EVAPORATIVE EVOLUTION OF MARTIAN BRINES BASED ON HALOGENS IN NAKHLITES AND MER SAMPLES. M. N. Rao[1] , S. R. Sutton[2] and D. S. McKay[3], [1]Lockheed Martin, Johnson Space Center, Houston. TX. 77058, [2]Department of Geophysical Sciences and CARS, University of Chicago, Chicago. IL. 60637, [3]ARES, Johnson Space Center, Houston. TX. 77058.

Introduction: We have recently reported the Cl and Br abundances determined by APS X-ray Microprobe and EMPA analyses of secondary aqueous minerals in Nakhla veins and discussed the significance of Cl – Br correlations with respect to the evolution of brine solutions on Mars [1,2]. In that study [2], we suggested that the low Br concentration (~10 ppm) in Lafayette Iddingsite [3] is indicative of early stage of evaporation during progressive evolution of Martian brine solutions, which is, in turn, consistent with the petrographic evidence of early deposition of salt sequence of carbonate-sulfate- and no halite [4,5] in Lafayette. We showed that the high Br concentrations of ~240 ppm in secondary salts in Nakhla veins similarly indicate late stages of evaporation in evolving Martian brine solutions which is again consistent with petrographic evidence of late stage deposition of salt sequence i.e. carbonate-sulfate-halite in Nakhla [4,5]. When sea water evaporates under equilibrium conditions, the most insoluble carbonates (siderite and calcite) deposit first, followed by sulfates (gypsum and anhydrite) and finally the water-soluble halides are precipitated when the water content is sufficiently low [6]. In the present study, we make a detailed comparison of Cl/Br ratios in secondary minerals in nakhlites with those in MER soils and rocks at Gusev and Meridiani and show that the compositions of solutions that inundated Lafayette iddingsite (early stage) and Nakhla veins (late stage) include the range of solution-compositions that gave rise to a variety of secondary salts at Gusev and Meridiani sites. Further, the results obtained here suggest that two kinds of brine solutions (one, late and the other, early or intermediate stage) seem to have inundated most of the rocks and soils to varying degrees and precipitated the secondary salts at Meridiani and Gusev sites.

Brines and halogens : Chlorine and bromine are known to be conservative tracers in sea water. Br usually does not form minerals of its own and, instead, is coprecipitated with chloride salts. Because of large differences in the natural abundance of Cl and Br, relatively small changes in the abundance of Br in a sample will give rise to large variations of Cl/Br ratios. During the evolution of a brine solution, the concentrations of Cl and Br increase as water is removed from the solution. Their elemental concentrations follow a linear progression such that the Cl/Br ratios remain constant, until chlorine begins to precipitate as an insoluble compound. Continued evaporation depletes the solution in Cl, but allows the concentration of Br to increase in the residual solutions. In evaporative deposition, though Cl and Br concentrations indicate the progression of evaporation in brines, prior to halite saturation, the Cl/Br ratios in brine solutions are more diagnostic in tracing the source of water from which the evaporites are being precipitated [6,7].

Results and Discussion: In Fig.1, we plot the Cl/Br ratios versus Cl concentrations for Nakhla salt veins [1,2], Lafayette iddingsite [3] and MER soils and rocks at Gusev and Meridiani sites by Spirit and Opportunity APXS instruments [8,9]. The Br measurements by APXS on MER soils and rocks [8,9] have errors ranging from ~10% (for high Br samples) and >80% (for low Br samples); and those by APS X-ray Microprobe in Nakhla salt veins (this study); and those by INAA in Lafayette iddingsite [3] have errors of ~30%. The halogen compositions of Gusev and Meridiani soils and rocks plot between the Cl/Br ratios determined for Lafayette iddingsite /Adirondack (Cl/Br ~280) and Nakhla /Dells Hi-Ho (Cl/Br ~20) representing early and late stages of evaporation respectively. This range is almost entirely covered by samples from each rover site where the early and late deposition samples at Meridiani are represented by Guadalupe (~120) and Dells Hi-Ho (~10) as well as Adirondack (~230) and Mazatzal (~10) at Gusev respectively. In general, the compositions of these rocks in Fig.1 tend to separate broadly into two groups, one with high Cl/Br ratios of 120-280 and the other with low Cl/Br ratios of 10-60 (large errors in the data do not permit us to meaningfully split them into further sub-groups). Further, Gusev soils, because of low Br contents, have high Cl/Br ratios. On the other hand, Meridiani soils such as HemaTrench 1, Trenchwall 2 and PHOTIDO Plains yield low Cl/Br ratios of ~25, similar to the rocks. The compositions in the lower part of Fig.1 seem to indicate that the low Cl/Br ratios correspond to late or more evolved brine solutions, whereas the high Cl/Br ratios in the upper part of the figure correspond to early or relatively less evolved brine solutions.

In the case of Nakhla, brine solutions at late stage of evaporation (low Cl/Br) seem to have inundated the rock (though for a short time [4]) and percolated into the rock fractures. In order to retain this highly evolved signature, desiccation needs to took place within the rock in a semi-closed system so that water is

expelled from the fractures without fractionation of Cl and Br. Salts produced in this way would have high Cl (and Br) concentrations whereas our analyses yield much lower concentrations. Thus our analysis volume in Nakhla veins must include other halogen-poor phases (such as silicates) to dilute the concentrations, but not change the ratio. This mixing ratio would vary from fracture to fracture within a single rock even though the brine composition was homogeneous. Similarly, the variations of the Cl contents in MER samples, given on the x-axis in Fig.1, may be largely due to variations in the mixing ratios of salts and silicates (which act as a diluent) in the sample volume where APXS is making measurements on MER samples.

An interesting feature of the MER halogen data set is the range of Cl/Br ratios exhibited by some weathered rock surfaces after different treatments such as "brush" and "RAT". Mazatzal (Gusev) shows the largest variation in Fig.1. Two "as-is" measurements (TX and OR, different locations) yield values of 220 and 120 (with large errors). The brush (NY) analysis was ~90, whereas RAT-1 and RAT-2 were 20 and 10 (small errors) respectively. These results indicate an apparent progression of interaction with solutions from early (or intermediate) stage at the surface to late stage in the interior of the weathered rock. The "as-is" analyses are of a light colored weathered rind consistent with the average Gusev soil ratio whereas the RAT analyses are more representative of the deposits from the late stage or highly evolved brine solutions at this site. Furthermore, Humphrey also shows this progression similar to Mazatzal, though less pronounced. One interpretation of this could be that the rock experienced an initial exposure to a highly evolved brine which penetrated deeply into the rock surface, followed by a later exposure to less evolved solutions which only affected areas close to the top most surface ("as-is"). However, in the case of Meridiani rock surface rinds (McKittrick, Flat Rock and Dells Hi-Ho), the halogen data yield low Cl/Br ratios (small errors) in both "as-is" and "RAT" measurements indicating that most of the Meridiani rocks(except for Guadalupe) were exposed to late stage or highly evolved brine solutions for sufficiently long time. In contrast, the rocks at Gusev seem to have been exposed to brine solutions belonging to both early (and intermediate) and late stages of brine evolution at different time periods.

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Figure Caption: Cl/Br versus Cl plot for secondary mineral assemblages in Nakhla veins [1.2], Lafayette Iddingsite [3] and MER soils and rocks at Gusev and Meridiani sites as given by Spirit and Opportunity APXS instruments [5,6]. Thick dashed lines are arbitrarily drawn to indicate approximate regions of high Cl/Br (large errors) and low Cl/Br (small errors) ratios, which correspond to early (or relatively less evolved) brine solutions and late (or highly evolved) brine solutions at these Martian sites. Thin solid lines connect data points from different areas of Mazatzal and Humphrey rocks and Nakhla veins. Also, they join various soils from Gusev. The individual numbers correspond to Meridiani samples, 1) GudalupeRAT, 2) FlatRock, 3) Trench wall, 4) Trench floor, 5) McKittrick, 6) McKittrick RAT, and 7) Dells Hi-Ho. Error bars are not shown in the figure to maintain clarity. (ai, for as-is; br,-for brush; r,-for rat).