INTRODUCTION: Mineralogical constraints can be placed on the martian surface by assuming chemical equilibria among the surface rocks, atmosphere and hypothesized percolating groundwater. We have initiated a study of possible martian surface mineralogy, as modified by the action of aqueous alteration, using the EQ3/6 computer codes [1]. These codes calculate gas fugacities, aqueous speciation, ionic strength, pH, Eh and concentration and degree of mineral saturation for complex aqueous systems. Thus, these codes are also able to consider mineralogical solid solutions. These codes are able to predict the likely alteration phases which will occur as the result of weathering on the martian surface. Knowledge of the stability conditions of these phases will then assist in the definition of the specifications for the sample canister of the proposed martian sample return mission.

MODELING: In our modeling we assumed that 1) all chemical reservoirs were in equilibrium, 2) the initial composition of the martian surface is adequately modeled by the mineralogy of the Shergotty meteorite [2-3] and 3) water was available to react with the rocks. The initial conditions are given below.

ATMOSPHERE: \( p_{O_2} = 10^{-5} \), \( p_{CO_2} = 10^{-2.2} \), \( pH_2O = 10^{-5} \), \( p_{N_2} = 10^{-4} \), \( P_{total} = 0.01 \ atm \)

WATER: \( 25^\circ C \), dissolved \( CO_2 = 10^{-3.3} \) m, dissolved \( O_2 = 10^{-7.7} \) m [4]

ROCKS: The modal mineralogy of the Shergotty meteorite [2-3]

These computer codes model a process of reacting solid mineral phases with a constant volume of solution. Thus, the "titrated" rocks will initially dissolve and then, as saturation of various components is reached, new phases precipitate. The codes have been operated in two modes; in the "closed" mode early-precipitated phases are free to re-equilibrate with later phases and solutions as the reaction proceeds, whereas in the "open" mode precipitating phases are removed from further reaction with the system. Thus, the latter operational mode more nearly resembles the action of a transient aqueous fluid while the former mode resembles a stagnant system.

Because of the lack of the requisite thermochemical data for minerals at temperatures below \( 0^\circ C \), these models were run for a temperature of \( 25^\circ C \). This figure is above the average martian surface temperature (\( \sim -23^\circ C \)), but within the range of values modeled by Viking IRTM data (\( -143 \) to \( 7^\circ C \)) [5]. The results presented here will be applicable to materials at lower temperatures, however, since aqueous alteration due to the action of "unfrozen water" has been documented well below \( 0^\circ C \) [6]. Obviously the rate of aqueous alteration would be the greatest at the highest temperatures, where liquid water would be more available and reaction rates faster. On Mars this would be in the mid to low latitudes in the spring and summer [5].

RESULTS: The results of the "closed" and "open" modeling modes were essentially identical, and are summarized in Figure 1. The alteration phases which form are shown along the vertical axis. The horizontal axis indicates (in a logarithmic scale) the percent of rock which has reacted at the point at which each alteration phase precipitates and, for some phases, redissolves. Narrow lines indicate where a mineral precipitates, and a wide line indicates where a mineral predominates among the precipitating phases.
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Lines pinch out where a mineral re-dissolves. The nontronite is more accurately a mix of ~88% Ca-Mg nontronite and ~12% beidellite. The calcite actually contains ~7% magnesite and <1% siderite.

DISCUSSION: Hematite and gibbsite are calculated to precipitate only during the earliest stages of aqueous alteration, re-dissolving as alteration proceeds. The obvious red coloration of martian fines, however, implies Fe³⁺ oxide pigmentation and indicates that compositional evolution was more complex than allowed by this single-stage model. No sulfates or chlorides are predicted to precipitate because the starting rock composition did not provide sufficient concentrations of these species. Nontronite is a dominant weathering phase in this model, which is consistent with some interpretations of the Viking XRF results [7]. Alteration to this smectite-dominated assemblage requires at least 0.1% reaction. However, unless degrees of alteration exceed approximately 0.01%, clay products should be dominated by nontronite and kaolinite, in contrast with the smectite-like composition inferred from Viking results. It is also interesting to note that if no more than approximately 0.5% of available rock is subjected to aqueous alteration carbonates should not form. Alteration to approximately 0.1-0.5% completion can apparently yield nontronite without carbonates. The subsequent behavior of the predicted alteration phases upon drying is beyond the scope of this simple model. Nevertheless, this model indicates that nontronite can form in cold non-saline environments, quite unlike the hot, saline environments which are characteristic of its most well-known terrestrial environments [8].


HEMATITE
GIBBSITE
NONTRONITE
KAOLINITE
QUARTZ
CALCITE
DAWSONITE

0.001 0.01 0.1 1 10 100
PERCENT OF ROCK REACTED WITH WATER
PHASE PRECIPITATES
PHASE PREDOMINATES

FIGURE 1