early Mars [e.g., *McEwen et al.*, 1999] would have produced igneous minerals containing ferrous iron and some degree of reduced gases to buffer photochemically produced oxygen, so it seems likely that oxygen levels were very low. For aqueous chemistry this means that ferrous iron (Fe^{2+}) would have been freely trans-

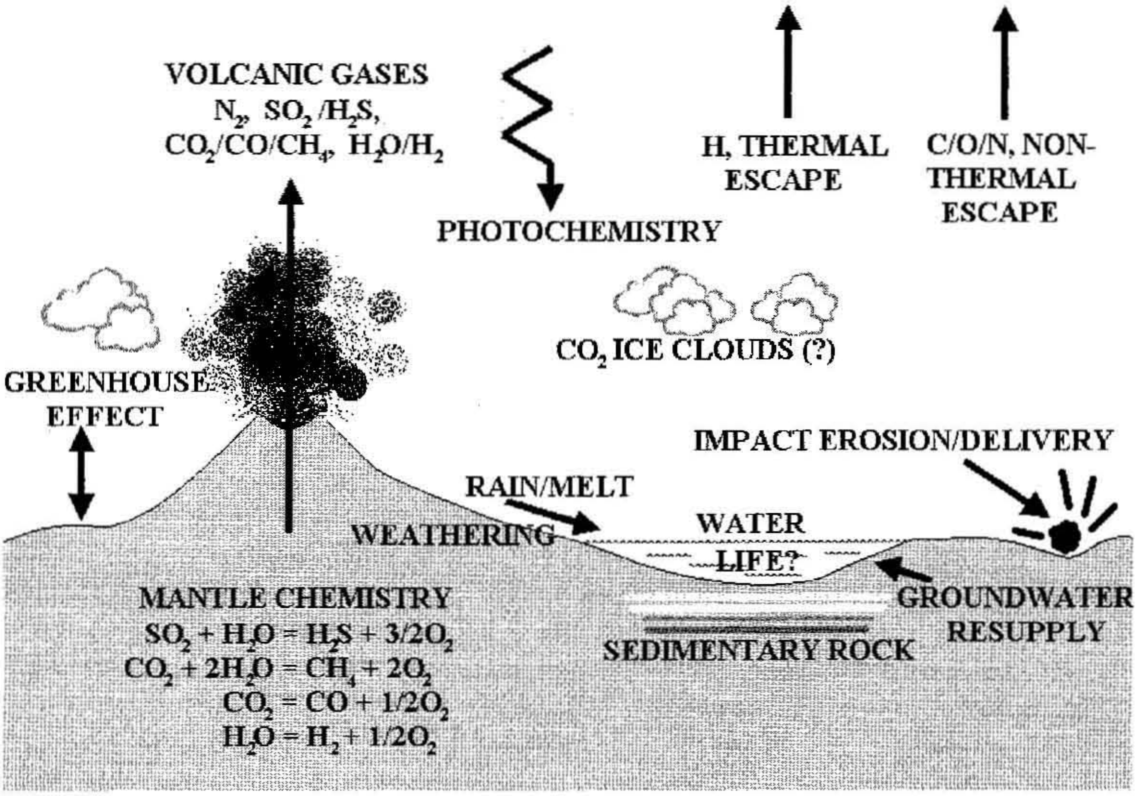

Figure 1. The geochemical environment on early Mars (shown schematically) was a complex interplay of geophysical phenomena.

ported in solution with the amount greater at the lower pH caused through equilibrium with the high levels of atmospheric CO_2. Indeed, the hypothesis that iron existed in the aqueous Fe^{2+} state on Mars earlier in its history (which implies very low oxygen levels) may be supported by the Mars Pathfinder magnetic properties experiment [*Hviid et al.*, 1997]. The possible presence of magnetic maghemite (γ-Fe_2O_3) implies Fe^{2+} leached from bedrock and subject to slow oxidation; otherwise, hematite (α-Fe_2O_3) or goethite (α-FeOOH) would have formed via fast oxidation.

2.2. Weathering on Early Mars

Rainwater, glacial melt, or near-surface groundwater on early Mars would consume atmospheric CO_2 to produce carbonic acid, which reacts with surface silicate rocks. For example, pure water in equilibrium with $P_{CO_2}=1$ bar is acidic with pH=3.9. Ferromagnesian silicates, typical of Martian igneous rocks, are dissolved by such acidic water to produce cations including Fe^{2+}, Mg^{2+}, Ca^{2+}, K^+, Na^+, and silica in roughly stoichiometric proportion to the mineral composition under low-oxygen conditions, according to laboratory experiments [*Murphy and Helgeson*, 1989; *Burns*, 1993]. This process consumes acid and raises the pH. The principal difference from conditions on contemporary Earth concerns the dissolution of iron: In highly oxygenated terrestrial surface waters, dissolution is incongruent and ferrous iron (Fe^{2+}) is almost instantly oxidized to insoluble ferric iron (Fe^{3+}) (except in the case of highly acidic hydrothermal springs). On early Mars, dissolved ions would be transported to basins and deposited as sediments. Here it assumed that these processes would be essentially inorganic. Again, this is unlike contemporary Earth, where carbonate and silica precipitation are almost entirely biologically mediated via skeletal remains of microscopic organisms like coccolithophorids and diatoms [e.g., *Holland*, 1978].

2.3. Basin Feedwater Composition

To make progress in estimating a likely sedimentary sequence, we must start with some rough approximation of the composition of early Martian water feeding a basin. Here we take the approach of estimating a baseline composition from terrestrial analogs and consider the effect of changing the composition variables later.

White et al. [1963] report various water compositions where leaching has occurred in different terrestrial igneous rock terrains. For the highland crust of early Mars, a mafic to ultramafic character is expected on the basis of the composition of Martian meteorites [*McSween*, 1994] and fundamental geochemical considerations [*Baird and Clark*, 1981]. Although approximate, for the purpose of quantitative estimation we shall assume White et al.'s average composition of ultramafic rock ground water to be roughly comparable to possible feedwater into a sedimentary basin on early Mars subject to some adjustments (Table 1). The necessary adjustments are analogous to those employed by *Garrels* [1987, 1988] for iron and silica where he estimated likely terrigenous feedwater for a sedimentary basin on early Earth.

Fe^{2+} is negligible in *White et al.*'s [1963] contemporary oxic terrestrial water but would not be so on early Mars, as mentioned previously. We set the molal concentration of Fe^{2+} relative to that of Mg^{2+} because these two cations behave very similarly during anoxic weathering of mafic rock and dissolve in proportion to their stoichiometry [e.g., *Burns*, 1993]. Igneous rocks on

Table 1. Average Groundwater Composition for Ultramafic Rocks on Earth and a Hypothetical Composition for Basin Feedwater on the Surface of Early Mars

Constituent	Molar Mass g	Average Terrestrial Ultramafic Rock Water[a]		Hypothetical Early Mars Water	
		ppm, mg L^{-1}	Molality, $\times10^{-3}$ mol kg^{-1}	ppm, mg L^{-1}	Molality, $\times10^{-3}$ mol kg^{-1}
SiO_2	60.084	40.7	0.678	60.1	1.0
Fe^{2+}	55.845	-	-	44.7	0.8
Mg^{2+}	24.305	26.3	1.08	24.3	1.0
Ca^{2+}	40.078	26.3	0.657	20.0	0.5
Na^+	22.990	18.4	0.80	18.4	0.8
K^+	39.098	2.9	0.074	2.7	0.07
Cl^-	35.453	23.0	0.65	23.0	0.65
HCO_3^-	61.017	205.2	3.364	274.0	4.49
SO_4^{2-}	96.064	17.3	0.18	17.3	0.18

Garrels [1987, 1988] used a similar approximation to estimate terriginous feedwater into a Proterozoic sedimentary iron formation basin, but in his case he was able to "tune" the composition to match observed sediments.

[a] From *White et al.* [1963].

Mars, on the basis of Martian meteorites, have Mg:Fe molar ratios ranging from the magnesian orthopyroxenes (1:0.4) of the ALH84001 meteorite [*Mittlefehldt*, 1994) to the iron-rich basalt of Shergotty (1:1.2). We adopt a nominal mean value of 1:0.8. In natural groundwaters, HCO_3^- is the main anion produced by weathering of igneous rock, and its molal concentration relative to the molal cation concentration depends on the mole ratios in dissolution reactions [*Garrels*, 1967]. For example, for ferrosilite (a pyroxene) and fayalite (an olivine) these weathering reactions are

$$FeSiO_3 + 3H_2O + 2CO_2 \rightarrow Fe^{2+} + 2HCO_3^- + Si(OH)_4 \quad (2)$$

$$Fe_2SiO_4 + 4H_2O + 4CO_2 \rightarrow 2Fe^{2+} + 4HCO_3^- + Si(OH)_4 \quad (3)$$

respectively. Consequently, to maintain electroneutrality in the solution, Fe^{2+} must be balanced with bicarbonate in a 1:2 ratio in dissolution.

Hydrolyzed silica is a product of ultramafic rock dissolution, as shown in (2) and (3). On contemporary Earth, dissolved silica is voraciously consumed by diatoms, radiolaria, and other microorganisms with siliceous shells, which generally leaves natural waters far below silica saturation. However, in the absence of such relatively complex organisms, which seems virtually certain for early Mars, silica would be closer to saturation. For amorphous silica, saturation occurs at ~ 115 ppm at 25°C. For our "near-saturated" baseline early Mars water, we arbitrarily set the initial concentration of silica to 60 ppm, that is, requiring about a halving of the water before precipitation. This is the value expected in Precambrian seawater prior to the evolution of silica-secreting organisms [*Siever*, 1992] and is at the upper limit of weathering fluids found on contemporary Earth, which have silica concentrations ranging from 2 to 60 ppm, depending on rock type [*Garrels and MacKenzie*, 1971, p.160].

The concentration and speciation of sulfur in our early Mars basin water is an issue of uncertainty. On present-day Mars the quantity of sulfur in the soil at the surface is high, about two orders of magnitude greater than average terrestrial soil, and appears to be present as sulfate [*Toulmin et al.*, 1977; *Banin et al.*, 1992]. For early Mars this is perhaps less relevant: The sulfur is widely postulated to have originated from volcanic gases (H_2S/SO_2) over the course of geological time [*Clark*, 1979; *Settle*, 1979], perhaps a large component in the last 10^9 years [*Banin et al.*, 1997]. On Earth, volcanic sulfur ends up as a major anion, SO_4^{2-}, in the oceans, second only to chloride, whereas on Mars this sulfur has had nowhere else to go but the soil. Of course, sulfate may have gone through aqueous speciation because of episodes of surface water. On early Mars an idealized CO_2-weathered mafic rock would produce little sulfur-bearing species, arising only from oxidation of possible minor iron sulfides (which is difficult because of the highly insoluble nature of iron sulfides), possible fluid inclusions, and other small sources. Sulfur would therefore enter into lakes on early Mars either through leaching of sulfates in surface soil or by direct dissolution of volcanic gases (H_2S/SO_2). The influence of sulfur is further discussed in section 4.3. For our baseline feedwater we assume a weakly reducing or weakly oxidizing environment consistent with the presence of both Fe^{2+} and sulfate. Sulfide would immediately precipitate highly insoluble iron sulfides although coprecipitation of iron carbonate and sulfide is also possible. For our baseline feedwater, sulfate is assumed to be at a similar level to that in fluid derived from weathered terrestrial ultramafics (Table 1).

3. Evaporative Sedimentation

3.1. General Considerations

When natural waters evaporate, the average ion concentration in solution increases and leads to the precipitation of salts; after mineral precipitation the rate of the concentration of the species concerned changes. Certain species can increase, decrease, or fluctuate as a result of the evaporation process. These solute fractionation processes are important for Mars because they would result in sedimentary layers and in potentially long-lived brines dominated by just a few chemical species. Besides evaporation, mineral precipitation can also occur through a variety of other mechanisms, for example, pH gradients from mixing acidic streamwater with a more alkaline standing body of water such as a lake or sea, temperature changes including freezing effects, and redox changes. Here we consider an evaporative thermodynamic model to investigate the chemical fate of water in a sedimentary basin on early Mars. The model calculates the endogenic precipitates in a water column (i.e., those directly precipitated) arising from sequential evaporation. This allows us to predict the mineral sequence that may result from evaporative concentration as well as the composition of the remaining brine. Since the model represents thermodynamic equilibrium states, it also allows us to make some qualitative assessment of other possibilities for solute fractionation listed above, such as the effect of changing the solution pH.

3.2. Model Description

The evaporation model uses the general methodology originally conceived by *Garrels and MacKenzie* [1967] for modeling Sierra Nevada spring water and relating the composition to the host bedrock. This methodology also forms the basis of evaporation models for terrestrial lacustrine environments by *Hardie and Eugster* [1970], *Eugster and Jones* [1970], *Al-Droubi et al.* [1980], *Garrels* [1987], *Herczeg and Lyons* [1991], and *Rajan et al.* [1996].

Possible variables are temperature T, total pressure P(total), P_{CO_2}, and the molalities m (i.e., mol kg^{-1})

and activity coefficients γ of the dissolved species. The species activity a_i is a dimensionless effective concentration that is related to molality by $a_i = \gamma_i m_i$. Some assumptions are made for practicality: (1) The water is assumed to evaporate isothermally in equilibrium with the atmosphere; $T = 25°\mathrm{C}$ is chosen because this is above the 0°C limit required for liquid water (or a low ionic strength solution) and is a standard temperature for which thermodynamic data are well characterized; however, we apply this with caution, noting that temperatures on Mars may have been closer to 0°C; (2) precipitated solids are assumed to be in equilibrium with the solution; and (3) thermodynamic data are used where P(total) is assumed as 1 atm standard because, unless the total pressure was higher by two or three magnitudes, the total pressure effect on the thermodynamics is very small [*Garrels and Christ*, 1965] and vastly outweighed by our uncertainties about the initial fluid composition. Thus total pressure effects are not considered to be relevant.

Since the solution must remain electroneutral, positive charges are balanced by negative. Arranging a charge balance equation such that pH-dependent species are on the right, we get

$$\begin{aligned} 2m_{\mathrm{Mg}^{2+}} + 2m_{\mathrm{Ca}^{2+}} + 2m_{\mathrm{Fe}^{2+}} + m_{\mathrm{Na}^+} + m_{\mathrm{K}^+} \\ -m_{\mathrm{Cl}^-} - 2m_{\mathrm{SO}_4^{2-}} \\ = m_{\mathrm{OH}^-} - m_{\mathrm{H}^+} + 2m_{\mathrm{CO}_3^{2-}} + m_{\mathrm{HCO}_3^-} \end{aligned} \tag{4}$$

where m_i is the molal concentration of dissolved species i. The molalities of the species that depend on the activity of the hydrogen ion, a_{H^+}, that is, that depend on the pH (where pH = $-\log_{10}(a_{\mathrm{H}^+})$, by definition), are given by *Stumm and Morgan* [1996, chap. 4]:

$$m_{\mathrm{OH}^-} = \frac{K_{\mathrm{H_2O}}}{(\gamma_{\mathrm{OH}^-})(a_{\mathrm{H}^+})} \tag{5}$$

$$m_{\mathrm{H}^+} = \frac{a_{\mathrm{H}^+}}{\gamma_{\mathrm{H}^+}} \tag{6}$$

$$m_{\mathrm{CO}_3^{2-}} = \frac{P_{\mathrm{CO_2}} K_{\mathrm{H}} K_1 K_2}{(\gamma_{\mathrm{CO}_3^{2-}})(a_{\mathrm{H}^+})^2} \tag{7}$$

$$m_{\mathrm{HCO}_3^-} = \frac{P_{\mathrm{CO_2}} K_{\mathrm{H}} K_1}{(\gamma_{\mathrm{CO}_3^{2-}})(a_{\mathrm{H}^+})} \tag{8}$$

Here $K_{\mathrm{H_2O}}$ is the dissociation equilibrium constant for water, K_{H} is Henry's Law constant for dissolved $\mathrm{CO_2}$, and K_1 and K_2 are the first and second dissociation constants of carbonic acid, respectively (Table 2).

From an initial estimate of the ionic strength, activity coefficients γ_i, and hence molaltites m_i, are calculated to allow the charge balance equation to be solved for pH. Activity coefficients are calculated from the Davies equation,

$$\log(\gamma_i) = -Az_i^2 \left(\frac{I^{0.5}}{1 + I^{0.5}} - 0.2I \right) \tag{9}$$

where z_i is the charge on each species, I is the ionic strength ($I = 0.5 \sum m_i z_i^2$) of the solution, and A is a constant (≈ 0.5 at 25°C) [*Stumm and Morgan*, 1996]. For the initial solution with no precipitates, the pH can be found easily by substituting the above expressions for m_{H^+}, m_{OH^-}, $m_{\mathrm{CO}_3^{2-}}$, and $m_{\mathrm{HCO}_3^-}$ into (4) to give a simple cubic in a_{H}. For the fluid with precipitates, iterative substitution of pH is repeated to calculate the m_i

Table 2. Equilibrium Constants Assumed in the Evaporation Model

Name	Equilibrium	$-\log K$	Symbol	Source
	Basic Components			
Water	$\mathrm{H_2O = H^+ + OH^-}$	14.000	K_w	1
Carbon dioxide	$\mathrm{CO_2(g) = CO_2(aq)}$	1.468	K_{H}	1
Bicarbonate	$\mathrm{CO_2(aq) + H_2O = H^+ + HCO_3^-}$	6.352	K_1	1
Carbonate	$\mathrm{HCO_3^- = H^+ + CO_3^{2-}}$	10.329	K_2	1
Siderite	$\mathrm{FeCO_3(s) = Fe^{2+} + CO_3^{2-}}$	10.45	K_{sid}	1
Calcite	$\mathrm{CaCO_3(s) = Ca^{2+} + CO_3^{2-}}$	8.47	K_{cal}	1
Hydromagnesite	$\mathrm{Mg_4(CO)_3(OH)_2(s) =}$ $\mathrm{4Mg^{2+} + 3CO_3^{2-} + 2OH^-}$	36.47	K_{hmag}	2
Amorphous silica	$\mathrm{Si(OH)_4(s) = SiO_2 + 2H_2O}$	2.70	K_{amsil}	1
Gypsum	$\mathrm{CaSO_4 \cdot 2H_2O(s) =}$ $\mathrm{Ca^{2+} + SO_4^{-2} + 2H_2O}$	4.58	K_{gyp}	1
	Complexes			
	$\mathrm{CaCO_3^0 = Ca^{2+} + CO_3^{2-}}$	3.22	$K_{\mathrm{CaCO_3^0}}$	1
	$\mathrm{FeCO_3^0 = Fe^{2+} + CO_3^{2-}}$	4.38	$K_{\mathrm{FeCO_3^0}}$	1
	$\mathrm{MgCO_3^0 = Mg^{2+} + CO_3^{2-}}$	2.98	$K_{\mathrm{MgCO_3^0}}$	1
	$\mathrm{CaSO_4^0 = Ca^{2+} + SO_4^{2-}}$	2.30	$K_{\mathrm{CaSO_4^0}}$	1

Values at 25°C. Sources: 1, *Nordstrom et al.* [1990]; 2, *Morse and MacKenzie* [1990].

of pH-dependent species (e.g., OH^-), solve the charge balance equation again for pH, and hence recalculate ionic strength and activity coefficients until convergence is achieved.

In solution, oppositely charged ions attract each other and can form soluble ion pairs, for example, $CaSO_4^0(aq)$. So next, the proportion of each species that exists as a free ion is computed by calculating how much of each species is paired using an iterative scheme similar to that originally developed by *Garrels and Thompson* [1962] for ion pairing to model seawater composition. *Adams* [1971] also uses a similar methodology. Essentially, in addition to charge balance, we also have mass balance equations for each species subject to complexing (i.e., the formation of polyatomic soluble entities). For example, for carbonate we have

$$m_{CO_3^{2-}} = m_{CO_3^{2-},\text{free}} + m_{CaCO_3^0} + m_{FeCO_3^0} + m_{MgCO_3^0} + \cdots \quad (10)$$

where $CaCO_3^0$, etc., are the soluble carbonate ion pairs considered in solution. The concentrations of the ion pairs are given by their respective equilibrium relations, such as

$$K_{CaCO_3^0} = \frac{(\gamma_{Ca^{2+}})m_{Ca^{2+}}(\gamma_{CO_3^{2-}})m_{CO_3^{2-}}}{(\gamma_{CaCO_3^0})m_{CaCO_3^0}} \quad (11)$$

where we assume unity for activity coefficients of uncharged species (i.e., $\gamma_{CaCO_3^0} = 1$). For numerical simplicity, we consider only those neutral ion pairs listed in Table 2. Other ion pairs also exist, such as $NaCO_3^-$ and $FeCl^+$, but an examination of equilibrium constants [*Nordstrom et al.*, 1990] shows that the divalent cation neutral pairs listed are the dominant ion pairs affecting precipitation for the typical solutions we consider. Because a proportion of the ions get complexed, this leaves a free ion concentration somewhat below the total ion concentration (e.g., $m_{CO_3^{2-},\text{free}} < m_{CO_3^{2-}}$), and this demands recalculation of the ionic strength and activity coefficients. Briefly, the method is to calculate ion pair concentrations from the equilibria (initially assuming free ion concentrations equal to total concentrations), revise free ion concentrations on the basis of mass balance equations for total ions, recalculate ionic strength and activity coefficients, and iterate the whole procedure until convergence on ionic strength is achieved (see *Adams* [1971] for details). After this, pH is recalculated (because activity coefficients have changed), and the whole procedure is repeated iteratively until convergence on pH is achieved. The effect of ion pairing is typically to delay the onset of precipitation products containing the complexed ions compared to the case with no complexes. Furthermore, through complexation, even ions not contained in a precipitate can affect a precipitate's formation. For example, Fe^{2+} and Mg^{2+} can suppress calcite precipitation through the effect of Fe^{2+} and Mg^{2+} pairing with CO_3^{2-}, which reduces the level of free CO_3^{2-}.

Given the concentration of the free ions, mineral precipitation is determined by checking for ion activity products. If ions precipitate, the ion activity product (IAP) of the free ions involved remains constant, equal to the solubility product, which can result in the concentration of a cation becoming pH-dependent. For example, if calcite precipitates, the Ca^{2+} concentration is determined by the IAP and depends on the pH through the pH-dependent concentration of CO_3^{2-}. The equation

$$CaCO_3(s) = Ca^{2+} + CO_3^{2-} \quad (12)$$

has equilibrium constant, the solubility product, given by

$$K_{cal} = a_{Ca^{2+}} a_{CO_3^{2-}} \quad (13)$$

where $a_{Ca^{2+}}$ and $a_{CO_3^{2-}}$ are the activities of calcium and carbonate. The latter depends on pH through (7) as well as equilibria for ion pairing. For silica the dissolved amount is simply allowed to increase until saturation of silica is reached.

The charge balance equation is recast such that the pH dependence of precipitating ions is incorporated on the right of (4) in subsequent calculations. Thus, with this methodology we obtain a final solution state for a particular degree of evaporation. A more detailed description of this general methodology is given by *Rajan et al.* [1996].

4. Modeled Evolution of the Basin Water

4.1. Baseline Results

Figure 2 shows the evolution of the baseline basin feedwater from a relatively dilute fluid, concentrated 1000-fold to a brine with an ionic strength I of 1.3 (compared to terrestrial seawater with $I = 0.7$). The change in concentration of the ions can be followed on the left-hand ordinate axis in Figure 2, while the corresponding pH for each concentration factor maps to the right-hand axis. The initial assumed concentration of bicarbonate in Table 1 is slightly decreased from 4.49 to 4.47 $\times 10^{-3}$ mol kg^{-1} by enforcing equilibrium with a specific atmospheric P_{CO_2}. This can be physically interpreted as allowing the fluid to come to equilibrium with the atmosphere by losing CO_2 with a consequent small increase in the pH.

Silica is precipitated first in the sequence at a concentration of about 2× since it is initially close to saturation because aqueously CO_2-weathered (ultra)mafic rock water is high in dissolved silica (section 2.3). The next precipitate is siderite ($FeCO_3$) at a concentration of about 4×. This is always the first carbonate to precipitate from solution because it is the most insoluble of the major common carbonates. Further evaporation of basin fluid leads to the precipitation of other carbonates: calcite and hydromagnesite. The latter tends to form rather than the pure carbonate phase because of

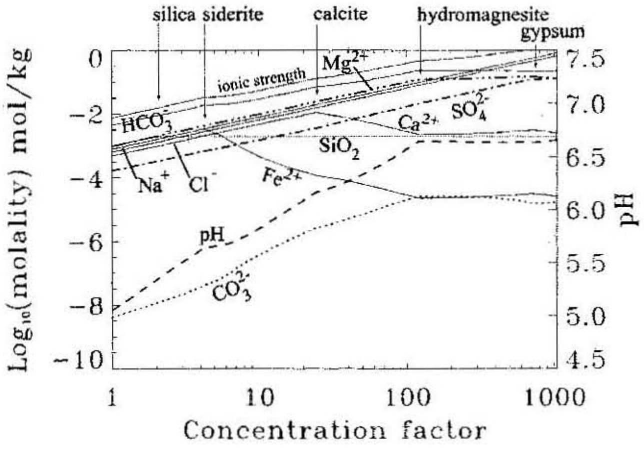

Figure 2. The ionic evolution of basin water as a function of concentration factor at $P_{CO_2} = 2$ bar. The ion concentrations are mapped to the left-hand ordinate axis; the pH is mapped to the right-hand ordinate axis. Arrows indicate the onset of precipitation events for various minerals at particular concentration levels.

the adherence of water molecules to the Mg^{2+} ion in precipitation. More evaporation leads to precipitation of gypsum, by which time the solution is somewhat more concentrated than average terrestrial seawater. Thus the overall sedimentary sequence of early precipitates for this fluid is silica, siderite, calcite, magnesite, then gypsum. At the end of the 1000-fold concentration a concentrated brine remains, dominated by Na-Mg-Cl-SO_4-CO_3 ions.

However, the early precipitates are important. In conditions of moderate summertime evaporation followed by winter/spring recharge of the basin water, following Figure 2, we would expect annual precipitation events leading to varves of siderite and chert. Such a sequence, siderite-chert, might be considered analogous to some microbanded sediments found in some Precambrian banded iron formations (BIFs). However, a direct analogy is probably misleading: Modern majority opinion contends that BIF siderite-chert sediment formed at the chemocline of either a deep marine environment or a continental shelf where ferrous iron and high CO_2 were maintained by ocean floor hydrothermal activity combined with oxidation of organic matter. This marine, hydrothermal hypothesis is largely based on the rare Earth element (REE) hydrothermal signatures in the sediments [*Beukes and Klein*, 1992] although the exact mechanisms of sedimentation and banding are still controversial.

Although not explicitly modeled, for the carbonate sequence we expect siderite to contain substantial Mg^{2+} and Ca^{2+} ions ($Fe_aMg_bCa_cCO_3$, where $a + b + c = 1$ and $a > b > c$) and the calcite to contain substantial Mg^{2+} ($Ca_xMg_{1-x}CO_3$, where $x < 1$). These occur rather than the pure components because of the innate tendency of Fe/Ca/Mg carbonates to form solid solutions. The degree of cation substitution depends upon the activity of the substituting cation in solution [*Woods and Garrels*, 1992]. Thus the hydromagnesite would be relatively pure because by the time it precipitates, the concentrations of Ca^{2+} and Fe^{2+} are so low (Figure 2) as to preclude significant cation substitution. Minor rhodochrosite ($MnCO_3$) is also an expected component although not explicitly included in the model.

For the carbonates the concentrations of the soluble neutral ion pairs are key factors in determining the stages at which the carbonates actually get deposited. Figure 3 shows the evolution of the soluble ion pairs corresponding to Figure 2. It can be seen that even in dilute solution, Fe^{2+} is a highly effective complexing agent for the CO_3^{2-} ion and considerably reduces the amount of free CO_3^{2-} in solution. Up to about 95% of the CO_3^{2-} gets tied up in the $FeCO_3^0$(aq) ion pair. This prevents the precipitation of other carbonates. On the basis of the total concentrations of Fe^{2+} and CO_3^{2-}, that is, the sum of free and bound ions that one would normally measure in the field, siderite is considerably supersaturated by the time a precipitate is formed. Calcite is also supersaturated by a factor of about 8 by the time it precipitates, on the basis of total ion concentrations, which compares fairly with the observation that noticeable calcite precipitation occurs only for supersaturations by a factor of ~ 10 in terrestrial waters [e.g. *Lui et al.*, 1995]. At a more concentrated stage in the model the calcium sulfate ion pair become appreciable (> 10% of total sulfate gets bound up in it).

Let us now consider the effect of various parameters, notably the high CO_2, and aqueous species in the solution.

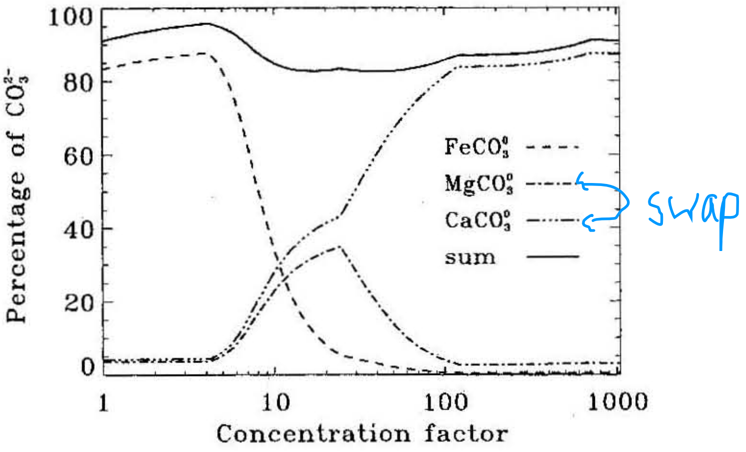

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Figure 3. Changes in the concentration of the major carbonate soluble ion pairs for the fluid evolution shown in Figure 2. Dashed lines show the concentration of the ion pair species as a percentage of the total carbonate present in solution. The solid line shows the percentage sum of the ion pair concentrations. The solid line shows that the amount of unbound, free CO_3^{2-} is always < 20% of the total CO_3^{2-} in solution.

4.2. Carbonates and P_{CO_2}

Siderite sediment may act as an indicator of high P_{CO_2} on early Mars because its formation is favored only at relatively high levels of P_{CO_2}, as we calculate below. Otherwise, alternative iron minerals such as silicates, hydroxides, or sulfides form, depending on the exact pH, oxidation potential, and composition of the solution. On early Earth this mineralogical approach seems to indicate a lack of high CO_2 needed to offset the effect of the faint young sun through greenhouse warming, perhaps implicating (biogenic?) CH_4 as the likely greenhouse gas. Indeed, *Mel'nik* [1982] suggested atmospheric $P_{CO_2} < 0.15$ bar on Archean Earth using this argument given the observational presence of silicates and lack of exclusive siderite facies in oldest Archean BIF sediments. Later, *Rye et al.* [1995] argued that the lack of siderite in paleosols (i.e., ancient terrestrial weathering profiles) would constrain the Earth's atmosphere to a $P_{CO_2} < 40$ mbar at about 2.1 Gyr ago. In contrast, on Mars one suspects that the presence of siderite sediments would indicate a past thick CO_2 atmosphere. Let us consider the necessary level of CO_2 in more detail.

In a low-oxygen environment in the presence of dissolved silica, if a Fe^{2+} mineral precipitates, it will be $FeCO_3$ if P_{CO_2} is high and one or more iron silicates if P_{CO_2} is low. Thus a possible indicator for P_{CO_2} in early Mars sediments is whether siderite or iron silicate gets deposited from a likely solution containing dissolved amorphous silica. Greenalite ($Fe_3Si_2O_5(OH)_4$), a black to dark green finely grained sediment, is the simplest of the possible ferrous silicates and a stable phase in sediments. The relative stability of siderite versus greenalite is governed by the equilibrium:

$$3FeCO_3 + 2SiO_2 + 2H_2O = Fe_3Si_2O_5(OH)_4 + 3CO_2 \qquad (14)$$

A thorough and self-consistent source of Gibb's free energy data on iron minerals is that compiled by *Mel'nik* [1982]. We use the values for amorphous precipitates since these apply directly to the real sedimentation process rather than values for crystalline solids (Table 3). Applying these values to (14), at 25°C, amorphous greenalite will be precipitated below a threshold of $P_{CO_2} \approx 0.1$ bar, rather than siderite. Two further relations define the deposition of siderite and greenalite,

$$Fe^{2+} + CO_2 + H_2O = FeCO_3 + 2H^+ \qquad (15)$$

$$\begin{aligned} &3Fe^{2+} + 2SiO_2 + 5H_2O \\ &= Fe_3Si_2O_5(OH)_4 + 6H^+ \end{aligned} \qquad (16)$$

respectively, and these yield

$$\mathrm{pH} + \tfrac{1}{2}\log a_{Fe^{2+}} = 4.6 - \log(\mathrm{pCO_2}) \qquad (17)$$

$$\mathrm{pH} + \tfrac{1}{2}\log a_{Fe^{2+}} = 5.2 \qquad (18)$$

for amorphous precipitates. These equations define the boundaries in Figure 4, a stability diagram for siderite and greenalite deposition in association with dissolved silica where the activity of aqueous divalent iron ($a_{Fe^{2+}}$) is a free parameter. Hence we would expect greenalite to be deposited as the Fe^{2+} comes out of solution when the P_{CO_2} level is lower than roughly 0.1 bar (uncertainties on the Gibb's free energy data do not allow us to be more exact than this). If the P_{CO_2} level is higher, siderite is favored. Consequently, if atmospheric P_{CO_2} was as high as climate models require for early Mars, we should expect there to be siderite facies at depth in sedimentary basins and not iron silicates.

Endogenic siderite does not form in contemporary lacrustine environments on Earth because in the terrestrial atmosphere P_{CO_2} is too low for siderite formation and P_{O_2} is too high for sufficient dissolved fer-

Table 3. Gibb's Free Energy Values Under Standard Conditions, $G_{f,298}$, Used in Calculations

Formula	Name	$G_{f,298}$ kcal mol^{-1}	Source
$FeCO_3$	siderite (crystal)	-162.0	1
		-162.4	2
$FeCO_3$	siderite (precipitate)	-160.0	1
$Fe_3Si_2O_5(OH)_4$	greenalite (crystal)	-717.2	1
$Fe_3Si_2O_5(OH)_4$	greenalite (precipitate)	-711.5	1
SiO_2	silica (amorphous gel)	-202.89	1
		-203.33	3
Fe^{2+}	aqueous ferrous ion	-21.54	1
		-18.85	4
CO_2	carbon dioxide gas	-94.26	4
H_2O	liquid water	-56.69	1

In general, the self-consistent data set of *Mel'nik* [1982] is used except where not available. In the literature, there are often discrepancies in $G_{f,298}$ values, which can lead to significant uncertainties in equilibrium calculations, so comparison data are also shown. Sources: 1, *Mel'nik* [1982]; 2, *Helgeson et al.* [1978]; 3, *Stumm and Morgan* [1996]; 4, *Lide* [1997].

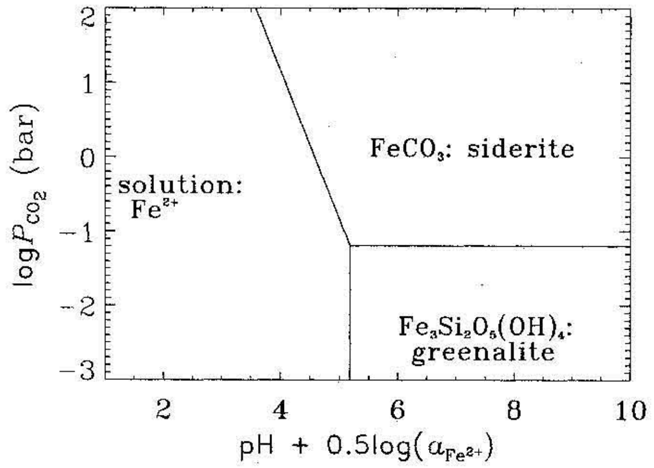

Figure 4. The stability of siderite and greenalite as a function of P_{CO_2}. As water in a closed basin evolves to more alkaline conditions, siderite will be deposited at high P_{CO_2} levels and greenalite will be deposited at low P_{CO_2} levels.

rous iron in the first place. Consequently, calcite is the ubiquitous carbonate form. However, there are two exceptions: Lake Nyos and Lake Monoun in Cameroon. These freshwater lakes, occupying maars, are fed with CO_2 by cold volcanic vents, and organic detritus keeps the lake floor sufficiently reduced for a significant hypolimnion concentration of Fe^{2+}. As a consequence, siderite is the only stable carbonate phase [*Bernard and Symonds*, 1989]. In this case the sediments formed are not in equilibrium with the atmosphere at all. Thus, while high CO_2 is required for siderite sediments, one must also bear in mind the depositional environment of sediments before ascribing bulk properties to the atmosphere on the basis of certain occurrences. If the Earth's atmosphere were indeed low in oxygen and P_{CO_2} sufficiently high, siderite would be common, replacing calcite as the predominant carbonate on a global basis. We hypothesize that this may have been the situation on early Mars.

P_{CO_2} can also affect the stage at which sedimentation takes place in Figure 2. The overall equation governing carbonate deposition (with divalent cation X) may be written as follows:

$$X^{2+} + 2HCO_3^- = XCO_3 + CO_2 + H_2O \qquad (19)$$

For a fixed initial fluid composition any increase in P_{CO_2} will shift the equilibrium to the left by Le Chatelier's principle and delay the onset of carbonate deposition. However, this simplistic interpretation does not take into account the fact that larger P_{CO_2} will increase the weathering rate, leading to greater cation concentrations, so that ultimately dynamic equilibrium is maintained between weathering processes and carbonate deposition to remove CO_2. This is a key point. However, such a simple situation exemplified by (19) may apply to ice-covered lakes where CO_2 becomes trapped and supersaturated or to sudden, rapidly evaporating floods of groundwater on Mars accompanied by temporary increases in P_{CO_2} [*Gulick et al.*, 1997]. An interesting consideration is that in this scenario, if P_{CO_2} is sufficiently high and the initial fluid has a large concentration of SO_4^{2-}, then gypsum saturation could be reached prior to calcite (cf. *Herzeg and Lyons* [1991] for a similar argument applied to terrestrial lakes). For example, consider the initial fluid in Table 1 but adjusted with $m_{Ca^{2+}}$ reduced to 0.3 mmol kg^{-1} and $m_{SO_4} > 2m_{Ca^{2+}} = 0.7$ mmol kg^{-1}, say, with the overall charge balance maintained by altering the concentration of nonprecipitating Cl^- and Na^+ to 0.3 and 1.1 mmol kg^{-1}, respectively. For this initial composition, Figure 5 shows the resulting saturation index (SI) of gypsum and calcite as a function of concentration factor for two different P_{CO_2} levels, where the SI, defined as IAP/(solubility product), is unity if saturation is reached. At $P_{CO_2} = 1$ bar the SI of gypsum is < 0.5 by the time calcite is precipitated. With increasing P_{CO_2}, calcite precipitation is delayed, and the gypsum SI becomes progressively higher at the stage of calcite precipitation until a threshold P_{CO_2} is reached. For $P_{CO_2} > 3.5$ bar, gypsum will be precipitated before calcite and will reduce the level of Ca^{2+} so that calcite deposition is reduced. This changes the whole precipitation sequence to silica-siderite-gypsum-hydromagnesite/calcite. Thus calcium would be deposited primarily in the form of gypsum beds and not as calcite on the Martian surface in this hypothetical case.

4.3. Influence of Sulfur and Redox State

As mentioned in section 2, sulfur is a minor species one expects from weathering of mafic rock, its appearance resulting only from minor sources in the host rock.

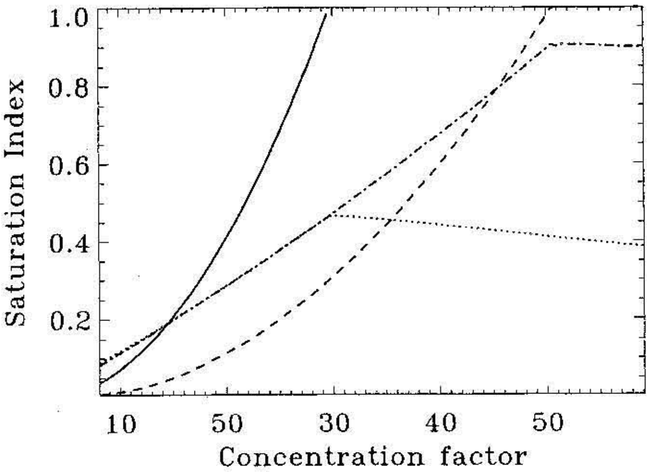

Figure 5. Evolution of the saturation index (SI) of gypsum and calcite for two different P_{CO_2} levels. At P_{CO_2}=1 bar, the solid line is the SI of calcite, and the dotted line is the SI of gypsum. At P_{CO_2}=3 bar, the dashed line is the SI of calcite and the dashed-dot line is the SI of gypsum.

However, what if there was significant subaerial input from volcanic gases (H_2S/SO_2) into lakes on early Mars?

The speciation and effect of sulfur in solution depend in a complicated manner on the redox state and pH. Also, sulfur affects the stability of iron minerals. Figure 6 shows the calculated equilibrium stability of iron minerals as a function of the total dissolved sulfur and electron activity (pe $= -\log a_{e^-}$) for a weakly acidic pH. If P_{CO_2} is increased, the effect is to enlarge the stability field of siderite, which is found to occupy two environmental regions: a highly reducing, low-sulfur zone and a weakly reducing/oxidizing zone. In this latter zone, near pe (or Eh) = 0, sulfate ions are stable. Indeed, if the pH is decreased, pH < 4, the latter siderite zone shifts upward on the diagram and occupies a region where pe > 0. Thus siderite becomes more stable in oxidizing environments. If the pH is increased, siderite will no longer be a stable phase and will be replaced with iron silicate. If the pH, solution composition, and P_{CO_2} level are constant, a change of redox potential is the only mechanism that can lead to mineral deposition. For high oxidation potential, iron will form a brown, gelatinous precipitate of $Fe(OH)_3$. This iron hydroxide is unstable and irreversibly converts in time to a stable oxide like magnetite or hematite, depending on the diagenetic environment. Figure 6 also indicates that we expect to find iron oxide sediments in association with siderite but not with iron sulfide. In general, the effect of a greater concentration of sulfur is to somewhat decrease the stability of siderite as a possible phase and could lead to iron oxide or iron sulfide sediments, depending on the precise combination of redox potential, pH, and P_{CO_2}.

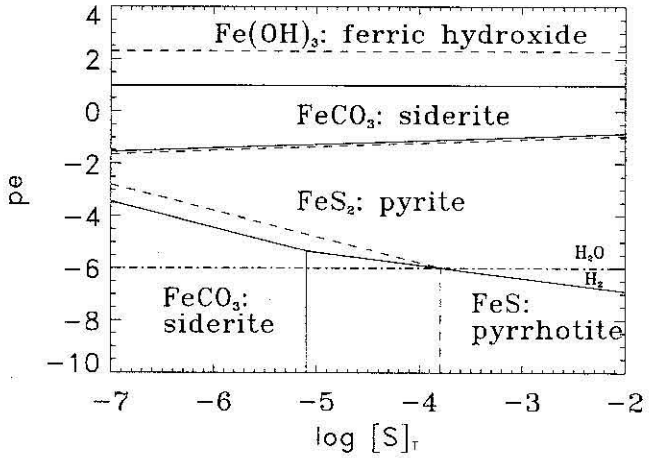

Figure 6. The stability of iron minerals as a function of electron activity (redox) and total dissolved sulfur (pH=5.5). Two cases are shown: (solid line) P_{CO_2} = 0.1 bar and (dashed line) P_{CO_2} = 2 bar.

5. Sedimentary Layering and Hidden Carbonates

Eventually, as the climate became unfavorable on Mars, a sedimentary basin would no longer be recharged with water and the lake would either totally evaporate or diminish under ice cover (because aeolian ablation of the ice would remove water). In the former case, after the initial sequence of carbonate sediments, further evaporation of the brine results in the deposition of highly soluble salts. Which salts get deposited depends mainly on the initial composition of the brine in the basin. In principle, evaporite salts therefore record the major ions of the ancient water composition. Table 4 lists the expected evaporite minerals from terrestrial evaporites based on the initial brine. From the calculations presented earlier we expect a Martian brine to be similar to the terrestrial "nonmarine" type but with Mg^{2+} as an additional major component. The extent to which the expected highly soluble evaporite salts apply to Mars is moderated by our knowledge of the different atmospheric composition which will affect the precipitation sequence. For example, trona (Na_2CO_3-$NaHCO_3 \cdot 2H_2O$) is a common sodium carbonate precipitate from saline alkaline lakes on Earth (e.g., Lake Magadi in Kenya, where it accumulates on the lake bed at a rate of 0.3 cm yr^{-1} [*Eugster*, 1970]) or, alternatively, natron ($Na_2CO_3 \cdot 10H_2O$) may form at lower temperatures (< 20°C). However, on Mars we would expect nahcolite ($NaHCO_3$) to be the predominant sodium carbonate in evaporites because it tends to form at higher P_{CO_2} on the basis of the equilibria:

$$\begin{aligned} &2NaHCO_3 + H_2O \\ &\rightleftharpoons Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O + CO_2 \end{aligned} \qquad (20)$$

$$2NaHCO_3 + 9H_2O \rightleftharpoons Na_2CO_3 \cdot 10H_2O + CO_2 \qquad (21)$$

However, to shift these equilibria to the left merely requires a minimum P_{CO_2} level of ~ 2–10 mbar for a temperature range of 0° to 40°C [*Monnin and Schott*, 1984]. Thus, while useful for studies of terrestrial paleoatmospheres (as originally suggested by *Eugster* [1966]), nahcolite would not be an effective tracer of the early Martian atmosphere given the present P_{CO_2} on Mars of ~ 6 mbar.

Siderite-calcite-magnesite facies would tend to be deposited early in the sequence and hidden beneath gypsum and halite layers. However, in a lake open to the atmosphere (i.e., unfrozen) they would be closest to the surface near the edges of a concave basin since the highly soluble salts pool at the center before finally precipitating from solution. A schematic diagram (Figure 7) shows a possible morphology. The sedimentary sequence shown represents the center of the basin and, although only salts are depicted, in reality there are likely to be clastic sediments also (such as clays). Surficial carbonate deposits were likely exposed to sulfurous

Table 4. Typical Minerals Evolved From the Final Stages of Evaporation of Brines in the Production of Terrestrial Evaporites After Deposition of Alkaline Earth Carbonates

Brine Type	Characteristic Evaporite Minerals	Key Type Indicators
"Nonmarine" $Na\text{-}K\text{-}CO_3\text{-}Cl\text{-}SO_4$	halite, Na carbonates/sulfates	sodium carbonates
"Marine" or marine/nonmarine mixtures $Na\text{-}K\text{-}Mg\text{-}Cl\text{–}SO_4$	gypsum, halite, Na/Mg sulfates, Mg/K chlorides	Mg/Na sulfates
Hydrothermal Na-K-Mg-Ca-Cl	gypsum, anhydrite, halite, Mg/K/Ca chlorides	KCl ± $CaCl_2$ with absence of Na_2SO_4 and $MgSO_4$; rare Earth elements

After *Hardie* [1991].

outpourings from volcanic activity later in Martian history (which may have been responsible for the high sulfur content of Martian soil). This would have destroyed carbonates according to

$$(Fe/Mg/Ca)CO_3 + SO_3 = (Fe/Mg/Ca)SO_4 + CO_2 \qquad (22)$$

where the SO_3 originates from photo-oxidation of volcanic SO_2 or H_2S [*Settle*, 1979]. This reaction has been demonstrated in the laboratory [*Clark et al.*, 1979]. In addition, it has been proposed by *Mukhin et al.* [1996] that surface carbonates on Mars are directly photodecomposed by shortwave ultraviolet; however, their experiments were conducted in high vacuum rather than CO_2, which makes their conclusion uncertain because the presence of CO_2 would obviously act chemically to oppose any decomposition. A further consideration for siderite, in particular, is photochemical oxidation. On Mars today near the surface one expects a heavily oxidized layer covered with the ubiquitous wind-blown

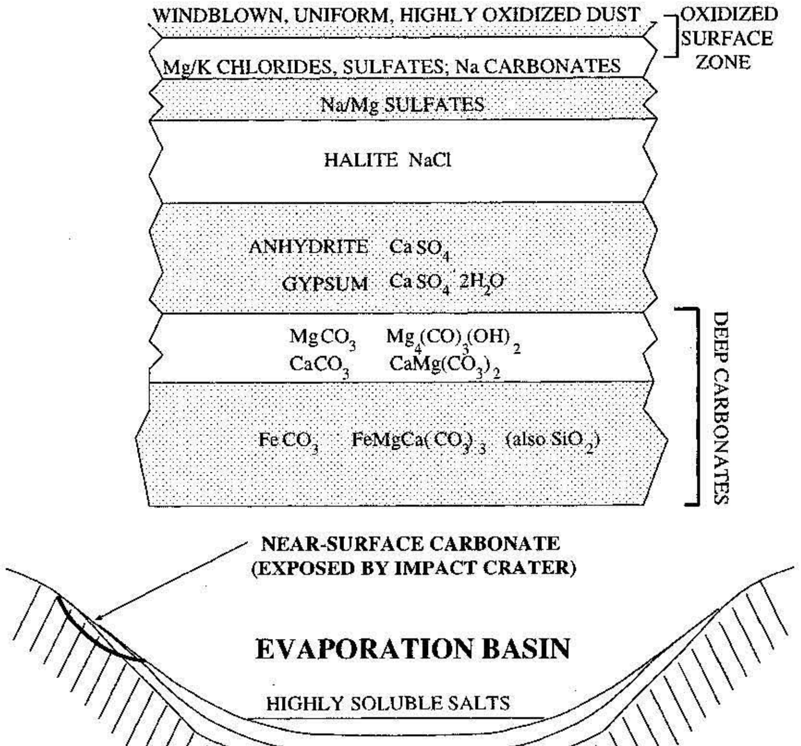

Figure 7. Hypothetical morphology of a sedimentary basin on Mars from a long-lived lake that evaporated. Lakes that were short-lived may be dominated by clastic sediments, and those that became ice-covered may also have different morphological features.

Martian dust of almost uniform composition on the basis of Viking and Pathfinder results [*Clark et al.*, 1982; *Rieder et al.*, 1997]. In the contemporary Martian atmosphere the OH number density may be typically 10-100 times less than in the Earth's atmosphere [*Hunten*, 1974], and there is only 0.13% by volume of oxygen compared to the Earth's copious biological supply. However, over a geologically short timescale on Mars, which unlike Earth lacks liquid water to dissolve photochemical oxidants, all the surface layers will have globally oxidized to a depth of several centimeters by oxidant diffusion [*Bullock et al.*, 1994; *Hartman and McKay*, 1995; *Quinn and Zent*, 1998]; mechanical mixing via cratering may have increased the global oxidation depth to a few meters [*Zent*, 1998]. Thus some Fe^{2+} compounds may be oxidized at the surface given the constant flux of oxidants due to photodissociation of water vapor in the atmosphere. Exposed at the surface, it is uncertain whether siderite, in particular, would remain stable against oxidation [*Gooding*, 1978]. Infrared remote sensing, which samples only the first few tens of microns, is therefore unlikely to reveal the identity of the most intriguing minerals relating to early Mars. These are buried and require in situ studies. Nevertheless, debris naturally excavated by impacts and strewn on the surface allows us to sample deep sediments without recourse to deep drilling. The survival of reduced compounds like siderite or even organics in the interior of such debris seems plausible given the small diffusion depth of photochemical oxidants, experimentally determined as < 10 cm [*Quinn and Zent*, 1998].

6. Discussion

Aqueous thermodynamic calculations were used to investigate the possible deposition of carbonates, sulfates/sulfides, silica, and silicates from sequential evaporation in a closed sedimentary basin fed by water from weathered igneous rock in a thicker CO_2 atmosphere.

Results of the calculations imply the following:

1. Assuming that conditions are neither strongly oxidizing nor strongly reducing, siderite ($FeCO_3$), the most insoluble of the major carbonates, is always the first carbonate mineral to precipitate and is predicted to be a significant facies component in early Martian carbonate sediments for this reason. If a basin is periodically recharged with fluid and continually evaporates, siderite sedimentary beds will build up.

2. If it is true that levels of P_{CO_2} were several times 0.1 bar on early Mars, then siderite facies (or their diagenetic alteration products) deposited in that epoch will act as an indicator of this high P_{CO_2}; otherwise, (dark-colored) hydrous iron silicates are more probable sediments. If such siderite sediments do not exist, it does not necessarily rule out high levels of P_{CO_2}. For example, we might find pyrite if a high concentration of sulfur was present in the water and conditions were more reducing; or we might find iron oxides only if our assumption about the anoxicity of the environment is somehow erroneous. However, endogenic hydrous iron silicate sediments would argue against high P_{CO_2} at the time of deposition. It is also worth noting that on Earth such silicate sediments are often found in assocation with iron oxides; in addition, greenalite, a possible silicate, is moderately magnetic, turning to a black, strongly magnetic ferric form if heated [*Joliffe*, 1935].

3. In general, the carbonate precipitation sequence consists of siderite, followed by calcite, followed by hydromagnesite. Solid solution chemistry, though not explicitly included, leads to some further conclusions. We expect considerable substitution of Mg and Ca cations into the siderite and some Mg substitution into the calcite on the basis of on the evolution of the concentration of these cations in solution. In contrast, the magnesite would be relatively pure because the Fe^{2+} and Ca^{2+} concentrations in solution are relatively very low by the stage that magnesite precipitates.

4. Carbonate precipitation is strongly influenced by the ion-pairing behavior of the divalent cations, as it is in terrestrial seawater [*Garrels et al.*, 1961]. In the model of Martian water, Fe^{2+} typically complexes 80-95% of the CO_3^{2-} into the $FeCO_3^0(aq)$ ion pair prior to siderite precipitation and thereby suppresses the precipitation of other carbonates by reducing the activity of the free CO_3^{2-} ion. At a more concentrated stage the $MgCO_3^0(aq)$ ion pair becomes the dominant carbonate complex.

5. Silica is expected to precipitate early in the sequence along with siderite. This is because silica is produced by aqueous CO_2 weathering of igneous rocks as a significant component of the initial solution and is likely to be close to saturation.

6. Gypsum precipitates from solution generally after calcite and hydromagnesite. However, under certain unusual circumstances, it is possible that gypsum could precipitate prior to calcite. For example, if the ratio of SO_4^{2-} relative to Ca^{2+} is increased in our baseline fluid to > 2, and P_{CO_2} is greater than about 3.5 bar, this chemical divide occurs, assuming no resupply of freshly weathered ions.

7. After carbonate and gypsum precipitation, the main components of the resulting brine depend upon our assumptions about the initial composition of the dilute fluid. However, on the basis of assumptions and calculations here, a Na-Cl-SO_4-Mg-CO_3 brine composition is expected at near neutral pH (although climatic lowering of P_{CO_2} after brine formation would raise the pH). Further evaporation would result in the deposition of salts such as halite (NaCl), sylvite (KCl), nahcolite ($NaHCO_3$), magnesium sulfates, sodium sulfates, and other highly soluble minerals. It is possible that abiotically fixed nitrate, which would be leached from the surface and enter groundwater, may be an evaporite salt component also although this species has been ignored in the model.

Finally, one should note that the model presented here is a "case study." There are certain assumptions concerning the nature of the early Mars water (e.g., using terrestrial analogs) that may differ from reality to a degree that remains unknown until we have more extensive observational data concerning Mars and its early conditions.

6.1. Possible Application to Carbonates in Martian Meteorites

All subgroups of the shergottites, nakhlites, and chassignites contain traces of salts, including carbonates and sulfates, that have been interpreted as minerals precipitated from water [*Gooding*, 1992]. Tiny amounts of evaporites in the fractures of Martian meteorites can be considered within the context of an evaporite model as what would happen if tiny droplets of the initial water were allowed to evaporate. It is interesting to note that the mineral assemblage resulting from the baseline evaporite model discussed here is consistent with the hypothesis of *Bridges and Grady* [1998] that salts in the Nakhla Martian meteorite, in particular, are derived from an ancient evaporite sequence that was incorporated into the basaltic melt and that predates the basalt. They report a Nakhla carbonate component dominated by siderite (about 20-90%) with lesser amounts of calcite ($< 6\%$), magnesite, and rhodochrosite; also, the more soluble salts comprise anhydrite ($CaSO_4$, a possible dehydration product of gypsum) and halite (NaCl). Bridges and Grady have suggested an evaporite origin based on several factors. These include the $\delta C^{13} \approx 50\%$ in the siderite compared to $\delta^{13}C \approx -12\%$ in the bulk Nakhla, which suggests derivation of the carbonate from the Martian atmosphere. The REE signature in the salts also suggests a nonhydrothermal origin.

The origin of salts in the ALH84001 meteorite is controversial. Because the carbonate globules are associated with hydrocarbons, alleged microfossils, and supposed biogenic minerals [*McKay et al.*, 1996], it is important to understand their origin. An evaporite origin for the carbonate globules in the ALH84001 meteorite has been proposed, where water perhaps dating from the Hesperian or Noachian percolated subsurface to precipitate minerals in tiny fractures [*Warren*, 1998]. *McSween and Harvey* [1998a, b] have suggested infiltration of a saline lake into shock-induced fractures at the base of a closed drainage basin, such as an impact crater. The carbonate globules have iron-rich cores and progress to pure magnesite rims [*Valley et al.*, 1997]. This is broadly consistent with the mineral assemblage resulting from the aquatic chemistry calculations presented in this paper for evaporating fluid. Formation of the carbonates from an evaporating droplet would develop on a central nucleus of Fe-rich carbonate. Physical factors, such as water stratification [*Warren*, 1998] or the occlusion of pore spaces by the carbonates [*McSween and Harvey*, 1998b], are needed to account for the lack of typical evaporite minerals like halite, which would be expected to accompany the carbonates. Unfortunately, the ALH84001 salts were likely subject to multiple shock events and melting on Mars prior to ejection [*Treiman*, 1998], so the considerable complexity of the salt chemistry is unlikely to lend itself to simple interpretation. However, an argument can be made that the original carbonate component was evaporite in origin [*Scott*, 1999].

6.2. Implications for Exploration

Upcoming sample-return missions could provide definitive answers that Martian meteorites cannot but only if samples are judiciously chosen; otherwise, returned samples may be just as complicated and controversial to interpret as the meteorites. What is clear is that future sample return missions or human exploration should focus on Noachian sedimentary and evaporite basins: These are places to search for vestiges of life as well as the past climate. Buried carbonate sediments, representative of early water chemistry, are best accessed by targeting basins where small, geologically recent impact craters within the basin have thrown up sediments from depth. Deep drilling is probably impractical in the near-term. The optimum scenario would be if the impact crater is in the outer part of a concave basin where carbonates may be closer to the surface (Figure 7). In the interior of debris thrown out from a crater, unoxidized sedimentary material could be protected from photochemical oxidants. For identifying siderite *in situ*, after removing oxidized surficial layers, a sensitive technique would be Mössbauer spectrometry; alpha-proton X-ray spectroscopy and infrared techniques would also be suitable. Similarly, it is important to look for hydrous ferrous silicates as possible products of aqueous alteration, which has also been suggested by *Calvin* [1998]. Returned samples, of course, would present the additional opportunity for dating mineral assemblages unambiguously through radioisotopes so that we can tie a particular environment, location, and sediment to a specific absolute time. In this way, we can have some hope of addressing the fundamental issue of the evolution of the Martian climate over geological time on a direct observational basis.

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