

Chemical divides and evaporite assemblages on Mars

Nicholas J. Tosca*, Scott M. McLennan

Department of Geosciences, State University of New York at Stony Brook, Stony Brook, NY 11794-2100, USA

Received 31 August 2005; received in revised form 13 October 2005; accepted 17 October 2005

Available online 28 November 2005

Editor: K. Farley

Abstract

Assemblages of evaporite minerals record detailed physical and chemical characteristics of ancient surficial environments. Accordingly, newly discovered regions of saline minerals on Mars are high priority targets for exploration. The chemical divide concept of evaporite mineral formation is used successfully to predict evaporite mineralogy and brine evolution on Earth. However, basaltic weathering largely controls fluid compositions on Mars and the robust predictive capabilities of terrestrial chemical divides cannot be used to interpret Martian evaporites. Here we present a new chemical divide system that predicts evaporite assemblages identified in SNC-type meteorites, ancient evaporites discovered on Meridiani Planum by the *Opportunity* rover, and Mars Express OMEGA data. We suggest that a common fluid type that has been buffered to different pH levels by basaltic weathering controls the variability among Martian evaporite assemblages and that evaporite mineralogy and brine evolution is essentially established by the initial composition of the dilute evaporating fluid.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Mars; Mars exploration rovers; evaporites; geochemistry; sulfates; carbonates

1. Introduction

The influx of new data from the Mars Exploration Rover (MER) and Mars Express (MEx) missions has significantly changed the current views of surficial environments on Mars. Sulfate salt minerals have been identified at many locations across the planet, manifested in soil analyses as well as in an ancient layered terrain [1–5]. In several of these localities, most notably Meridiani Planum, an intricate sedimentary record has been preserved [5]. Additional evidence for saline mineral formation on Mars comes from alteration mineral assemblages identified in the SNC-type meteorites,

which are markedly different than the assemblages inferred for Meridiani Planum sediments [6]. The characterization of evaporative environments is important because, just as they do on Earth, assemblages of saline minerals hold the most potential for constraining the characteristics of ancient aqueous fluids once present at the Martian surface and subsurface. In addition, geological settings that contain saline minerals are commonly the host of fossil biosignatures on Earth [7] and accordingly, are targets of high priority for future exploration by both orbiting and landed missions.

For terrestrial evaporite systems, Hardie and Eugster [8] demonstrated that the single most important parameter responsible for the variety of brine compositions and evaporite mineral assemblages is the composition of the dilute water at the onset of concentration. In countless terrestrial examples (where diagenetic modification of chemical sediments is insignificant), the end-

* Corresponding author. Tel.: +1 631 632 1936; fax: +1 631 632 8240.

E-mail address: ntosca@ic.sunysb.edu (N.J. Tosca).

product of evaporative concentration can be traced back to the initial chemistry of the evaporating fluid. With evaporite mineral precipitation creating turning points (or “chemical divides”) in the geochemical evolution of brines, a robust scheme has been developed to place constraints on the aqueous conditions necessary for the formation of evaporites on Earth [8,9].

A simple definition for the concept of chemical divides states that of two ions precipitated as a salt mineral, one will increase in solution and one will decrease in solution as evaporation proceeds [8,9]. This variance in ion concentration is determined by the molar ratio of the two ions in solution compared to the ratio present in the salt. For example, upon gypsum precipitation, if the Ca to SO_4 molar ratio in solution is greater than that of gypsum, SO_4 will eventually decrease to the point of exhaustion while Ca will continue to increase. Alternatively, the inverse may take place if Ca is less than SO_4 , resulting in a Ca-deficient fluid. This chemical divide created by gypsum precipitation largely determines the chemical evolution and subsequent precipitation pathway of the evaporating fluid. Therefore, the two most important factors that will determine the chemical evolution of evaporating brines, as well as the character and sequence of saline precipitates, are: (1) the chemistry of the dilute fluid being evaporated and (2) the nature of the precipitates creating chemical divides. These two factors appear to be fundamentally different for Martian evaporative systems when compared to terrestrial evaporative systems. Accordingly, chemical divides for terrestrial evaporites are not transferable to Martian environments. It is imperative then, that chemical divides be evaluated for these unique systems in order to provide useful constraints on the saline mineral assemblages expected at the Martian surface as well as the chemical evolution of resulting brines.

Here, we present a new system of chemical divides that is likely to be encountered during the production of saline mineral assemblages at the Martian surface. The resulting scheme for brine evolution on Mars captures the variability of saline mineral assemblages expected, their precipitation pathways, and the major brine types formed as a result of evaporative concentration. Our results establish a “roadmap” for the interpretation of saline mineral assemblages identified at the Martian surface and place constraints on the aqueous conditions necessary for their formation. The system of chemical divides developed here for the Martian surface independently predicts the saline mineral assemblages observed in SNC-type meteorites as well as assemblages inferred from MER and MEx data. The new chemical divide system also demonstrates that the SNC-type, Meridiani

Planum, and OMEGA-derived evaporite mineral assemblages could have evolved from a similar parent fluid, but simply buffered to different pH levels by basaltic weathering. As a result, two distinct geochemical environments for the production of saline minerals on Mars have been delineated: (1) acid–sulfate dominated environments and (2) mixed carbonate–sulfate dominated environments. Utilizing new data returned from MER and MEx missions in combination with thermodynamic modeling and other geochemical constraints, we suggest that the results obtained by the *Opportunity* rover point to a geochemical process which may have been common across the Martian surface, but is extremely rare on Earth—saline mineral formation from acidic fluids derived from basaltic weathering.

2. Controls on solution chemistry

Analogous to the Earth’s surface, solute acquisition at the Martian surface will be controlled mainly by the chemical weathering of crustal materials. The resulting fluid chemistry, however, differs markedly from the majority of dilute inflow waters on Earth that lead to brine formation. Compared to terrestrial dilute surface waters, Martian fluids are enriched in Mg, SiO_2 , Ca and most importantly, under acidic conditions, Fe [10–12]. Fluid composition is a critically important factor to assess because the final outcome of evaporative concentration is often sealed at the time dilute waters have acquired their solutes [13].

In general, chemical weathering reactions will be driven by acid input and the consumption of this acidity by mafic mineral dissolution will ultimately cause the pH to increase. The most significant sources of acidity at the Martian surface are the influx of volcanic gases rich in SO_2 , other minor volatile species such as Cl, and a predominantly CO_2 atmosphere [14,15]. The three major anions to be considered for Martian fluids then are HCO_3^- , SO_4^{2-} , and Cl^- . Given that the cation chemistry will be set by chemical weathering reactions, the most important variable to consider in assessing a wide range of fluid compositions ultimately leading to evaporite production is the relative proportion of these three major anions. The relative proportions are closely related to pH.

A simple way to account for the combined effects of acidity from various anion sources is to first consider both HCO_3^- and SO_4^{2-} equilibria. Beginning with a SO_4^{2-} and Cl^- free solution at equilibrium with a high pCO_2 atmosphere, acidity is largely controlled by carbonate equilibria. For pure water, pH as a function of pCO_2 can be calculated in a straightforward manner

using equilibrium thermodynamics. For water containing some amount of dissolved solute where the pH has increased from cation exchange by mineral dissolution, carbonate alkalinity ($[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$) will increase as CO_2 becomes more soluble. However, if the same water is simply titrated with acid (analogous to the addition of H_2SO_4 or HCl from an external source), the solution will eventually become SO_4^{2-} (or Cl^-) dominated and both the pH and carbonate alkalinity will decrease. This relationship is illustrated in Fig. 1, which simulates acid titration into a fluid derived from basaltic weathering (the cation concentrations used for the simulation are listed in Table 1). It is important to note that the relative amounts of carbonate, sulfate and chloride will determine two major factors: (1) the pH of weathering, and (2) the mineralogy of saline minerals precipitated upon evaporation.

Taken together, all of the factors above can be expressed by means of a simple model that captures a broad range of possible dilute fluid compositions at the Martian surface. Prior to evaporation, the initial anion composition of aqueous solutions (i.e., from volatile input) will fall along the x -axis of Fig. 1. The anion composition will be continuously modified by an increasing pH that results from basaltic weathering. Basaltic weathering reactions will in turn set the cation proportions in solution and serve to buffer acidity generated by SO_4^{2-} (or Cl^-) dominated solu-

Table 1

Cation proportions used in thermodynamic calculations

Cation	Concentration ($\mu\text{mol/kg}$ water)	Relative percent
Mg^{2+}	497	47
Fe^{2+}	356	34
Ca^{2+}	165	16
Na^+	25	2
K^+	10	1
Total	1053	100

From Tosca et al. [10].

tions, eventually increasing both carbonate alkalinity and carbonate mineral saturation. Such a scenario will be the most favored in rock-dominated, subsurface environments where atmospheric volatile input is limited and the water-to-rock ratio is low. At the opposite end of the spectrum, acidic volatile input may be so substantial that carbonate alkalinity remains negligible, and solutions are SO_4^{2-} or Cl^- dominated and highly acidic. Highly acidic solutions will take up to several orders of magnitude longer to buffer to higher pH levels by chemical weathering. This is especially true if the weathering reactions are in competition with fluid evaporation at the surface, a process which continuously decreases the pH of slightly acidic fluids. This scenario was suggested by Tosca et al. [16] to have been responsible for sustaining an acid-dominated chemical environment at Meridiani Planum.

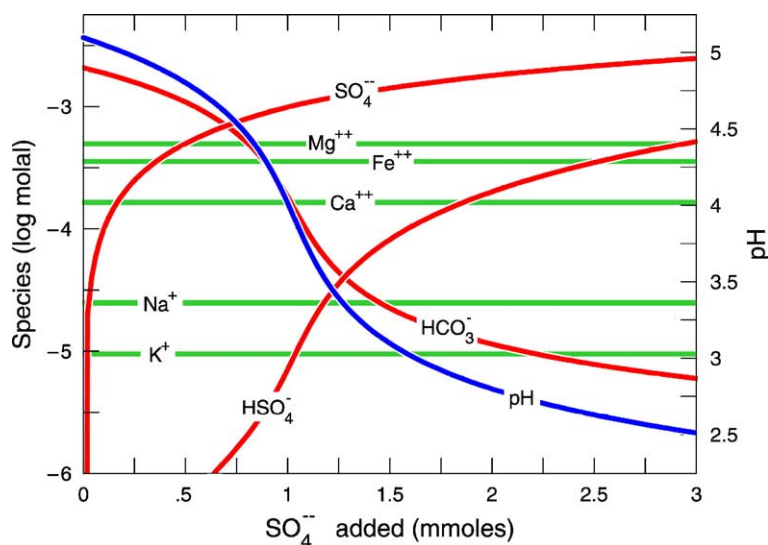


Fig. 1. Major chemical species present during addition of sulfate to a basaltic weathering fluid in equilibrium with 1 bar of CO_2 . As sulfate is added to the solution, carbonate alkalinity is titrated and the pH decreases substantially, shifting from bicarbonate dominated to sulfate dominated. This calculation represents a condition where the cation proportions are set by chemical weathering reactions and the anion composition changes as a result of acidic volatile input. The buffering of acid–sulfate dominated solutions by water–rock interaction will have an opposite effect on pH and carbonate alkalinity.

3. Approach and methods

A series of evaporation calculations based on equilibrium thermodynamics was performed in this study to construct a new system of chemical divides applicable to the Martian surface. Thermodynamic calculations of mineral solubility upon evaporation were performed with the Geochemist's Workbench® software (GWB) [17]. The Pitzer ion interaction approach was used for all activity coefficient calculations. All Pitzer parameters and mineral solubility data used are the same as those reported in Tosca et al. [16]. In addition, the database reported in [16] has been expanded to include the carbonate system. Parameterization for the carbonate system was performed using data and methods presented by Marion and colleagues [18,19]. The equilibrium constant for siderite solubility at 25 °C was taken from Ptacek and Blowes [20] and the solubility constants for magnesite and calcite at 25 °C were taken from Marion [18]. For all calculations, no back-reactions between minerals were allowed and dolomite formation was suppressed because this phase does not typically occur as an evaporative precipitate owing to kinetic effects on its precipitation. Electroneutrality was maintained by charge balance on H^+ , and so pH was allowed to vary in all calculations.

The system presented here is one characterized by initial pH values of less than or equal to about 6 with any relative proportion of HCO_3^- , SO_4^{2-} and Cl^- . We assume that dilute waters are dominated by Mg, Fe^{2+} and Ca, and contain lesser amounts of Na and K. In the context of evaporitic phases, we ignore $SiO_2(aq)$ and Al^{3+} . Accordingly, the formation of clay minerals is not considered here as the process is limited mainly to particular stages of basaltic weathering where the pH is allowed to increase over time. Instead, for simplicity, we have chosen to focus purely on the process of fluid evaporation. It is important to note, however, that localized occurrences of clay minerals have been identified by the OMEGA instrument aboard the Mars Express spacecraft [21]. Although the formation of clay minerals generally takes place at high pH (e.g., circumneutral and higher), clay minerals and the saline minerals discussed in this study are not mutually exclusive—before evaporation, some clays may indeed precipitate toward the higher range of fluid pH levels considered in this study. The exact cation proportions for the remaining components used in this study were taken from acidic weathering experiments performed by Tosca et al. [10] on synthetic olivine-bearing basalt and are listed in Table 1.

Sensitivity of the results to variation in cation proportions was also assessed. Variation of cation proportion has a direct effect on the proportion of each critical precipitate produced upon evaporation. The insoluble alkaline earth carbonates are the most susceptible to these variations, but the effect on brine evolution after their precipitation remains the same. Extensive variation in cation proportion so as to prevent critical precipitates from forming was not considered. Such variation would demand additional chemical divide systems for hypothetical fractionation of fluid compositions and would not be relevant to the basaltic weathering processes discussed here. It is also important to note that for practicality, all calculations discussed in this study were performed at 25 °C—a temperature for which well established thermodynamic data for our system exist. Temperature effects on mineral precipitation, specifically in Fe-rich systems, should continue to be investigated [19]. However, in the context of chemical divides, the same concept holds for freezing as for evaporation at 25 °C. The results presented in this study are not anticipated to change significantly upon recalculation to 0 °C and lower temperatures. In fact, while the hydration states of predicted critical precipitates are known to change with temperature, changes in the chemical evolution of brines are likely to remain the same [19].

The interpretation of evaporite sedimentation on the Martian surface is subject to the same complications identified for terrestrial environments. Of particular importance, for example, are kinetic effects on mineral precipitation (e.g., the inhibitory effects from Mg^{2+} on calcite precipitation [22]) that cause disparities between thermodynamic calculations and observed mineral assemblages. Although such kinetic factors have been identified for terrestrial environments, some remain inadequately understood. In dealing with a new geochemical system such as the one investigated in this study, it is anticipated that additional kinetic complications will indeed prove to be important. However, beginning with a fundamental thermodynamic approach and integrating as much knowledge of terrestrial environments as possible is the first step toward understanding these factors.

In the calculations that follow, redox equilibrium between Fe and atmospheric oxygen is not assumed. Although thermodynamic equilibrium demands $Fe^{2+}(aq)$ instability in contact with atmospheric oxygen, the kinetics of Fe(II) oxidation typically prevent equilibrium from being reached—this is a ubiquitous condition in aqueous environments on Earth [23,24]. Inadequate constraints on the oxygen content of an-

cient Martian evaporative environments make quantitative calculation of Fe(II) oxidation kinetics difficult. What is known, however, is that the present oxygen content of the Martian atmosphere is approximately 27,000 times less than that of Earth [25]. In addition, several authors have calculated the oxygen content of the ancient Martian atmosphere to be even lower and hence slightly more reducing than current conditions resulting from increased volcanic activity buffering photochemically produced oxygen [11,25,26]. Combining these suggestions with lines of evidence implying acidic conditions at the near Martian surface [27] demands that the kinetics of Fe-oxidation by $O_2(g)$ were indeed slower, possibly by orders of magnitude than acidic environments currently present at the Earth's surface [12,25]. Accordingly, we suggest that Fe-redox equilibrium during chemical weathering and saline mineral production should not be assumed and the transport of Fe^{2+} in solution be considered [16]. The identification of siderite in SNC-type meteorite samples (discussed in more detail below) supports this suggestion [6]. However, it is important to note that the majority of Fe identified in Meridiani Planum sediments exists in the ferric state [27]. Although oxidizing conditions are certainly implied by this finding, the materials are ancient and are also consistent with attainment of redox equilibrium possibly over much longer diagenetic timescales than those of the weathering/evaporation cycles resulting in saline mineral production considered in the calculations below (see Tosca et al. [16] and McLennan et al. [28] for additional discussions). In summary, Fe^{3+} is not explicitly included in this model of chemical divides and we note that if Fe is oxidized in solution and subsequently depleted by precipitation, fractionation of Fe analogous to Fe^{2+} -bearing saline mineral formation will result. Conspicuous evidence suggesting such a process would be the identification of Fe-oxides co-genetic with other carbonate minerals such as calcite and magnesite.

4. Chemical divides at the Martian surface

Fig. 2 depicts the major chemical divides, precipitation pathways, and brine compositions encountered during the evaporation of fluids where the initial chemistry is controlled by basaltic weathering under acidic conditions. Our thermodynamic calculations suggest that upon evaporative concentration (moving downward on Fig. 2), the first major precipitate formed is dependent on the proportion of HCO_3^- to SO_4^{2-} in the fluid. Accordingly, the first major chem-

ical divides encountered in this system are arranged on Fig. 2 from left to right as a function of decreasing HCO_3^- relative to SO_4^{2-} (paths A–E on Fig. 2). Fig. 2 can essentially be viewed as a transect of evaporation calculations along the x -axis of Fig. 1 with variable Cl^- content. If Fe^{2+} is held in solution, the first major precipitate to form when the system is dominated by HCO_3^- is siderite ($Fe^{2+}CO_3$). Under the condition that $HCO_3^- \gg Fe$ (path A), siderite precipitation will exhaust Fe from the fluid. Upon further evaporative concentration, gypsum and/or alkaline earth carbonates are responsible for the next chemical divide, depleting the solution in either Ca, HCO_3^- , or SO_4^{2-} . Depending on the proportion of HCO_3^- remaining in the solution (conditions I, II, or III in Fig. 2), the phases will be Mg-rich and dominated by either carbonates or sulfates. It is important to note that solid solution behavior of carbonate minerals has not been included in our calculations. However, previous studies have shown that the sequence of carbonate precipitation in the Mg–Fe–Ca system generally leads to early siderite precipitation (with minor Ca), subsequent calcite (with minor Mg) precipitation, and the later formation of Mg–carbonate phases if enough Mg persists after the precipitation of the other carbonates [29]. Under the geochemical conditions used in these calculations, taking path A and the condition that $Ca > SO_4^{2-}$, gypsum always precipitates before calcite and magnesite except under very low SO_4^{2-} concentrations where gypsum precipitation occurs together with the alkaline earth carbonates. The overall effect on solution chemistry, however, does not change.

The next major chemical divide may occur when Fe is present in the same proportion as HCO_3^- (path B on Fig. 2), at which point siderite precipitation will deplete the solution of both Fe and HCO_3^- . The resulting brine will be rich in other cations, in this case, Mg and Ca. The resulting mineralogy will be sulfate or chloride-dominated, consisting of gypsum and epsomite, or Mg- and Ca-dominated chloride minerals, respectively.

If the evaporating fluid contains less HCO_3^- than Fe (path C on Fig. 2), precipitation of siderite will instead deplete the solution of HCO_3^- . Gypsum precipitation is responsible for the next chemical divide, at which point SO_4^{2-} may or may not be depleted leading to either Cl^- dominated or SO_4^{2-} dominated saline mineral assemblages, respectively. Paths B and C predict only one carbonate phase, siderite, which depletes all remaining HCO_3^- . Therefore, paths B and C can be distinguished from path A, which demands the formation of a sub-

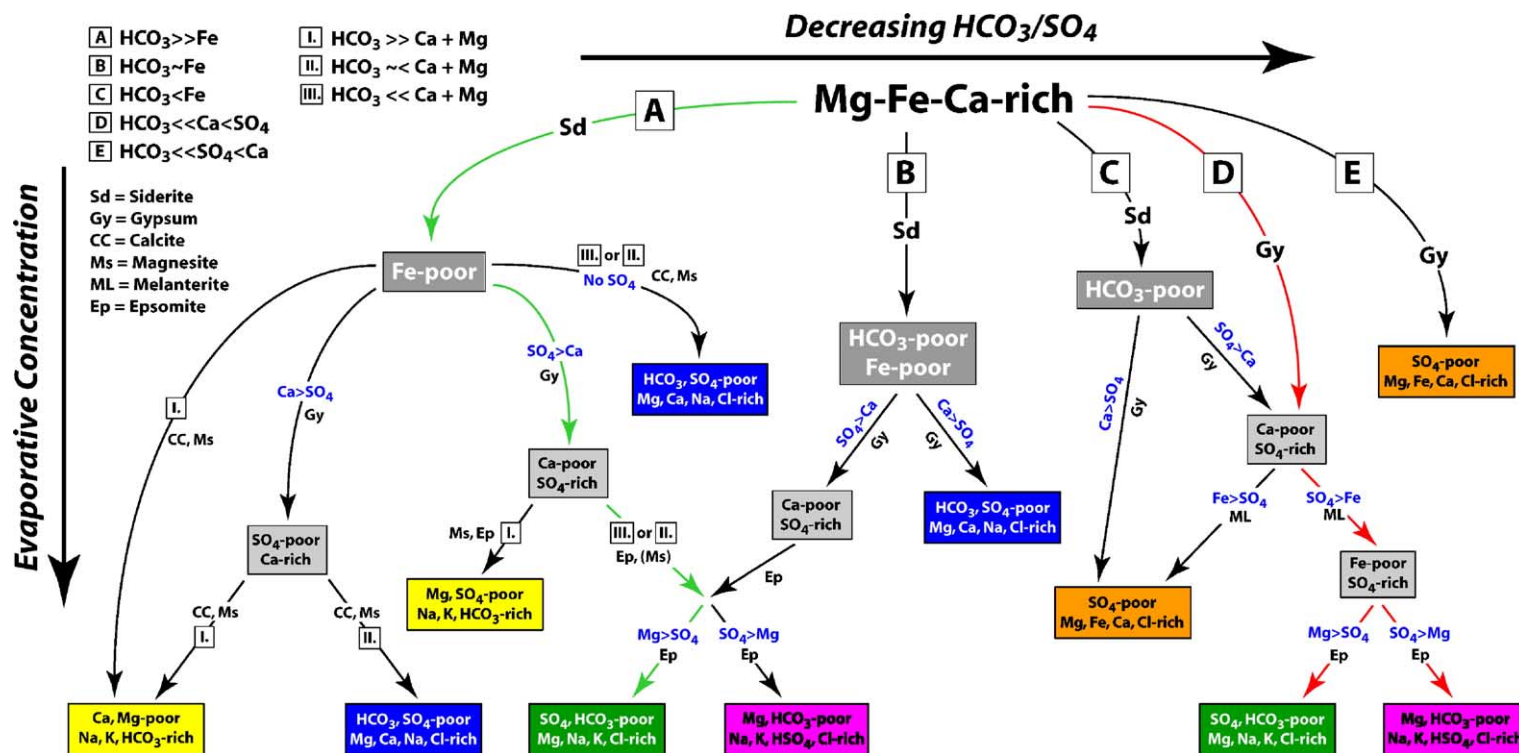


Fig. 2. Flow chart for the chemical evolution of evaporating fluids derived by basaltic weathering. Evaporative concentration increases downward and the relative amount of HCO_3^- to SO_4^{2-} decreases to the right. Precipitates causing chemical divides are indicated as are conditions leading to chemical fractionation from mineral precipitation. The resulting brines and their characteristics are described in boxes. The precipitation pathways for the Nakhla (green arrows) and Meridiani Planum (red arrows) evaporite assemblages correspond to two distinct geochemical environments for saline mineral formation on Mars.

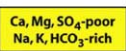
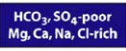
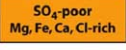
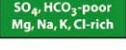
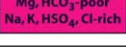
sequent carbonate phase (or phases) because HCO_3^- is not completely exhausted after siderite precipitation.

If HCO_3^- is present in negligible amounts where carbonate precipitation does not occur upon evaporation (path D on Fig. 2), then the saline mineral assemblage will be dominated entirely by sulfate minerals, including melanterite and epsomite if SO_4^{2-} remains in high proportion.

The last major pathway depicted on Fig. 2 may occur when HCO_3^- is negligible in solution and any SO_4^{2-} is depleted by gypsum precipitation, creating a Mg, Fe, Ca-chloride brine (path E).

An important result of the chemical divide system presented here is that only five major types of late-stage brines are produced (three of which are Mg- and Cl-dominated, varying in the less abundant components), and they are composed of only a few major components. Table 2 lists the five major brine types that are formed upon successions of chemical divides shown in Fig. 2. Perhaps the most important conclusion to be drawn from Table 2 is that the brines are unique—all are extremely acidic and only very few chemical analogs exist on Earth. Highly soluble mineral phases will precipitate from these brines upon even further evaporative concentration and the major precipitates predicted to form from such brines based on our thermodynamic calculations are also listed in Table 2.

Table 2
Major late-stage brine types formed from basaltic weathering fluid evaporation^a

Brine type	Symbol	Characteristics	Typical precipitates
TYPE I		Acid brine (pH 3–4), Na > K - Bicarbonate brine	Nahcolite, kalcanite
TYPE II		Acid brine (pH 0–2), Mg > Ca > Na - Chloride brine	Halite, sylvite, bischofite, antarctite
TYPE III		Acid brine (pH 0–2), Mg > Fe > Ca - Chloride brine	Halite, sylvite, bischofite, antarctite
TYPE IV		Acid brine (pH 0–2), Mg > Na > K - Chloride brine	Halite, sylvite, bischofite
TYPE V		Acid brine (pH 0–2), Na > K > HSO4 - Chloride brine	Bloedite, polyhalite, glauberite, thenardite

^a All brines were produced with the same cation proportions in solution, but varying anion composition and all evolve to extremely acid pH upon near complete evaporation. Also listed are mineral phases predicted to form upon further evaporative concentration of these brines, based on our thermodynamic calculations. Nahcolite = NaHCO_3 , Kalcanite = KHCO_3 , Halite = NaCl , Sylvite = KCl , Bischofite = $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, Antarcticite = $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, Bloedite = $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, Polyhalite = $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, Glauberite = $\text{Na}_2\text{Ca}(\text{SO}_4)_2$, Thenardite = Na_2SO_4 .

5. Discussion and implications

Chemical divides have been applied to numerous terrestrial evaporative environments placing powerful constraints on their geochemical evolution. As a result, the chemical divide concept has demonstrated a robust predictive ability for the precipitation of major saline mineral assemblages from a wide range of fluid compositions. Of the numerous applications on Earth, chemical divides have been used to interpret the evolution of seawater composition over geologic time [30,31] as well as the geochemical evolution of countless lacustrine deposits [9,13]. We anticipate that applying the same concepts to Martian evaporative environments will prove to be of comparable value.

All available evidence for evaporite minerals at the Martian surface shows that, analogous to Earth, significant variability in saline mineral assemblages has been observed. In the following discussion, we describe three examples from Mars where the system of chemical divides presented above can be used to interpret the geochemical evolution of specific Martian evaporite assemblages. In addition, using these chemical divides, we show that the variability observed in evaporite mineral assemblages on Mars (from SNC meteorite studies, MER and MEx results) can be explained by a single dilute fluid type with variable anion concentration. As discussed above, the variation in anion concentration is simply controlled by pH buffering during basaltic weathering.

Alteration mineral assemblages identified in several SNC-type meteorites are consistent with low-temperature formation by evaporating fluids [6]. It has been demonstrated by numerous lines of supporting evidence that these assemblages are of pre-terrestrial origin [6]. In general, the assemblages are carbonate-dominated with some containing sulfate and chloride minerals as well as clays [6]. The Nakhilites, for example exhibit siderite with gypsum (and anhydrite), sulfates and halite [32]. Specifically, Nakhla provides the most detailed information on evaporite mineral assemblages on Mars, because the evaporite mineral assemblage contains several phases indicative of late-stage evaporation and precipitation. The entire evaporite mineral assemblage identified in Nakhla is consistent with one specific precipitation pathway presented above. In addition, significant quantities of siderite have been identified in Nakhla (and in two other Nakhilites). These observations, together with more recent identification of minor siderite in Y000593 and NWA998 [33], provide evidence that siderite was indeed an important critical precipitate in chemical divides on Mars. This results

mainly from the fact that Fe-oxidation and precipitation had not been so extensive as to deplete the fluid of Fe.

According to Fig. 2, the precipitation sequence of the Nakhla evaporite assemblage began with siderite (path A), which depleted the solution of any remaining Fe^{2+} . The carbonates identified in Nakhla are Fe-rich (with minor Ca) and also contain significant Mg, suggesting that Fe was essentially depleted with siderite and more Mg-rich carbonate compositions subsequently precipitated [29]. This suggests that there was more available HCO_3^- in the fluid than Fe, pointing to path A on Fig. 2, rather than path B or C. Subsequent gypsum precipitation led to a Mg- and SO_4^{2-} rich solution, which then precipitated epsomite. According to our system of chemical divides, epsomite precipitation likely depleted the remaining SO_4^{2-} and led to a brine rich in Na and Cl. Halite has also been identified in Nakhla and textural relationships among mineral phases show that this phase is a late-stage precipitate [32]. Halite precipitation likely resulted from a late-stage brine similar to Type IV (Table 2), which subsequently precipitates halite under further concentration, whereas Type V does not. The precipitation pathway inferred from Fig. 2 is consistent with textural relationships among saline minerals. In addition to Nakhla, Lafayette and Governador Valadares each contain siderite (Governador Valadares also contains gypsum), indicating that the precipitation pathways of these evaporite minerals occurred along the left hand portion of Fig. 2 (paths A or B). Carbonate minerals (plus gypsum) identified in some shergottites and Chassigny, as well as carbonates found in ALH84001, also provide evidence for carbonate-dominated and mixed carbonate–sulfate precipitation pathways [6]. The composition of the carbonate minerals differs somewhat among the meteorites and is controlled by cation proportions in the parent fluid. This is not unexpected however, because the meteorite host lithologies vary and as a result, weathering fluids will show some variation in their cation proportions. The carbonate compositions in ALH84001 and the Nakhrites are consistent with the relationships described above for Mg–Fe–Ca– CO_2 – H_2O systems [6,34].

The results obtained by the *Opportunity* rover from Meridiani Planum have revealed a markedly different evaporitic mineral assemblage than typified by the SNC-type meteorites. Bulk compositional measurements on outcrop sandstones suggest that Mg- and Ca-sulfates are important components, which is also consistent with Mini-TES spectral deconvolution [5]. Mössbauer spectroscopy has identified the Fe^{3+} -sulfate jarosite, hematite and an ambiguous spectral feature

attributed to other Fe^{3+} -bearing sulfates or oxides (the so-called Fe3D3 component) [27]. No carbonate minerals have been identified by Mini-TES or inferred from any data collected to date [5,35]. It is clear that the outcrop is composed of re-worked evaporite sandstone and so the exact mineral proportions cannot be taken to be representative of a primary evaporite sequence. It is also possible in such depositional settings that evaporite minerals may be absent; although the striking similarity of the S- and Cl-free outcrop composition to typical Martian basalts [28] suggests that most major components are likely represented. If this is indeed the case, Fig. 2 can be used as a guide with which to interpret the chemical evolution of evaporating waters at Meridiani Planum.

In the context of chemical divides, there are two possibilities for the geochemical evolution of evaporating fluids at Meridiani Planum. The first possibility is that the initial fluid first precipitated siderite (and possibly other carbonates) and subsequent Ca- and Mg-sulfates (paths A–C). If this was the case, the carbonates would need to be replaced by sulfate to facilitate the production of Fe-sulfates such as jarosite and remove carbonate minerals from the point of detection. The second possibility is that the initial evaporitic fluid was acidic to the point that HCO_3^- was negligible which, upon evaporation, precipitated a sulfate-dominated mineral assemblage beginning with gypsum, and Fe- and Mg-sulfates (path D). Ferrous Fe-bearing sulfates have not been detected at Meridiani Planum. However, the identification of ferrous Fe bearing siderite in several SNC-type meteorites suggests that at the time of Meridiani Planum sediment formation, oxidation may have been sluggish enough where Fe^{2+} remained in solution upon evaporation. Analogous to siderite precipitation under carbonate-dominated aqueous conditions, we suggest that melanterite is expected to be an Fe^{2+} -bearing evaporite phase that will cause a late-stage chemical divide during surficial brine evolution. Interestingly, such phases are highly unstable toward oxidation and dehydration, leaving open the possibility that they have been oxidized and altered during one of the diagenetic events that has taken place at Meridiani Planum [16,28]. This alteration pathway, in turn, would have produced additional Fe-bearing sulfate or oxide phases, possibly contributing to hematite concretion formation and/or the Fe3D3 Mossbauer spectral component [16,28]. Such a hypothesis is consistent with much available data collected on outcrop material to date. This latter precipitation pathway for Meridiani Planum is illustrated in Fig. 2. Although a siderite pathway is possible, there is no evidence to

suggest that carbonates have initially formed and were altered to sulfates. The simplest explanation, and one consistent with the majority of chemical and mineralogical data collected on the outcrop, is that the second path (highlighted on Fig. 2) was the mineral precipitation pathway leading to the formation of evaporite minerals which were deposited as sandstones and subsequently altered by groundwater-mediated diagenetic reactions.

Detailed mineralogical data of the Martian surface obtained by the OMEGA instrument show that similar to Meridiani Planum, specific occurrences of sulfate-dominated lithologies with no detectable carbonate minerals have been observed [2,3]. Kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), gypsum, and a feature presently attributed to polyhydrated sulfates have been mapped in specific locations across the Martian surface, including regions of Valles Marineris, Margaritifer Terra and Terra Meridiani [2]. Additional saline minerals may be present however, that do not exhibit spectral features in the OMEGA range (e.g., halite) [2]. It is not yet known whether discrete deposits of kieserite and gypsum are part of the same precipitation sequence and have not been significantly fractionated by sedimentary processes. However, these mineral occurrences are consistent with a precipitation pathway beginning on Fig. 2 where gypsum is the first critical precipitate and not siderite, similar to the pathway discussed for Meridiani Planum (paths D or E). According to Fig. 2, the presence of late-stage Mg-sulfates suggests that HCO_3^- was depleted along the evaporation sequence, or that carbonate minerals never formed. Also, kieserite detection suggests that Fe was quantitatively precipitated, either as Fe-sulfates of ferrous, ferric, or mixed-valence forms, or as insoluble ochreous precipitates such as oxides or hydroxysulfates. This interpretation stems from thermodynamic modeling studies suggesting that during evaporation of Fe-rich basaltic weathering fluids, such phases are typically of equal or lower solubility than Mg-sulfates [16]. Such an Fe-bearing component, if the kieserite and gypsum-dominated lithologies have evolved from the same fluid, is consistent with the interpretation of associated polyhydrated sulfate spectral signatures in such regions [2]. Although complete mineralogical characterization is still needed for these environments, the coupling of these observations with other remotely sensed datasets as well as detailed geologic relationships holds the most potential for utilizing the constraints presented in Fig. 2.

The examples discussed above suggest two fundamentally different geochemical environments leading to saline mineral formation on Mars: (1) acid–sulfate dominated surficial environments and, (2) environ-

ments where acidity is buffered by basaltic weathering reactions, leading to an increase in carbonate alkalinity. The precipitation pathways for these two environments correspond to the right-hand (paths D and E) and left-hand portions (paths A–C) of Fig. 2, respectively. Catling [11] presented a model for evaporite mineral formation on Mars which is consistent with the geochemical environment depicted by the left-hand side of Fig. 2 and martian meteorite salts. The recent identification of evaporite sediments at Meridiani Planum has indeed revealed another evolutionary pathway, corresponding to the acid–sulfate dominated surficial environments discussed above and illustrated on the right hand portion of Fig. 2. The results obtained by the OMEGA instrument provide additional evidence for the importance of this setting. It is important to recall that the sediments analyzed by the *Opportunity* rover are inferred to be of Late Noachian to Early Hesperian in age [5,36]. However, age relationships of sulfate-rich deposits identified by OMEGA are less clear. The similar sulfate-dominated, carbonate-poor assemblages apparent from both datasets suggest that the aqueous conditions inferred for Meridiani Planum may have been common on the surface of Mars, but the duration is not well constrained. These discoveries do show however, that the full range of sulfate- and carbonate-dominated evaporite mineral assemblages now needs to be considered in the interpretation of evaporative environments on Mars. It is important to highlight that although carbonates have not been found at the surface and shallow subsurface as a result of prevailing acidic chemical conditions, our interpretation of the SNC meteorite results suggests they may be present at the subsurface, resulting simply from atmospheric cutoff and pH buffering to higher levels in low water-to-rock ratio, bedrock-dominated environments.

The characterization of environments containing saline minerals will hold the key to constraining aqueous and environmental conditions at the surface of Mars. Future landed and orbiting missions, with ever increasing spatial resolution and analytical capabilities, will provide the data with which these relationships can be tested and improved. Accordingly, the chemical and mineralogical relationships presented above provide a “roadmap” for which the results of future exploration of aqueous environments on Mars can be compared and interpreted. Finally, and perhaps one of the most important conclusions to be drawn from the results presented in this study, is that the system described above is unique compared to almost any evaporitic environment on Earth. The uniqueness is manifested in this system of chemical divides from at least three factors

fundamental to Martian surficial processes: (1) acidic environments controlled largely by SO_4^{2-} , HCO_3^- and Cl^- input, (2) increased mobility and concentration of Fe in aqueous systems, and (3) dilute water chemistry dominated by the weathering of basalt. Taken together, this system combines aspects of classical evaporite geochemistry and sedimentology with systems such as acid mine drainage and basaltic weathering. This study shows that while seemingly complex, considerable advances can be made in understanding evaporite geochemistry on Mars if such systems are considered at a simple and fundamental level, analogous to their terrestrial counterparts.

Acknowledgements

The authors would like to thank Joel Hurowitz, John Grotzinger, Andrew Knoll, Rebecca Parsons, and the Athena Science Team for thorough reviews and helpful discussions. The authors would also like to thank two anonymous reviewers for insightful comments.

References

- [1] R. Gellert, R. Rieder, R.C. Anderson, J. Bruckner, B.C. Clark, G. Dreibus, T. Economou, G. Klingelhöfer, G.W. Lugmair, D.W. Ming, S.W. Squyres, C. d'Uston, H. Wanke, A. Yen, J. Zipfel, Chemistry of rocks and soils in Gusev from alpha particle X-ray spectrometer, *Science* 305 (2004) 829–832.
- [2] A. Gendrin, N. Mangold, J.-P. Bibring, Y. Langevin, B. Gondet, F. Poulet, G. Bonello, C. Quantin, J.F. Mustard, R.E. Arvidson, S. LeMouelic, Sulfates in Martian layered terrains: the OMEGA/Mars express view, *Science* 307 (2005) 1587–1591.
- [3] Y. Langevin, F. Poulet, J.-P. Bibring, B. Gondet, Sulfates in the north polar region of Mars detected by OMEGA/Mars Express, *Science* 307 (2005) 1584–1586.
- [4] R. Rieder, R. Gellert, R.C. Anderson, J. Bruckner, B.C. Clark, G. Dreibus, T. Economou, G. Klingelhöfer, G.W. Lugmair, D.W. Ming, S.W. Squyres, C. d'Uston, H. Wanke, A. Yen, J. Zipfel, Chemistry of rocks and soils at Meridiani Planum from the alpha particle X-ray spectrometer, *Science* 306 (2004) 1746.
- [5] S.W. Squyres, J.P. Grotzinger, R.E. Arvidson, J.F. Bell III, P.R. Christensen, B.C. Clark, J.A. Crisp, W. Farrand, K.E. Herkenhoff, J.R. Johnson, G. Klingelhöfer, A.H. Knoll, S.M. McLennan, H.Y. McSween, R.V. Morris, J.W. Rice, R. Rieder, L.A. Soderblom, In-situ evidence for an ancient aqueous environment at Meridiani Planum, Mars, *Science* 306 (2004) 1709.
- [6] J.C. Bridges, D.C. Catling, J.M. Saxton, T.D. Swindle, I.C. Lyon, M.M. Grady, Alteration assemblages in Martian meteorites: implications for near-surface processes, *Space Sci. Rev.* 96 (2001) 365–392.
- [7] S. Bonny, B. Jones, Microbes and mineral precipitation, Miette Hot Springs, Jasper National Park, Alberta, Canada, *Can. J. Earth Sci.* 40 (11) (2003) 1483–1500.
- [8] L.A. Hardie, H.P. Eugster, The evolution of closed-basin brines, in: *Mineralogical Society of America Special Publication*, vol. 3, 1970, pp. 273–290.
- [9] H.P. Eugster, L.A. Hardie, Saline Lakes, in: A. Lerman (Ed.), *Chemistry, Geology, and Physics of Lakes*, Springer, New York, 1978, pp. 237–293.
- [10] N.J. Tosca, S.M. McLennan, D.H. Lindsley, M.A.A. Schoonen, Acid-sulfate weathering of synthetic Martian basalt: the acid fog model revisited, *J. Geophys. Res.—Planets* 109 (E05003) (2004), doi:10.1029/2003JE002218.
- [11] D.C. Catling, A chemical model for evaporites on early Mars: possible sedimentary tracers of the early climate and implications for exploration, *J. Geophys. Res.* 104 (E7) (1999) 16453–16469.
- [12] R.G. Burns, Rates and mechanisms of chemical weathering of ferromagnesian silicate minerals on Mars, *Geochim. Cosmochim. Acta* 57 (19) (1993) 4555–4574.
- [13] H.P. Eugster, Geochemistry of evaporitic lacustrine deposits, *Annu. Rev. Earth Planet. Sci.* 8 (1980) 35–63.
- [14] A. Banin, B.C. Clark, H. Wanke, Surface Chemistry and Mineralogy, in: H.H. Kieffer, B.M. Jakosky, C.W. Snyder, M.S. Matthews (Eds.), *Mars*, University of Arizona, Tucson, 1992, pp. 594–625.
- [15] B.M. Jakosky, R.J. Phillips, Mars' volatile and climate history, *Nature* 412 (2001) 237–244.
- [16] N.J. Tosca, S.M. McLennan, B.C. Clark, J.P. Grotzinger, J.A. Hurowitz, A.H. Knoll, C. Schroeder, S.W. Squyres, Geochemical modeling of evaporation processes on Mars: Insight from the sedimentary record at Meridiani Planum, *Earth Planet. Sci. Lett.* 240 (1) (2005) 125–151.
- [17] C.M. Bethke, The Geochemist's Workbench, Release 4.0: A User's Guide to Rxn, Act2, Tact, React, and Gtplot, University of Illinois, 2002, 224 pp.
- [18] G.M. Marion, Carbonate mineral solubility at low temperatures in the Na–K–Mg–Ca–HCl–SO₄–OH–HCO₃–CO₃–CO₂–H₂O system, *Geochim. Cosmochim. Acta* 65 (12) (2001) 1883–1896.
- [19] G.M. Marion, D.C. Catling, J.S. Kargel, Modeling aqueous ferrous iron chemistry at low temperatures with application to Mars, *Geochim. Cosmochim. Acta* 67 (2003) 4251–4266.
- [20] C.J. Ptacek, D.W. Blowes, Influence of siderite on the pore-water chemistry of inactive mine-tailings impoundments, in: C.N. Alpers, D.W. Blowes (Eds.), *Environmental Geochemistry of Sulfide Oxidation*, American Chemical Society, Washington, D.C., 1994, pp. 172–189.
- [21] J.-P. Bibring, Y. Langevin, A. Gendrin, B. Gondet, F. Poulet, M. Berthe, A. Soufflot, R.E. Arvidson, N. Mangold, J.F. Mustard, P. Drossart, O. team, Mars surface diversity as revealed by the OMEGA/Mars Express observations, *Science* 307 (2005) 1576–1581.
- [22] Y.P. Zhang, R.A. Dawe, Influence of Mg^{2+} on the kinetics of calcite precipitation and calcite crystal morphology, *Chem. Geol.* 163 (2000) 129–138.
- [23] D.K. Nordstrom, Aqueous redox chemistry and the behavior of iron in acid mine waters, in: R.T. Wilkin, R.D. Ludwig, R.G. Ford (Eds.), *Workshop on Monitoring Oxidation–Reduction Processes For Ground-Water Restoration*, U.S. Environmental Protection Agency, Dallas, TX, 2002.
- [24] D.K. Nordstrom, J.L. Munoz, *Geochemical Thermodynamics*, Blackwell, Boston, 1994, 493 pp.
- [25] D.C. Catling, J.M. Moore, The nature of coarse-grained crystalline hematite and its implications for the early environment of Mars, *Icarus* 165 (2003) 277–300.
- [26] M.W. Schaefer, Are there abiotically-precipitated iron formations on Mars?, in: M.D. Dyar, C. McCammon, M.W. Schaefer

- (Eds.), *Mineral Spectroscopy: A Tribute to Roger G. Burns*, Geochemical Society Special Publication, vol. 5, The Geochemical Society, Houston, 1996, pp. 381–393.
- [27] G. Klingelhöfer, R.V. Morris, B. Bernhardt, C. Schroeder, D.S. Rodionov, P.A. de Souza, A. Yen, R. Gellert, E.N. Evlanov, B. Zubkov, J. Foh, E. Kankeleit, P. Gutlich, D.W. Ming, F. Renz, T. Wdowiak, S.W. Squyres, R.E. Arvidson, Jarosite and hematite at Meridiani Planum from Opportunity's Mossbauer spectrometer, *Science* 306 (2004) 1740.
- [28] S.M. McLennan, J.F. Bell III, W.M. Calvin, P.R. Christensen, B.C. Clark, P.A. de Souza, J. Farmer, W. Farrand, D. Fike, R. Gellert, A. Ghosh, T. Glotch, J.P. Grotzinger, B.C. Hahn, K.E. Herkenhoff, J.A. Hurowitz, J.R. Johnson, S.S. Johnson, B.L. Jolliff, G. Klingelhöfer, A. Knoll, Z.A. Learner, M.C. Malin, H.Y. McSween, J. Pockock, S.W. Ruff, L.A. Soderblom, S.W. Squyres, N.J. Tosca, W.A. Watters, M.B. Wyatt, A. Yen, Provenance and diagenesis of the evaporate-bearing Burns Formation, Meridiani Planum, Mars, *Earth Planet. Sci. Lett.* 240 (2005) 95–121.
- [29] T.L. Woods, R.M. Garrels, Calculated aqueous-solution–solid-solution relations in the low-temperature system CaO–MgO–FeO–CO₂–H₂O, *Geochim. Cosmochim. Acta* 56 (1992) 3031–3043.
- [30] J.P. Grotzinger, J.F. Kasting, New constraints on Precambrian ocean composition, *J. Geol.* 101 (1993) 235–243.
- [31] R.J. Spencer, L.A. Hardie, Control of seawater composition by mixing of river waters and mid-ocean ridge hydrothermal brines, in: R.J. Spencer, I.-M. Chou (Eds.), *Fluid–Mineral Interactions: A Tribute to H.P. Eugster*, Geochemical Society Special Publication, vol. 2, Geochemical Society, 1990, pp. 409–419.
- [32] J.C. Bridges, M.M. Grady, Evaporite mineral assemblages in the nakhlite (martian) meteorites, *Earth Planet. Sci. Lett.* 176 (2000) 267–279.
- [33] J.C. Bridges, P.H. Warren, M.R. Lee, Olivine decomposition features in the Y-000593 and NWA998 nakhlites, *Meteorit. Planet. Sci.* 39 (8) (2004) A18–A18 (Suppl. S).
- [34] D.C. Golden, D.W. Ming, C.S. Schwandt, R.V. Morris, S.V. Yang, G.E. Lofgren, An experimental study on kinetically-driven precipitation of calcium–magnesium–iron carbonates from solution: Implications for the low-temperature formation of carbonates in martian meteorite Allan Hills 84001, *Meteorit. Planet. Sci.* 35 (2000) 457–465.
- [35] P.R. Christensen, M.B. Wyatt, T.D. Glotch, A.D. Rogers, S. Anwar, R.E. Arvidson, J.L. Bandfield, D.L. Blaney, C. Budney, W. Calvin, A. Fallacaro, R.L. Fergason, N. Gorelick, T. Graff, V.E. Hamilton, A.G. Hayes, J.R. Johnson, A.T. Knudson, H.Y. McSween, G.L. Mehall, L.K. Mehall, J. Moersch, R.V. Morris, M.D. Smith, S.W. Squyres, S.W. Ruff, M.J. Wolff, Mineralogy at Meridiani Planum from the Mini-TES experiment on the Opportunity rover, *Science* 306 (2004) 1733.
- [36] R.E. Arvidson, F.P. Seelos, K.S. Deal, W.C. Koepfen, N.O. Snider, J.M. Kieniewicz, B.M. Hynek, Mantled and exhumed terrains in Terra Meridiani, Mars, *J. Geophys. Res.* 108 (E12) (2003), doi:10.1029/2002JE001982.