Final Report: Aqueous chemical modeling of sedimentation on early Mars with application to surface-atmosphere evolution

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Abstract

This project was to investigate models for aqueous sedimentation on early Mars from fluid evaporation. Results focused on three specific areas: (1) First, a fluid evaporation model incorporating iron minerals was developed to compute the evaporation of a likely solution on early Mars derived from the weathering of mafic rock. (2) Second, the fluid evaporation model was applied to salts within Martian meteorites, specifically salts in the nakhlites and ALH84001. Evaporation models were found to be consistent with the mineralogy of salt assemblages— anhydrite, gypsum, Fe-Mg-Ca carbonates, halite, clays-- and the concentric chemical fractionation of Ca-to Mg-rich carbonate rosettes in ALH84001. We made progress in further developing our models of fluid concentration by contributing to updating the FREZCHEM model. (3) Third, theoretical investigation was done to determine the thermodynamics and kinetics involved in the formation of gray, crystalline hematite. This mineral, of probable ancient aqueous origin, has been observed in several areas on the surface of Mars by the Thermal Emission Spectrometer on Mars Global Surveyor. The "Opportunity" Mars Exploration Rover has also detected gray hematite at its landing site in Meridiani Planum. We investigated how gray hematite can be formed via atmospheric oxidation, aqueous precipitation and subsequent diagenesis, or hydrothermal processes. We also studied the geomorphology of the Aram Chaos hematite region using Mars Orbiter Camera (MOC) images.

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1.0 SUMMARY OF RESEARCH

1.1 Scientific Objectives and Motivation

Mars is a high priority target for exploration because of its intriguing geological surface features and geochemical similarities to the Earth. The possibility that it may have harbored simple life forms early in its history (McKay et al., 1996) has, in part, reinvigorated exploration efforts. Because life requires liquid water, the consensus scientific recommendation has been to target future NASA landers and rovers at regions where there is apparent evidence of past hydrological activity and therefore the possibility of sediments and perhaps vestiges of life (e.g. Gulick (1998) and references therein). Although sedimentary minerals are prime targets, prior to this research and other research in the past few years, aquatic chemistry studies describing the detailed mineralogy of sedimentary basins and evaporites on Mars were largely restricted in the literature to a sparse selection of occasional short abstracts. Other literature dealing with aqueous processes were not very detailed in their chemistry and did not consider the more subtle chemical details (e.g. chemical complexes, different carbonates, and redox state). Most previous work concerns other issues, such as the geomorphology of basins or valleys formed by aqueous means and discussions of the total amount of CO_2 that may have been sunk as carbonate sediments (e.g. Goldspiel and Squyres, 1991) or the timescale for loss of atmospheric CO_2 (Schaefer, 1990; 1993). Given the intention of NASA's exploration efforts to focus on sedimentary environments, this project was conceived to work towards a comprehensive theoretical chemical analysis of aqueous sedimentation on early Mars. The high-level goals of this work were therefore as follows:

- To model and understand plausible sedimentary environments on early Mars in terms of the theoretical sequence of minerals using numerical aqueous chemistry simulations (e.g., What is the sedimentary mineral sequence expected from a typical solution derived from aqueously-weathered Martian igneous rocks in equilibrium with an atmosphere representative of early Mars? How might this indicate the past chemistry and composition of the atmosphere?)

- To relate the consequent understanding of sediment formation, in as much as it is possible, to the global environment and geochemical nature of Mars including its past atmosphere

This work has strong relevance to NASA's current exploration program. The Mars Exploration Rover (MER) mission has detected geochemical and sedimentological signs of evaporites on the surface of Mars. Also in the future, the MECA (Microscopy Electrochemistry and Conductivity Analyzer) experiment on the 2007 Phoenix Lander will directly measure soluble salts by mixing soil with water. The salt chemistry, relative proportions, and what they mean need to be understood with recourse to models of their origin: for example, did they come from volcanic or aqueous precursors? Similarly, any interpretation of sediments as biogenic precipitates must first take into account inorganic processes that could lead to the same mineralogy. Inorganic aqueous chemistry sedimentation processes were the focus of this research.

In part, this work addressed how the composition of the atmosphere of ancient Mars would have affected the geochemistry of surface waters and left signatures in sedimentary or evaporite deposits. The scientific motivation for this study may be summarized as follows. Our basic hypothesis was that because early Mars had liquid water, it must have produced a sedimentary record which would reflect environmental parameters such as pCO_2, temperature at the time of precipitation, rock compositions which were leached, ancient water composition, and whether the solution froze, evaporated or was ice-covered. Sediments therefore hold a key to determining the environmental conditions on early Mars, certainly locally and to some degree globally. The purpose of this work was to evaluate this hypothesis quantitatively by assessing how the early Mars environment would have been reflected in the chemistry of the sediments using numerical models.

1.2 Work accomplished

1) Martian evaporites incorporating iron minerals

The work started with the PI's modeling of Martian evaporites. Although others had previously considered the thermodynamic stability of minerals on Mars (e.g., Gooding, 1978), Catling (1999a) was the first numerical model of an evaporite sequence on Mars in a peer-reviewed journal. It was also a "first principles" model developed from scratch, because off-the-shelf models did not contain adequate iron chemistry, if indeed they contained any iron chemistry. Since then, the idea of modeling Martian evaporites has become popular and others have addressed similar problems (e.g., Bridges and Grady, 2000; Marion et al. 2003, 2004; Moore and Bullock, 1999).

Principal findings: A sedimentation model driven by sequential evaporation was used to calculate the evaporite mineral sequence in a closed basin lake subject to high pCO_2, a widely discussed atmospheric possibility on early Mars. The initial fluid was derived from weathered igneous rock similar to Martian meteorite basalts. The high pCO_2 and the presence of aqueous iron meant that siderite ($FeCO_3$) was found to be the first major carbonate to precipitate. Thus siderite was predicted to be an important facies component in ancient Martian sediments along with silica, which was also an early precipitate. These would form varves in lakes that undergo cycles of evaporation and water recharge. After silica and siderite, the sequence was magnesian calcite, nearly pure hydromagnesite, and gypsum, followed by highly soluble salts like NaCl. The presence of siderite sediments was shown to generally require an atmospheric pCO_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 pCO_2 of approximately several bar, gypsum precipitation occurred before calcite upon evaporation if the initial SiO_2:Ca^{2+} ratio was high and there was no water recharge. The PI has also contributed to the process of adding sophistication to evaporite modeling through collaboration with Giles Marion. FREZCHEM is a program that can model brine evaporation and freezing at subzero temperatures. Originally FREZCHEM did not include the complexity of the carbonate system. But appropriate carbonate and iron chemistry have now been incorporated into the FREZCHEM model to produce an evaporite/freezing model including carbonates (Marion et al., 2003).

2) *Salts in Martian meteorites*

Principal Findings. The PI found that:

- secondary minerals in Martian meteorites could have been precipitated from brines with seawater-like composition, high bicarbonate content, and acidic nature.

- the co-existence of Fe-carbonate and clays in the nakhlites suggests that the pCO_2 level in equilibrium with the parent brine may have been ~0.05 bar or more (i.e. ~10 times the present atmospheric level).
- the nakhlite and ALH84001 salt assemblages were precipitated under more reducing conditions than the ferric iron-rich Martian soil has experienced.
- the volume of carbonates in the meteorites extrapolates to a crustal abundance equivalent to 0.25 bar of CO_2 being trapped in the uppermost km of the crust.

These results were summarized in a review paper by Bridges, Catling, et al. (2001).

3) *Gray, crystalline hematite*

A low abundance of carbonate has been detected in Martian dust by the Thermal Emission Spectrometer (TES) on the Mars Global Surveyor (MGS), but TES did not find evidence for abundant evaporites. In contrast, the MER "Opportunity" rover and the OMEGA experiment on Mars Express have found abundant sulfates. The most interesting mineral deposit discovered by MGS TES during the course of this research was gray hematite. Significant deposits of such gray hematite are spectrally inferred to exist in Sinus Meridiani, Aram Chaos and Vallis Marineris (Christensen *et al.* 2000, 2001), where they cover areas of >175,000 km^2, ~5000 km^2, and 25-800 km^2, respectively. Consequently, the chemical formation of gray hematite was investigated as part of this research.

Principal Findings: In Catling & Moore (2003), we examined the geological context of Aram Chaos as well as the geochemical requirements to form gray hematite in this region. We examined the geology of Aram Chaos because we reasoned that its unique topographic relief and chaotic terrain perhaps offer more clues to the formation of the hematite than the more featureless flat terrain (as seen from orbit) of Sinus Meridiani. Much of Aram Chaos' interior is surfaced by a prominent light-toned caprock. The major exposures of this caprock appear heavily pitted and fluted in Mars Orbiter Camera (MOC) narrow angle (NA) images. In MOC NA images, the main gray hematite-bearing material appears to emerge from beneath the caprock and rarely extends more than 15 km from the last exposure of the caprock. We interpreted this relationship to infer that the hematite unit is more susceptible to erosion than the caprock. The relatively smooth texture of the caprock immediately superjacent to the hematite-bearing outcrops in Aram Chaos may be a consequence of the caprock immediately above the hematite rock being mechanically homogeneous and perhaps massive and relatively impermeable. From an examination of MOLA topography in concert with the MOC images, we also found that the hematite layer lies within a restricted stratigraphic layer within the Aram Chaos crater. Recently, Glotch and Christensen (2003) have come to the same conclusion with regard to Aram Chaos hematite stratigraphy. We proposed a hydrothermal or diagenetic origin for the Aram Chaos hematite for three reasons, described in detail in Catling and Moore (2003): (1) thermal processing at a temperature greater than about 90°C is always necessary to produce gray crystalline hematite based on geochemical thermodynamics, (2) the chaotic terrain of Aram Chaos is associated with probable geothermal melting of ground ice or the expulsion of groundwater, causing a loss of support and collapse of overlying material, (3) the restricted stratigraphic topography of the gray hematite in Aram Chaos is consistent with an ancient aquifer, which at one point, we postulate, was hydrothermally charged.

In Catling and McKay (2000) we considered the redox environment on early Mars. The basic issue is that today Mars loses hydrogen and oxygen in 2:1 ratio because of a coupling in atmospheric chemistry.

However, in the past the escape must have been different – with a greater escape rate of hydrogen relative to oxygen – because the Martian surface is net oxidized. We presented some detailed calculations in Catling and Moore (2003) to show that on early Mars, the levels of free molecular oxygen in the atmosphere would have been very low ($<10^{-12}$ bar compared to 7.8×10^{-6} bar on current Mars) given a plausible output of reducing gases from volcanoes. The implication is that the early Martian atmosphere would have been relatively hydrogen-rich, i.e. weakly reducing, which would promote hydrogen escape to space as a means to create oxidized, ferric iron on the surface of Mars. We thus linked the oxidized state of the Martian surface to the evolution of the atmosphere.

1.3 Publications and Scientific Dissemination Resulting from this Work

This research produced the following publications:

(a) Peer-reviewed papers:

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, 16,453-16,470, 1999a.

D. C. Catling and J. Moore. The nature of coarse-grained crystalline hematite and its implications for the early Martian environment, *Icarus,* 165, 277-300, 2003.

J.C. Bridges, D. C. Catling, J. M. Saxton, T. D. Swindle, I. C. Lyon and M. M. Grady, Alteration assemblages in Martian meteorites: Implications for near-surface processes, *Space Science Reviews*, 96, 365-392, 2001.

G. M. Marion, D. C. Catling, and J. S. Kargel. Modeling aqueous iron chemistry at low temperatures with application to Mars, *Geochim. Cosmochim. Acta*, 67, 4251-4266, 2003.

G. M. Marion, J. S. Kargel, D. C. Catling, and S. D. Jakubowski. The effect of pressure on complex chemical equilibria at low temperatures. *Geochim. Cosmochim. Acta,* in press.

(b) Conference abstracts and presentations:

D. C. Catling, A model for the chemical composition of early Mars evaporites: Implications for landing site selection and *in situ* analysis. In *International Symposium on the Mars Exploration Programme and Sample Return Missions*, Centre National d'Etudes Spatiales (CNES), Paris, O2/S3, 1999b.

D. C. Catling and J. M. Moore. A Case for Hydrothermal Gray Hematite in Aram Chaos, *Sixth International Conference on Mars*, July 20-25 2003, Pasadena, California, #3245

D. C. Catling and J. M. Moore. Sedimentary hematite on Mars and its implications for the early Martian environment. *32nd Lun. Plan. Sci. Conf.*, #2053, 2001.

D. C. Catling and J. M. Moore. Iron oxide deposition from aqueous solution and iron formations on Mars, *31st Lunar and Planet. Sci. Conf.*, 2000.

D. C. Catling and C. P. McKay, (Invited Keynote Talk) Aqueous iron chemistry on early Mars: Was it influenced by life? *Goldschmidt 2000 International Geochem. Conf.*, Sept 3-8, 2000, Oxford, UK, *J. Conf. Abstracts* 5, 291.

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1.4 Relevance of findings to NASA programs and the Planetary Geology and Geophysics Program

A key focus for NASA's Mars Exploration Program is the search for evidence of life, which is generally agreed to require liquid water. This work was focused on chemical processes in geology that may indicate the presence of past aqueous activity. Aqueously deposited sediments will hold important keys to the paleoclimate, paleohydrology and paleogeology of Mars. We helped contribute to unraveling this history of Mars by examining new data and presenting predictive, theoretical calculations for evaporite minerals and the formation of gray, crystalline hematite.

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