Fig. 3. The zone of compositions that would produce the 21.5–22.5% LR reabsorption upon both the second and third injections. The ionic strength of wet martian regolith is unknown; a range of 2×10^{-3} to 1.3 has been assumed. The pressure of atmospheric CO_2 trapped in the cells after loading, thermal equilibration and venting is estimated to have been 2 mbar. The pHs are the values that would be observed if 0.5 mL samples of regolith were sealed in 10 mL volumes with martian atmosphere at 6 mbar and wet with 0.5 mL of deionized H_2O at 25°C.

one would expect from consideration of the equilibria involved. Qualitatively, the addition of more liquid into the system would have two effects. First, the amount of CO_2(aq) would increase because the amount of liquid phase increases, causing a decrease in the amount of labeled CO_2(g). Second, and more important, more $MeCO_3$(s) dissolves, increasing the exchange pool and causing the fraction of the $^{14}CO_2$(g) in the gas phase to decrease.

The equilibria and the decreased responses on successive injections are described quantitatively by the (1) mass balance and (2) charge balance equations. Allowance has been made for ionic strength using assumed limits and for activity coefficients at various ionic strengths as calculated using the Davies equation. Thermodynamic equilibrium constants have been adjusted to 283 K. The effects of K_s and of the amount m_0 of soluble acid or base present in the sample are shown in Fig. 2.

There is a narrow zone of composition that will produce the observed reabsorption effect for a particular injection. The similar magnitudes of successive injection reabsorption limits the zone of acceptable compositions still further. The zones for two extreme ionic strengths are shown in Fig. 3. Since the ionic strength is unknown, compositions between these zones must also be considered as possible.

Conclusions: This theoretical analysis has been confirmed experimentally by quantitative simulations of the reabsorption effects [9]. The kinetics of the LR oxidation reaction provide additional evidence that $CaCO_3$(s) must be present.

This analysis shows that $CaCO_3$ (either as calcite or aragonite) has the correct K_{sp} to have produced the Viking LR successive injection reabsorption effects. Thus $CaCO_3$ or another $MeCO_3$ with very similar solubility characteristics must have been present on Mars. A small amount of soluble acid, but no more than 4 µmol per sample, could also have been present. We conclude that the pH of the regolith is 7.2 ± 0.1. This is the value that would be observed if 0.5 mL sample of regolith were sealed in a 10-mL volume with a martian atmosphere at 6 mbar and wetted with 0.5 mL of deionized H_2O at 25°C. The variation in pH values is very small, which is a consequence of carbonate buffering.

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THE MINERALOGIC EVOLUTION OF THE MARTIAN SURFACE THROUGH TIME: IMPLICATIONS FROM CHEMICAL REACTION PATH MODELING STUDIES.
G. S. Plumlee[1], W. I. Ridley[1], J. D. De Braal[2], and M. H. Reed[2], [1]Mail Stop 973, U.S. Geological Survey, Denver Federal Center, Denver CO 80225, USA, [2]Department of Geological Sciences, University of Oregon, Eugene OR 97403, USA.

This report summarizes results to date of the MSATT-sponsored project, "Chemical Reaction Path Modeling at the Martian Surface Through Time." We have used chemical reaction path calculations to model the minerals that might have formed at or near the martian surface (1) as a result of volcano- or meteorite impact-driven hydrothermal systems [1]; (2) as a result of weathering at the martian surface during an early warm wet climate [2,3]; and (3) as a result of near-zero [4] or sub-zero °C brine-regolith reactions in the current cold climate.

Fundamentals of Chemical Reaction Path Modeling: Computer-driven chemical reaction-path modeling [5] quantitatively predicts the changes in water chemistry, amounts of minerals precipitated or dissolved, and amounts of gases formed as the result of specified geochemical processes such water-rock reactions, fluid mixing, or fluid boiling. The modeling is based upon equilibrium chemical thermodynamics, and takes into account both chemical reactions (through equilibrium constants) and mass balance relations between all solid, aqueous, and gaseous phases in a specified

water-rock-gas system. A wide variety of reaction-path calculations can be performed to address potential variations in starting conditions and other factors that influence particular chemical processes. The chemical speciation and reaction path programs SOLVEQ and CHILLER [5,6] were used in this project.

It is important to note the limitations of the reaction-path modeling. First, the validity of modeling results are highly dependent on the quality of the thermodynamic data upon which the modeling is based. Thermodynamic data determined through laboratory experiments are generally the most accurate; experimentally derived data, especially those for reactions involving aqueous species, are best-developed at or near 25°C, are somewhat less available at hydrothermal temperatures above 50°–100°C, and are not well developed at near-zero or sub-zero °C temperatures. When experimentally derived data are not available, they are generally estimated instead by various techniques or are extrapolated from experimentally derived data at 25°C. Another limitation of the reaction-path modeling is that minerals predicted to be thermodynamically stable for a given set of geochemical conditions may not actually precipitate in nature due to kinetic factors. For example, minerals such as chalcedony, kaolinite, aluminum hydroxides, and ferrihydrite are kinetically stable and much more likely to precipitate at 25°C than thermodynamically stable quartz, illites, smectites, other aluminosilicate minerals, hematite, and goethite [7]. The relative chemical effects of such kinetic controls on mineral precipitation can be evaluated in the modeling by carrying out runs in which kinetically inhibited minerals are allowed to precipitate, and runs in which these minerals are suppressed, thereby allowing kinetically more stable but thermodynamically less stable minerals to precipitate.

Chemical Modeling of Possible Martian Hydrothermal Processes: Hydrothermal systems associated with volcanos and impact events have been proposed to play important roles in the development of the martian regolith and the valley networks [8–10]. Our chemical modeling results [1] indicate that such hydrothermal processes would produce a variety of alteration minerals and mineral precipitates that can be readily searched for using remote sensing techniques. For example, condensation of SO_2- and CO_2-rich volcanic gases in the throats of martian volcanos would probably generate highly acidic (pH < 1.5) fluids capable of altering the volcanic wallrocks to zoned silica-alunite-anhydrite-hematite-nontronite-smectite-carbonate assemblages. If the gases condensed into hydrothermal waters circulating within the volcanos, then such acid alteration assemblages could extend well away from the immediate vicinity of the volcano throats. If interactions between the hydrothermal fluids and volcanic gases were negligible, then hydrothermal systems circulating within the volcanos would alter the basaltic volcanics to quartz-pyrite-carbonate-epidote-albite alteration assemblages. Hydrothermal fluids that reacted with the regolith (such as permafrost meltwaters generated by a meteorite impact) were likely acidic (pH 3–5) and saline, and produced nontronite, anhydrite, kaolinite, Mg-smectite, Mg-chlorite, and quartz alteration assemblages within the regolith. Near-surface quenching of hydrothermal fluid outflows from impact- or volcano-driven hydrothermal systems should have produced extensive silica- and/or carbonate-rich precipitates analogous to the silica sinter and travertine terraces formed by terrestrial geothermal systems.

Chemical Modeling of Weathering in an Early Warm Wet Climate: In the reaction-path calculations modeling weathering in

an early warm wet climate [2], a range of initial water compositions was used to account for reasonable variations in ambient partial pressures of atmospheric CO_2 and O_2, and possible variations in the input of acidic volcanic gases such as SO_2 and HCl. Our results indicate that weathering processes in an early warm wet climate (temperature = 25°C) with at least some free atmospheric O would have altered basalts to mixtures of ferric and manganese hydroxides, chalcedony, kaolinite, apatite (or other phosphate minerals), dolomite, and calcite. Smectite clays are predicted to be thermodynamically stable in many of the weathering reaction paths considered; such clays may have formed if kinetic barriers to their nucleation were overcome. Acid rain (resulting either from high atmospheric CO_2 or influx into the atmosphere of acid volcanic gases such as HCl and SO_2) would have enhanced the extent of the weathering reactions and increased the proportions of minerals such as carbonates and gypsum in the weathering assemblages. Reaction paths modeling the limited evaporation of waters that had previously reacted with basalt predict the formation of gypsum, calcite, dolomite, sodium and potassium feldspars, dawsonite (a hydrated sodium-aluminum carbonate mineral), and phosphate minerals. Calculations modeling more extensive evaporation generally do not predict the precipitation of common halides such as halite or sylvite. Rather, unusual minerals such as Cl-bearing apatite (see below) or MgOHCl are predicted to form. We are currently evaluating whether the predicted lack of precipitation of halite and sylvite is geochemically and kinetically reasonable. Waters initially high in dissolved sulfate and chloride (such as acid rain) require substantially less evaporation to reach saturation with gypsum (and other readily soluble salts) than waters that derive their sulfate and chloride solely from the rocks. These results lend support to the premise that acid rain may have helped generate the high sulfate and chloride values measured in the martian regolith.

Our calculations show that weathering of P-bearing basalts would probably result in the transport of aqueous phosphate, the formation of phosphate alteration minerals such as apatite or crandallite, and the possible evaporative enrichment of phosphate in the regolith. Based on these results, we speculated in an earlier report [2] that Cl-bearing apatite could serve as a residence for chloride in the regolith. Recent infrared reflectance studies (T. V. V. King, 1992, oral communication) do not support the presence of Cl-apatite in detectable amounts in the martian regolith; however, further work is needed to evaluate if the chloride could be tied up in some other phosphate phase.

Regolith Weathering by Aqueous Solutions in a Cold Climate: We are currently modeling potential interactions of martian regolith and basaltic rocks with near-zero °C waters or sub-zero °C brines that may have been or are currently stable at or near the martian surface [3,4]. Model groundwaters at 0.1°C in equilibrium with the current martian atmospheric CO_2 and O_2 pressures are predicted to be acidic (pH 6) and oxidizing, while model groundwaters that have no contact with the atmosphere are predicted to be very alkaline (pH 11) and reducing. Calculations modeling weathering of a Shergotty basalt composition by the near-zero (0.1°C) groundwaters predict alteration assemblages that consist of Mg-nontronite, $MgCO_3 \cdot 3H_2O$, chalcedony, kaolinite, trona ($Na_3CO_3HCO_3 \cdot 2H_2O$), spurrite ($Ca_5$[$SiO_4$]$2CO_3$), potassium feldspar, alunite, and MgOHCl, in order of decreasing abundance. If the nontronite and potassium feldspar were kinetically inhibited from precipitating, then the alteration

assemblages are predicted to contain abundant Fe-, Mn-, and Al-hydroxides in addition to the dolomite, chalcedony, and kaolinite. Subsequent evaporation of the groundwaters after reaction with basalt is predicted to form, with progressive evaporation, dolomite, $MgCO_3*3H_2O$, apatite (or other phosphate minerals), calcite, dawsonite, and gypsum. Halite and sylvite are not predicted to form, even with extensive evaporation. Reactions of the regolith with groundwaters near 0°C are predicted to result in acidic waters and alteration assemblages containing abundant Fe- and Al-hydroxides (or smectites), Mn-hydroxides, and kaolinite.

The portion of the project in which we model sub-zero brine-regolith interactions has required extensive modifications to the computer programs that carry out the reaction-path calculations and the thermodynamic database that serves as the basis for the calculations. Modeling calculations below 0°C are still in progress.

Summary: Although the chemical reaction-path calculations carried out to date do not define the exact mineralogical evolution of the martian surface over time, they do place valuable geochemical constraints on the types of minerals that formed from an aqueous phase under various surficial and geochemically complex conditions. Based on these results, we believe that further chemical reaction-path modeling efforts are needed as new remote sensing data and other lines of evidence are acquired on possible surficial mineralogies. By integrating such geochemical modeling calculations with remote sensing studies, more realistic and geochemically valid models for the evolution of the martian surface through time can be developed.

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CONTROLS ON THE CO_2 SEASONAL CYCLE. J. B. Pollack[1], F. Forget[1,3], R. M. Haberle[1], J. Schaeffer[2], and H. Lee[2], [1]NASA Ames Research Center Moffett Field CA 94035-1000, USA, [2]Sterling Software, Inc., Palo Alto CA, USA, [3]University of Paris, FRANCE.

The meteorology experiment on the Viking landers carried out accurate measurements of the surface pressure over the course of several martian years [1]. These data show substantial variations in pressure on seasonal timescales that are characterized by two local minima and two local maxima. These variations have widely been attributed to the seasonal condensation and sublimation of CO_2 in the two polar regions. It has been somewhat of a surprise that the amplitude of the minimum and maximum that is dominated by the CO_2 cycle in the north was much weaker than the corresponding amplitude of the south-dominated extrema. Another surprise was that the seasonal pressure cycle during years 2 and 3 of the Viking mission was so similar to that for year 1, despite the occurrence of two global dust storms during year 1 and none during years 2 and 3.

We have attempted to model the observed seasonal pressure variations with an energy balance model that incorporates dynamical factors from a large number of general circulation model runs in which the atmospheric dust opacity and seasonal date were systematically varied [2,3]. The energy balance model takes account of the following processes in determining the rates of CO_2 condensation and sublimation at each longitudinal and latitudinal grid point: solar radiation, infrared radiation from the atmosphere and surface, sub-surface heat conduction, and atmospheric heat advection. Condensation rates are calculated both at the surface and in the atmosphere. In addition, the energy balance model also incorporates information from the GCM runs on seasonal redistribution of surface pressure across the globe, a process that has very little effect on CO_2 condensation and sublimation per se, but which can alias surface pressure measurements at local sites.

Numerical experiments with the energy balance model show that the following factors make important contributions to the seasonal pressure variations measured at local sites: albedo and emissivity of the seasonal CO_2 polar caps, topography of the polar regions, atmospheric heat advection, and seasonal redistribution of the surface pressure. The last factor contains contributions from seasonal variations in atmospheric dynamics and from scale height changes in the presence of topography. The model-derived values of cap emissivity may contain an influence from CO_2 ice clouds that are particularly prevalent in the north during its fall and winter seasons [4]. Atmospheric dust influences each of the above factors, albeit in different ways. For example, atmospheric heat transport to the poles rapidly increases as the dust opacity increases from 0 to 1, but then tends to approach an asymptotic value. We suggest that the similarity of the seasonal CO_2 cycle between years with and without global dust storms may reflect this type of saturation effect. Indeed, runs with the energy balance model performed using Viking-lander-measured opacities during years 1 and 2 [5] tend to substantiate this hypothesis.

We have used estimates of the surface temperature of the seasonal CO_2 caps [4] to define the infrared radiative losses from the seasonal polar caps. This information implicitly incorporates surface topography, a quantity that is poorly known in the polar regions. We have been able to closely reproduce the seasonal pressure variations measured at the Viking lander sites. Our best models are characterized by a lower cap emissivity in the north than in the south. We attribute this difference to the influence of CO_2 ice clouds [4]. According to our calculations the reduced amplitude of the north-cap-influenced pressure extrema, when compared to that of the south-cap-influenced extrema, are due to the following: lower cap emissivity in the north (due to a greater frequency of CO_2 ice clouds in the north), greater heat advection during northern winter when the dust opacity is elevated, and a larger amplitude to the seasonal pressure redistribution during northern winter when the dust opacity is higher. Opposing these factors is a lower CO_2 ice temperature in the south due to its higher elevation.

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