

MARTIAN BRINES: CLUES FROM SULFUR AND CHLORINE IN SALTS FROM SOME MARTIAN METEORITES AND MER SAMPLES. M. N. Rao¹, D. S. McKay², S. J. Wentworth¹ and D. H. Garrison¹, ¹Jacobs-ESCG, NASA Johnson Space Center, Houston, TX. 77058 (sitarao@sbcglobal.net), ²AERS, NASA Johnson Space Center, Houston, TX. 77058 (david.s.mckay@jsc.nasa.gov).

Introduction: For studying the aqueous alteration records in rocks and soils on Mars, halogens and sulfur seem to be better suited [1]. The coupling and decoupling of these mobile elements such as S and Cl in salt-bearing mineral assemblages in Martian meteorites and MER samples are complex partly due to leaching and deposition of sulfates and chlorides by brine solutions on Mars. While reviewing the extensive Martian meteorite data, Treiman [2] noted that the differences between the alteration materials in nakhlites and shergottites are great enough to suggest the occurrence of two different altering fluids on Mars. Here, we explore selected nakhlites, shergottites and Meridiani samples to decipher the nature of these brines by studying the distribution of S and Cl abundances in salts produced from fluids that interacted with the regolith materials on Mars.

Results and Discussion: NAKHLITES: We analyzed several veins in Nakhla olivines bearing iddingsite and carbonates as fracture-filling materials by EMPA and SEM/EDS techniques. Typical results are: Iddingsite [Cl:1.43%(ave), range 0.75-3.06%; SO₃: 0.18% (ave), range 0-0.46%] and Carbonates (Fe-carb, Fe-Mn-carb, Fe-Mg-carb) [Cl: 1.5% (ave), range 0.51- 2.23%; SO₃: 0.7% (ave), range 0.1-0.26%]. The errors in Cl are small whereas the errors in SO₃ values are relatively large (2σ). Gooding et al. [3] used a different approach to study S and Cl abundances in Nakhla salts. They pyrolyzed the interior Nakhla sample (.369) and analyzed the evolved Cl (Cl & HCl) and S (oxidized SO₂ and reduced S₂ & H₂S) components using quadrupole mass-spectrometric methods. The total Cl released amounted to 0.4-0.5% in this sample, whereas the total S varied between 0.05-0.08%. During pyrolysis of .369, they noticed a one-to-one correspondence between the release of Cl and Na in the temperature interval 850-1050 °C (NaCl decomposition), followed by monotonic release of Cl at >1300 °C probably due to the decomposition of refractory Cl-bearing phases such as Cl-apatite or merrillite.

In iddingsite and carbonate bearing veins in Nakhla, sulfur seems to be subordinate to the dominant chlorine abundance. Because iddingsite does not contain major concentrations of S, its formation probably did not occur by the oxidation of indigenous FeS. Instead, it appears that iddingsite is a silicate alteration product formed through the action of fluids enriched in halides [4,5].

Nakhlites presumably originate from relatively deep subsurface regions in Martian megaregolith [6] and it is likely that the salts preserved in the fracture zones in Nakhla precipitated from aqueous fluids within that subsurface environment. If this inference is valid, it appears that the aqueous fluids that gave rise to the alteration products in Nakhla might represent chlorine-rich and sulfate-poor subsurface brines on Mars.

SHERGOTTITES: In contrast to the poorly shocked nakhlites, the shergottites show evidence of heavy shock. In some shergottites, sizeable impact-produced glass pockets containing large abundances of Martian atmospheric volatiles occur. These glasses consist of molten Martian regolith [7] and are known as GRIM (Gas- Rich, Impact -Melt) glasses. They contain assemblages of secondary alteration products produced from brine solutions that permeated the basaltic rocks and soils on Martian regolith [8,9]. We studied these GRIM glasses (.77; .78; .18; .20; .506; .153 in EET79001) by EMPA and SEM/EDS techniques. In some, we found relatively large abundances of SO₃ and CaO which are somewhat positively correlated (r²=0.6) with each other suggesting the occurrence of CaSO₄ [7]. This inference is consistent with the direct findings of ~10 μm needles and laths of CaSO₄ (gypsum/ anhydrite) trapped in these GRIM glasses during impact-melting of porous regolith materials at EET790001 site on Mars [8,9].

Below, we examine the correspondence between S (as sulfate) and Cl (as chloride) in GRIM glasses from two shergottites, EET79001 and Shergotty. In the case of EET79001 GRIM glasses (mentioned above), the SO₃ abundance varied from ~0.3 to 2.0 % (it is ~0.4 % in Lith A). The Cl abundance varied from 0.02 to 0.05% (~ thousand sites rastered). While measuring Cl, precautions were taken using a defocused electron beam to avoid volatility effects (also cross checking for epoxy). As in the case of nakhlites, Gooding et al. [3] also studied two shergottite GRIM glasses for S and Cl abundances using similar techniques. They pyrolyzed a GRIM glass (EET79001,180) belonging to the parent glass pocket (.27) from which our sample (.77) was also generated using continuous heating techniques, and analyzed the evolved gases by quadrupole mass-spec methods. They found high abundance of S (0.134% as SO₂ and 0.131% as S₂+H₂S). However, the Cl content is below the detection limit.

The S - Cl trend observed by us in the subsample ,77 is in agreement with that found by Gooding et al. [3] in subsample ,180 using pyrolysis techniques. During pyrolysis of another subsample ,234, belonging also to parent (,27), Gooding et al.[3] found small amounts of HCl and Cl in the temperature interval 800-1100 °C (NaCl decomposition) and high abundance of S ($\text{SO}_2 + \text{S}_2 + \text{H}_2\text{S}$) similar to that in ,180. Several of these GRIM glasses in EET79001, LithA seem to yield high sulfur and low Cl (as NaCl) abundances. In contrast to Lith A, a GRIM glass ,507 in LithB yielded a SO_3 abundance as high as 18% (average ~11%; range 1 to 20%) showing an excellent positive correlation with FeO [10]. This result indicates that some Fe-hydroxysulfate (jarosite?) compound produced by acid-sulfate weathering on Mars regolith materials was trapped in this GRIM glass during impact. The ,507 glass yields a Cl abundance of only ~0.1 to 0.2% suggesting that GRIM glasses in LithB also yield high S and low Cl abundances as in the case of LithA. Similarly, in another shergottite, Shergotty, GRIM glass inclusions (,DBS a-c) which are chemically similar to ,507 from EET79001, LithB also yielded high SO_3 and low Cl abundances during EMPA/ SEM studies. Typical results are (a) 4% SO_3 (ave), range 2.2-4.4%; 0.02% Cl (ave), range 0-0.5%, (b) 2.6% (ave), range 2.0-3.9%; 0.12% Cl (ave), range 0.06-0.17%, and (c) 0.72% SO_3 (ave), range 0.19-0.26%; 0.16% Cl (ave) range 0-0.25%. In Shergotty, the GRIM glasses also yielded high sulfur and low Cl abundances as in the case of EET79001, Lith A & B.

Shergottites presumably originate from shallow surface regions in Martian megaregolith ~180 Ma ago [6]. Furthermore, it appears that the Rb-Sr isotopic data for these GRIM glasses in EET79001 are consistent with their host-rock (Lith A & B) crystallization ages [11]. If salts such as CaSO_4 and Fe-hydroxy sulfate (jarosite?) were precipitated from surface fluids on Mars and trapped in GRIM glasses during incipient melting of the regolith materials by impact [12], results for GRIM glasses suggest that the surface brines were sulfate-rich and chloride-poor.

MER SAMPLES: At Meridiani Planum, the rover Opportunity found large abundances of SO_3 (~21% (ave), range ~17 to 26%) in samples from stratigraphic locations A to G in Endurance crater and in some from Eagle and Fram [13]. But the Cl in samples from stratigraphic locations between A and K-East amounted to only ~0.5% yielding a SO_3/Cl ratio of ~40 to 50. On the other hand, samples from K-East to Gm showed Cl abundance of ~1.5%, yielding a SO_3/Cl ratio of ~15. A possible explanation for the observed elemental fractionation in Meridiani samples could be, according to Kargel [14]: First, an acid-

sulfate brine (high SO_3/Cl) permeated the laminated volcanic tuff, and precipitated a sequence of impure Mg, Ca and Fe-sulfates and a different chloride-rich brine (low SO_3/Cl) later infiltrated into the same area and redissolved and mobilized some of the more soluble sulfates, such as MgSO_4 . It appears that this acid-sulfate fluid is sulfate-rich and chloride-poor, whereas the chloride brine is chloride-rich and sulfate-poor as found in the case of nakhlite and shergottite samples.

ALTERING FLUIDS: Subsurface fluids and crustal heat sources drive hydrothermal systems on Earth producing two types of aqueous fluids: (a) neutral-chloride type (high Cl with low S/Cl ratios) or (b) acid -sulfate type (high sulfate with high S/Cl ratios) [15]. It is possible that similar processes might have occurred on Mars under favorable conditions back in time [16,17]. Neutral chloride type fluids might have interacted with nakhlites, whereas acid-sulfate type fluids might have reacted with shergottites and Meridiani samples in the near surface environment on Mars. In addition to these hydrothermal fluids, volcanic aerosols [18] similarly interact with regolith materials on Mars producing fractionation between sulfate and chloride in these salts. The chemical reactions with these fluids presumably took place at low water/rock ratios and low temperatures <120 °C. It is likely that selective mobilization by Martian fluids (under different pH conditions) seem to have produced the observed sulfate - chloride fractionation in nakhlites, shergottites and MER samples. However, more detailed studies are needed to quantify these inferences.

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