

MARTIAN FLUIDS THAT PRODUCED SALT ASSEMBLAGES IN MERIDIANI ROCKS AND IN MARTIAN METEORITES: A COMPARISON. M. N. Rao¹, L. E. Nyquist², S. J. Wentworth¹, D. H. Garrison¹, J. S. Herrin¹ and S. Sutton³, ¹ESCG-Jacobs, NASA, Johnson Space Center, Houston. TX. 77546, ²ARES, NASA, Johnson Space Center, Houston. TX. 77546, ³Department of Geological Sciences, University of Chicago, Chicago. IL.

Introduction: Secondary salt assemblages containing sulfates, chlorides, and carbonates of Mg, Ca and Fe are ubiquitously found as fracture-filling materials in crevices and voids of Martian meteorites [1-3]. Somewhat similar salts (sulfates and chlorides but no carbonates) are inferred to be occurring in rocks and soils at Meridiani, Gusev and Pathfinder based on APXS results [4 -7]. Mössbauer spectrometer on Opportunity detected jarosite and other poorly crystalline Fe-mineral phases at Meridiani [8]. During mineralogical mapping of Mars' surface by MGS-TES, gray hematite was found at Meridiani by [9]. At Meridiani Planum and Valles Marineris, Mg- and Ca-sulfates were detected by OMEGA EXPRESS [10]. Several models have been proposed to explain the formation and distribution of aqueously altered minerals as fracture-fills in Martian meteorites [2,3,11] and in rocks and soils analyzed during different Mars Missions [6,7,12-14]. Studies of major anions in the secondary mineral assemblages likely provide clues for understanding the nature and conditions of the Martian fluids that gave rise to these salts, whereas studies of major cations- (such as Ca, Mg, Fe and Na) compositions could throw light on the nature of rocks and soils with which these Martian fluids chemically-interacted, dissolved and mobilized the constituent mineral phases [15]. Based on mobile anion (SO_3 , Cl and Br) abundances determined by Opportunity APXS in RAT rocks at Meridiani, we present a model for salt-formation and deposition by progressive evaporation of fluids infiltrating into rocks/outcrops at Endurance, Fram and Eagle craters and compare the resulting fluid compositions with those deduced earlier from studies on salt assemblages trapped as fracture filling materials in nakhlite and shergottite meteorites [16-20]. Here, we suggest that aqueous activity was the norm rather than exception near Mars surface based on geochemical evidence obtained from the salt assemblages in Martian meteorites (recent) and from the salt deposits in Meridiani rocks (ancient).

Sulfate, Cl and Br abundance data by APXS for rocks and soils at Meridiani and Gusev are from [4-6] and from the PDS data base. The mobile element abundances in secondary mineral assemblages in nakhlites and in GRIM glasses in shergottites are from [11, 16-20].

Results and Discussion:

Sulfate – Chloride systematics in Meridiani solutions: Sulfate and chloride abundances determined for Meridiani RAT rocks are plotted as SO_3/Cl (ordinate) vs Cl (abscissa) in Fig. 1 for 20 rocks/outcrops from Eagle, Fram and Endurance craters. The data from Gusev Plains and Columbia Hills RAT rocks are also plotted in Fig. 1. For purposes of comparison, the mobile element data for iddingsites and carbonates in nakhlites and for GRIM (gas-rich impact-melt) glasses in shergottites [20] are also plotted in Fig.1. Note that the nakhlite data points plot close to X-axis whereas the shergottites data points plot close to Y-axis in Fig.1.

As the solutions bearing conservative elements undergo evaporative concentration in a closed basin, they can generate a linear array of concentrations. The concentrations of conservative ions in the solutions increase in such a way that their ratios remain constant as water is removed from the system [21]. That is, in the case of conservative elements, when we plot an element (e.g. Cl) along the ordinate and the ratio (e.g. SO_3/Cl) along the abscissa , the data points yield a hyperbolic distribution if both Cl and SO_3 are fully conserved [21,22].

The data points for the Meridiani RAT rocks in Fig.1 plot into a sausage-shaped curved field approximating a hyperbolic distribution. Using this relation between SO_3/Cl and Cl in secondary mineral assemblages deposited in sedimentary rocks at Meridiani, the data could be fitted to an equation of the type $(\text{SO}_3/\text{Cl})_m = a / (\text{Cl})_m + b$, which defines a hyperbola when the x-variable is $(\text{Cl})_m$. The numerical values of "a" and "b" define the position and the curvature of the best-fit hyperbola [21,22]. This relation, in principle, is transformable into a straight line by plotting the X-coordinate as the inverse of the Cl abundance i.e. $1 / (\text{Cl})_m$. In this case, the above hyperbola - equation is transformed into an equation of the type $(\text{SO}_3/\text{Cl})_m = ax + b$ which corresponds to a straight line with slope "a" and intercept "b" on the Y –axis [21,22]. The underlying assumption in this methodology is that the interacting species behave conservatively with respect to each other. This inverse relation between SO_3/Cl and Cl remains linear when the compositions of the resulting sulfate and chloride salt assemblages are not modified by random processes after the deposition of a given mineral phase. To examine the validity of the relationship between these two species, the SO_3/Cl

ratios for Meridiani RAT rocks are plotted against $1/\text{Cl}$ in Fig.2. An equation is fitted to the data yielding a regression line with $r^2 = 0.97$. The goodness of the fit for the data points indicates that neither the chloride contents nor the sulfate /chloride ratios in the deposited salt assemblages had undergone any disturbance after they were originally deposited at the Endurance crater (Karatepe-west / Burns formation). This inverse correlation further justifies that SO_3 and Cl behave as conservative mobile ions in the aqueous system at Meridiani. This kind of relation between SO_3 and Cl could be best maintained if the solutions at Meridiani were acidic in character.

Evaporation Model: Early on, sedimentary rocks (sandstones) near Endurance, Fram and Eagle craters at Meridiani presumably formed from sulfate/chloride salts and siliclastic materials resulting from aqueous interactions of fluids with basaltic rocks in this region and subsequently the altered mineral components were deposited by aeolian activity at these sites [13,23]. The chemical compositions of the salt assemblages determined by APXS in the rocks/outcrops at the Karatepe-West and Burns formations seem to provide evidence for interactions with two kinds of solutions. One solution is referred to as SOL-I which is sulfate-high, chloride-low and bromide-high and it is fairly acidic in nature. The second one is SOL-II which is chloride-high, sulfate-low and bromide-low and it is weakly acidic. The SOL-I and SOL-II solutions may correspond to fluids in the 3rd and 4th water-influx events (presumably from the ground water-table) in the diagenetic model for the Burns formation by McLennan et al.[12]. Depending on the fluid/rock ratio, secondary minerals formed at reaction sites are locally mobilized and left behind after dessication / precipitation.

Evolution of solution I and brine I in rocks above Whatana contact: When the SOL-I solutions infiltrated into the Meridiani sedimentary rock/outcrop complex up to the rim-top of Endurance crater, they dissolved the already-existing CaSO_4 (gypsum?), FeSO_4 (melanterite?) and MgSO_4 (epsomite?) and other chlorides in these sandstones and partially mobilized them locally. On equilibration with dissolved solutes after diagenetic alteration, SOL-I solutions became enriched in Ca-, Mg-, and Fe- bearing phases and evolved into a new brine-I. This SOL-I could be similar to the solutions in the 3rd – influx event in the McLennan et al. [13] model where the water level rose up to the surface at Endurance crater. On progressive evaporation of brine-I at Endurance crater, sparingly-soluble gypsum/anhydrite and less soluble melanterite are successively deposited from one evaporation step to another leaving behind the residual solutions rela-

tively enriched in highly soluble Mg-bearing sulfate and chloride phases. When the residual brines percolate into the adjoining sedimentary rock fractures/crevices and dessicate (when the water level starts falling gradually during progressive evaporation), the resulting salts yield lower CaO/MgO and FeO/MgO ratios compared to those in the previous step. As the evaporation progressed, these elemental oxide ratios thus decreased from one evaporation step to another from the top-rim of the Endurance crater down to the Whatanga diagenetic contact. Furthermore, these results suggest that the CaO/SO_4 and FeO/SO_4 ratios in these solutions (SOL-I) at the start of evaporation are <1, as expected based on operation of the “geochemical divide” principle in these evaporating solutions [24].

Evolution of solution II and brine II in rocks below Whatanga contact: Sometime after the first aqueous-fluid infiltration event involving SOL-I, a second infiltration event involving SOL-II solutions seems to have taken place into the outcrop complex at Karatepe-West/ Burns formation in Endurance crater. At that time, the SOL-II solutions, instead of rising to the rim-top of the crater as in the case of SOL-I, rose only up to an intermediate level named Whatanga diagenetic contact [13,23]. At and below this level, SOL-II fluids presumably interacted with the salts and siliclastic materials already occurring in fracture zones of sedimentary outcrops/rocks by partly dissolving, remobilizing and recrystallizing the constituent mineral components, leading to significant diagenetic alteration. As a result, SOL-II solutions have evolved into a new brine-II, whose composition is different from that of brine-I, discussed above. In this case, the SOL-II fluids are SO_3 -low and Cl-high relative to SOL-I. Further, brine-II solutions seem to be weakly acidic compared to brine-I. It appears that the weakly acidic (relatively high pH) SOL-II solutions did not dissolve and remobilize the sparingly-soluble CaSO_4 and less soluble FeSO_4 salts already existing from an earlier generation in the sedimentary rock layers below the Whatanga contact. Instead, the SOL-II solutions seem to have dissolved highly soluble Mg-bearing phases (sulfates and chlorides) and allowed them to equilibrate with other dissolved solutes. Thus, the brine-II fluids became enriched in Mg-sulfate and chloride bearing phases and remained relatively unaltered with respect to Ca-and Fe-bearing phases. As the brine-II fluids underwent progressive evaporation and became more and more concentrated, MgSO_4 started precipitating sequentially from one evaporation step to another on the rocks below the Whatanga contact (refer to Fig.5 of [6]). This decreasing trend of MgO abundance in these rocks from one evaporation step to another sug-

gests that the MgO/SO_4 ratio is <1 in the brine-II fluids before the onset of evaporation, according to the “chemical divide” principle operating in these solutions [24]. As the CaO and FeO contents in the sedimentary rocks from the earlier episode of salt deposition are not significantly altered, the lower and lower MgO contents deposited from these evaporating solutions will result in higher and higher CaO/MgO and FeO/MgO ratios in the rocks below the Whatanga contact.

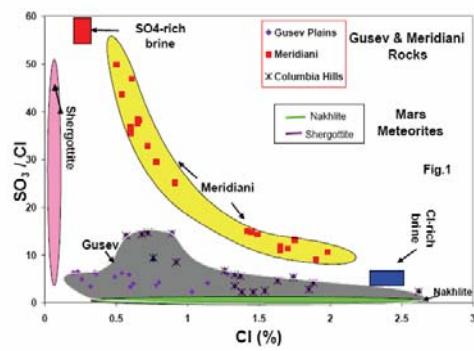


Fig.1. SO_3/Cl versus Cl (APXS) in rocks from Meridiani and Gusev (Columbia Hills); GRIM (gas-rich impact-melt) glasses from Shergotty, EET79001 Lith A and B and secondary salts in Nakhla & Lafayette fracture zones (EMPA/SEM). MER data are for RAT rocks only. Note that nakhelite data plot close to the X-axis whereas the shergottite data plot close to the Y-axis. The Whatanga contact separates the lower and upper part of hyperbola.

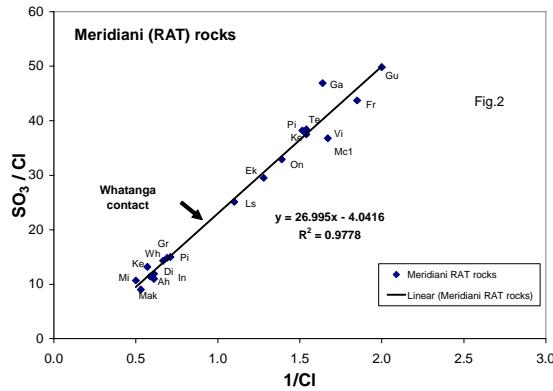
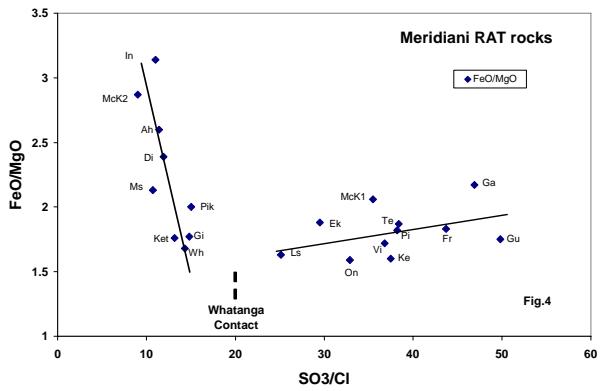
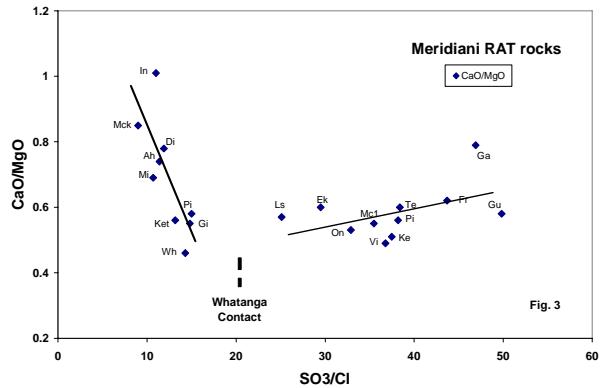


Fig.2. SO_3/Cl versus $1/\text{Cl}$ plot for Meridiani RAT rocks. The hyperbolic distribution in Fig.1 is trans-

formed into a regression line with $r^2 = 0.97$. The rock nomenclature is taken from Clark et al.[6].



Figs. 3 and 4. SO_3/Cl vs CaO/MgO and FeO/MgO ratios in RAT rocks from Karatepe-west / Burns formation in Endurance crater. CaO/MgO and FeO/MgO ratios decrease as the SO_3/Cl ratios decrease from the rim-top down to the Whatanga contact in the stratigraphic section preserved at Karatape-West / Burns formation in Endurance crater. These observations suggest that the CaO/SO_4 and FeO/SO_4 ratios in the parent solutions above Whatanga contact before the onset of evaporation is likely to be <1 . However, in rocks below the Whatanga contact, these ratios systematically increase as the SO_3/Cl ratio continues to decrease. This is perhaps due to the fact that in these rocks MgSO_4 is precipitated from the evaporating solutions as pointed out by [6]. These results suggest that in the evaporating solutions below Whatanga contact, the MgO/SO_4 ratios are likely to be <1 and the CaO and FeO abundances in the sedimentary rocks remained unaltered during the second event. This is possible if the solutions in the second event remained only weakly acidic (relatively high pH).

Evolution of Chlorine-Bromine ratios in the brines:

Cl and Br also behave as conservative tracers in Martian fluids [11]. This inference is based on the results obtained by comparing halogen abundances determined in salt-assemblages in nakhelite fracture-filling materials using EMPA/SEM and APS Synchrotron-Microprobe techniques [11,19]. Salt assemblages in Nakhla yield high Br and low Cl/Br ratios suggesting salt deposition from relatively concentrated fluids belonging to late stages in a progressive evaporation sequence.

As in the case of the SO₃-Cl system for Meridiani rocks (Fig.2), we plot Cl/Br vs 1/Br (Fig.5) for the same RAT rocks above the Whatanga contact at Endurance. The data fit to regression line with $r^2 = 0.94$ indicating that Cl/Br inversely correlates with Br. These observations provide support for the progressive evaporation scenario discussed above. Further, this chemical affinity is similar to that observed between sulfate and chloride in the solutions that interacted with the rocks above the Whatanga contact. However, occurrence of little Br in rocks below the Whatanga contact shows that brine-II fluids may be different from brine-I.

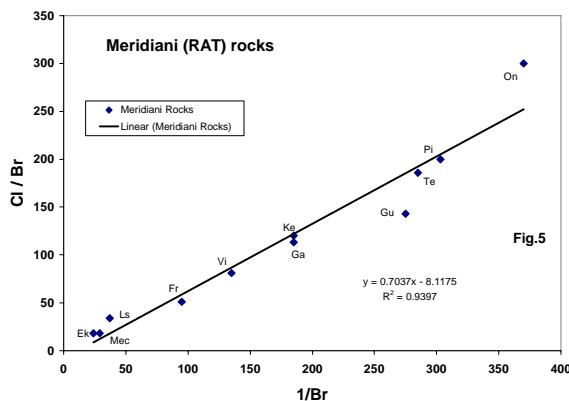


Fig.5. Cl/Br vs 1/Br plot for rocks above the Whatanga contact in Endurance crater at Meridiani. The Br abundance for rocks below the Whatanga contact is below the detection limit. The rock nomenclature is same as given in [6].

CONCLUSIONS:

a) Brines (SOL-I) that interacted with sedimentary rocks above Whatanga contact in Endurance crater at Meridiani are SO₃-high, Cl-low and Br-high in composition. These solutions are fairly acidic.

b) Brines (SOL-II) that interacted with rocks below Whatanga contact are SO₃-low, Cl-high and Br-low relative to SOL-I. These solutions are weakly acidic.

c) Excellent regression line-fits for Meridiani rock data indicate that these solutions had undergone pro-

gressive evaporation with little disturbance after their formation at the Endurance crater.

d) In these brines, the sulfate, chloride and bromide anions behaved as conservative tracers.

e) The GRIM glasses in shergottites show that their constituent minerals are produced from solutions which are SO₃-high and Cl-low in composition, as discussed earlier [11,18,20]. These solutions seem to be similar to SOL-I fluids at Meridiani.

f) The iddingsites and carbonates in nakhellites indicate that they might have formed from SO₃-low and Cl-high solutions, as discussed earlier [11,18,20]. These solutions may be similar to SOL-II fluids at Meridiani.

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