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Jarosite as an indicator of water-limited chemical weathering on Mars

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The Mars Exploration Rover Opportunity identified the ferric sulphate mineral jarosite and possible relicts of gypsum at the Meridiani Planum landing site¹. On Earth, jarosite has been found to form in acid mine drainage environments, during the oxidation of sulphide minerals², and during alteration of volcanic rocks by acidic, sulphur-rich fluids near volcanic vents³. Jarosite formation is thus thought to require a wet, oxidizing and acidic environment. But jarosite on Earth only persists over geologically relevant time periods in arid environments because it

rapidly decomposes to produce ferric oxyhydroxides in more humid climates⁴. Here we present equilibrium thermodynamic reaction-path simulations that constrain the range of possible conditions under which such aqueous alteration phases are likely to have formed on Mars. These calculations simulate the chemical weathering of basalt at relevant martian conditions. We conclude that the presence of jarosite combined with residual basalt at Meridiani Planum indicates that the alteration process did not proceed to completion, and that following jarosite formation, arid conditions must have prevailed.

The occurrence of sulphate alteration phases in martian meteorites^{5,6} and previous observations of significant concentrations of sulphur at the Viking⁷ and Pathfinder⁸ landing sites support the recent Mars Exploration Rover (MER) evidence that sulphur has played an important role in Mars' surface geochemical processes. Atmospheric sulphur released by volcanic outgassing^{9,10} appears to have been incorporated into the regolith through aqueous alteration or solid–gas interactions to produce sulphur-bearing phases^{11–14}. Analyses of Viking and Pathfinder Lander data indicate that sulphur observed in Mars' regolith is probably associated with magnesium sulphate salts^{6,15}. However, early thermodynamic simulations predicted iron sulphates to be the most likely phases to form at Mars' surface conditions. It should be noted that in this previous model iron sulphates were thought to form from solid–gas alteration of troilite and pyrrhotite, not through aqueous alteration processes¹⁶. Two models have been presented to account for the salts observed in the surface materials. The first assumes that early Mars was warm and wet, creating salty oceans that later evaporated, leaving behind evaporite minerals¹⁷. The second suggests that the sulphur phases formed relatively recently as a result of 'acid fog' reacting with surface materials to form secondary salts¹¹.

Equilibrium thermodynamic reaction-path simulations that constrain the range of possible conditions under which aqueous alteration phases are likely to form are presented here. Using the numerical thermodynamic reaction-path model REACT¹⁸ we have simulated chemical weathering of basalt at Mars-relevant conditions. The results provide a basis for interpreting the geochemical history of acidic chemical weathering on Mars. In these equilibrium models, a given quantity of a basaltic mineral assemblage¹⁹ consisting of diopside, enstatite, ferrosilite, K-feldspar, anorthite, albite, fayalite, forsterite and magnetite is titrated into 1 litre of aqueous fluid containing variable concentrations of sulphate and trace amounts of Na⁺, K⁺, Ca²⁺, Fe²⁺, Mg²⁺, Al³⁺ and dissolved SiO₂. The model includes kinetics only through the suppression of mineral phases unlikely to form in a geologically relevant time period. Suppression of mineral phases is done at the discretion of the operator based on the feasibility of such minerals forming as initial chemical weathering products under wet, oxidizing, low-temperature conditions, as recommended by the author of the modelling package¹⁸. Phases suppressed in the models include epidote, phlogopite, muscovite, K-feldspar, andradite, annite, minnesotaite, greenalite, phengite, tremolite, haematite, goethite and nontronite. In acid mine drainage environments, goethite is the thermodynamically stable phase but it is rarely observed. Rather, the metastable phases jarosite and ferric hydroxides occur in this environment because goethite (and haematite) formation rates are very slow^{4,18}.

The model system is charge-balanced with H⁺, and is buffered by current martian atmospheric oxygen and carbon dioxide fugacities²⁰ at 298 K and 10⁴ Pa total atmospheric pressure. Although CO₂ fugacity may have been greater early in Mars' geologic history, increasing CO₂ fugacity has little effect on jarosite stability. However, photolysis of CO₂ to form O₂ would have resulted in higher atmospheric oxygen fugacity than at present, expanding the pH range over which jarosite would form. The temperature used in the models (298 K) is higher than current martian surface conditions (average 220 K). If the weathering fluids at Meridiani Planum were

approximated by the system $H_2O-FeSO_4$, liquid water could have been stable to temperatures as low as 271.3 K, or as low as 211 K if the fluid were an aqueous sulphuric acid solution²¹. The REACT model is only valid along the liquid–vapour curve for water, from 273 K to 573 K. A temperature of 298 K was used in the models because the thermodynamic data are more complete at this temperature. A few models were run at 273 K for comparison, with no obvious differences from those run at 298 K. The difference in pressure between the model conditions and current atmospheric pressure on Mars (~600 Pa; ref. 22) is likely to have little effect on the thermodynamic properties of the aqueous–solid system²³. Some phases observed on the martian surface today (such as anhydrite and haematite) were probably produced by later dehydration of salts and clays. By varying the fluid composition and water:rock mass ratio, we have constrained the range of conditions at which ferric sulphates are likely to form on Mars.

Alteration assemblages containing ferric sulphate (a Na-end member jarosite phase and/or K-end member jarosite) always include a SiO_2 phase (probably amorphous or microcrystalline when precipitated) and an amorphous iron hydroxide phase (Fig. 1). The minimum concentration of sulphate in aqueous solution required to produce a ferric sulphate phase is of the order of 10^{-5} molal, and the oxygen fugacity of the system must be greater than 10^{-50} . Sodium concentrations $>10^{-7}$ molal are required to produce Na-jarosite (the ferric sulphate phase predicted to precipitate in greatest abundance), while potassium concentrations must exceed 10^{-11} molal to precipitate K-jarosite. The ubiquitous presence of SiO_2 in the alteration assemblages suggests that the widespread high-silica signature observed in Mars' surface thermal emission spectra²⁴ represents secondary silica coatings on surface materials.

Under most conditions jarosite is also accompanied by kaolinite (although kinetics may favour the formation of its polymorph halloysite²⁵ or amorphous allophane²⁶) and gypsum. For gypsum to form, calcium concentrations greater than 10^{-3} molal are required. Subsequent lower humidity levels would probably dehydrate gypsum to form anhydrite, facilitating physical weathering of alteration rinds. This dehydration process may also alter jarosite to less hydrous ferric sulphates and alter iron hydroxides to haematite. Dolomite and calcite are also predicted to form in most models, while dawsonite and the zeolite clinoptilolite are also predicted to form in some cases when initial sulphate concentrations are varied.

The water:rock ratio does not affect the weathering path through E_h –pH space (bold line in Fig. 2), but reaction progress along this path is controlled by the amount of water available to react with the rock (symbols on bold line in Fig. 2). The initial sulphate-rich fluid has a pH of 1. However, the fluid pH increases as the basalt is weathered. This results in the precipitation of jarosite and gypsum

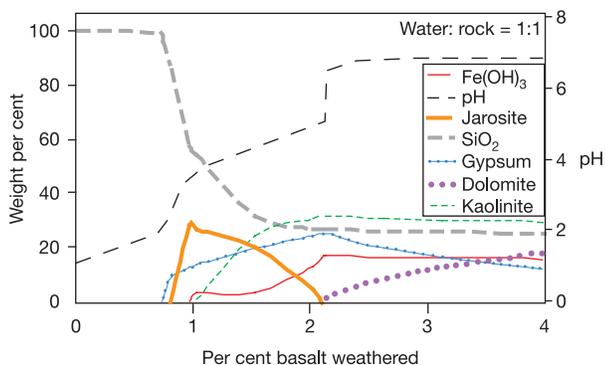


Figure 1 Predicted alteration minerals, reported as weight per cent of alteration assemblage at a water:rock ratio of 1:1. Note that jarosite is only stable during the very earliest stages of basalt weathering.

early in the weathering process. Jarosite becomes unstable and is replaced by other Fe-bearing phases in the alteration assemblage as weathering proceeds and pH increases (Figs 1 and 2). The final pH of the system (as defined by that point at which the fluid is in equilibrium with the mineral assemblage present) increases with decreasing water:rock ratio, thus moving the extent of the reaction farther along the weathering path into the iron hydroxide + gypsum field. As a result, the presence of jarosite within alteration assemblages can be used as an indicator of the extent of chemical weathering at Mars' surface conditions. It is only possible for jarosite to form and remain stable if the alteration process is arrested after only a few per cent of basalt weathering occurs.

As the water:rock ratio is decreased, jarosite is formed earlier in the chemical weathering process (>80% of basalt must weather to produce jarosite at water:rock = 100:1, while <20%, <2% and <0.2% of basalt must be weathered at water:rock = 10:1, 1:1 and 1:10, respectively). This suggests that jarosite may form in two ways: (1) from the complete reaction of a large quantity of water with a small amount of rock, that is, a large amount of water altering only a thin outer layer of rock; or (2) from a small amount of water partially weathering a large quantity of rock. In both cases, water must be removed from the system (probably via evaporation) in order to arrest the alteration process before the weathering fluid pH increases and is no longer in the jarosite stability field. This in turn suggests that the weathering rind formed in a geologically short period of time. However, the presence of gypsum without accompanying jarosite would indicate that chemical weathering was extensive, allowing sufficient interaction with the basalt to raise the pH of the weathering fluid beyond the jarosite stability field.

Thermodynamic simulations indicate that reaction of acidic aqueous fluids with basalt under oxidizing conditions produces jarosite and gypsum. However, for jarosite to survive in the

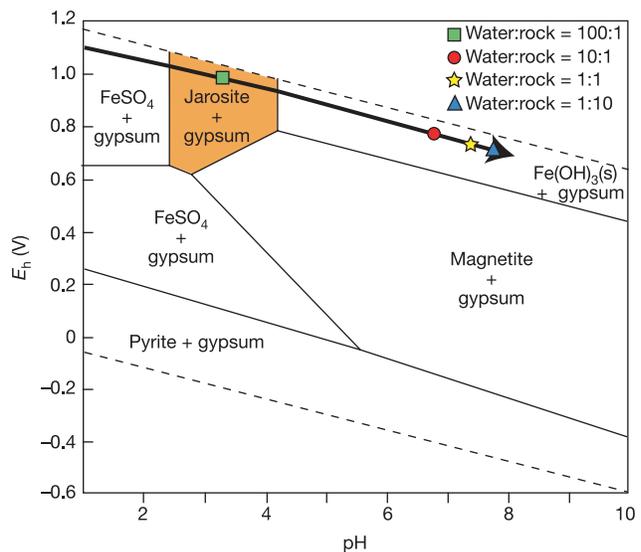


Figure 2 E_h –pH phase diagram of the Fe–S–Ca–Na– HCO_3 – H_2O system at 298 K. Activities of SO_4^{2-} , Ca^{2+} and Na^+ are set at 10^{-2} , 10^{-2} and 10^{-3} , respectively. The dashed parallel lines represent the upper and lower bounds on water stability. The bold line at the upper left of the diagram shows the reaction path followed during weathering of basalt by sulphate-bearing aqueous fluids, buffered by the present martian atmosphere. Symbols on this line represent the extent of the reaction corresponding to different water:rock ratios, as shown in the key at upper right. As the reaction path moves to higher pH, it passes through the jarosite + gypsum stability field. However, if pH continues to rise with increased weathering of the basalt, the reaction path moves out of the jarosite stability field, resulting in dissolution of jarosite and reprecipitation as other ferric iron-bearing minerals in the alteration assemblage. Therefore, observations of jarosite would suggest a short-lived period of water-limited aqueous alteration.

weathering assemblage, alteration must have ceased well before the basalt had been significantly weathered (Fig. 1) and subsequent conditions must have remained dry. This suggests that liquid water was only active at the Opportunity landing site in Meridiani Planum for a geologically short period of time. Thus, while other studies indicate that liquid water was present for a relatively long period of time early in Mars' history¹⁷, its distribution must have been spatially variable. Alternatively, the jarosite observed at Meridiani Planum may have formed later in Mars' history during periods of transient liquid water stability; such conditions could have resulted from extremes in orbital obliquity²⁷ and/or large additions of volatiles to the atmosphere from volcanic eruptions²⁸ or bolide impacts²⁹. In any case, the occurrence of residual (unweathered) basalt along with jarosite requires that liquid water was only present for a limited period of time at this location.

On the basis of thermodynamic simulations, one possible chemical weathering scenario for the Meridiani Planum site is that, as weathering proceeded, the weathering fluids were incorporated into hydrated phases (that is, the rocks literally absorbed the water to form hydrous phases) while simultaneously evaporating. The evaporated water would have over time been lost from the atmosphere by photolytic decomposition, reprecipitated as ice at the poles, or consumed by further weathering rind formation in subsequent periods of aqueous alteration. The lack of liquid water eventually 'stalled' the chemical weathering process early in its history, leaving jarosite or other ferric sulphates as stable alteration phases within the partially weathered basalt. Continued water loss from the planet's atmosphere by photolytic decomposition gradually reduced the relative humidity to levels where hydrous phases exposed to the atmosphere could dehydrate, producing haematite and anhydrite from iron hydroxides and gypsum. Subsequent physical erosion and transport of such alteration rinds may have produced the globally distributed salty fines enriched in sulphur that have been observed at the Viking and Pathfinder field sites³⁰. □

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No enhancement of fusion probability by the neutron halo of ⁶He

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Quantum tunnelling through a potential barrier (such as occurs in nuclear fusion) is very sensitive to the detailed structure of the system and its intrinsic degrees of freedom^{1,2}. A strong increase of the fusion probability has been observed for heavy deformed nuclei³. In light exotic nuclei such as ⁶He, ¹¹Li and ¹¹Be (termed 'halo nuclei'), the neutron matter extends much further than the usual nuclear interaction scale. However, understanding the effect of the neutron halo on fusion has been controversial—it could induce a large enhancement of fusion⁵, but alternatively the weak binding energy of the nuclei could inhibit the process⁶. Other reaction channels known as direct processes (usually