EVIDENCE FOR INCREASING AND CORRELATED HALITE AND FLUORITE DURING MT. SHARP ASCENT FROM THE SAMPLE ANALYSIS AT MARS INSTRUMENT SUITE. P. D. Archer, Jr.[1], C. R. Webster[2], J. V. Clark[3], A. E. Hofmann[2], G. J. Flesch[2], P.-Y. Meslin[4], O. Forni[4], Amy C. McAdam[5], and H. B. Franz[5], [1]Jacobs, NASA Johnson Space Center, Houston, TX 77058, doug.archer@nasa.gov, [2]Jet Propulsion Laboratory, Pasadena, CA, [3]Geocontrols, NASA Johnson Space Center, Houston, TX, [4]IRAP, Université Toulouse 3, CNRS, Toulouse, France, [5]NASA Goddard Space Flight Center, Greenbelt, MD.

Introduction: The Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) rover Curiosity has detected increasing HF and HCl, and a strong correlation between the two, in drilled samples as the rover ascends Mt. Sharp. These data are further evidence of increasing lake salinity or evaporite deposits as the rover moves upsection and is also evidence for co-precipitation of Cl and F-bearing salts.

The MSL rover landed on Mars over 9 years ago and is currently at the boundary of the clay-sulfate transition as mapped from orbit, posited to be caused by a shift in environmental conditions at the time of sediment deposition [e.g. 1]. The SAM instrument suite includes two ovens that can heat a sample to ~850 °C and the gases evolved from the sample are monitored directly with a quadrupole mass spectrometer (QMS) in evolved gas analysis (EGA) mode and a pre-selected portion of the gas can be sent to either the Tunable Laser Spectrometer (TLS) or a trap for subsequent gas chromatograph/mass spectrometry (GCMS) analysis. The TLS was designed to measure C, O, and H isotopes from CO_2, H_2O, and CH_4 but it was discovered that there are other gases (such as HF and CH_3Cl) that can be measured because some of their absorption lines fall within the spectral window of the TLS detectors. For this work, we focus on the detection of HCl by EGA and HF detected by the TLS.

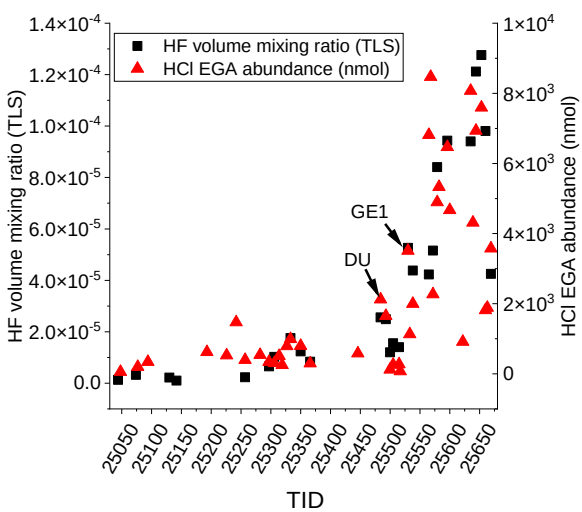

Fig 1 – HF volume mixing ratio (vmr) from the TLS (black squares) and nmol HCl from EGA (red triangles) plotted vs. SAM TID (test identification number). The Duluth and Glen Etive samples are labeled. Note that TLS data are not collected in every run (TLS and GCMS are mutually exclusive at this point in the mission due to power constraints) which is why there are more red than black points in figure 1.

Data: Beginning with the Duluth sample collected immediately below the Vera Rubin Ridge, then continuing with the Glen Etive sample, the first collected in the Carolyn Shoemaker formation, the HF and HCl abundances measured by SAM have increased significantly above what had been seen in samples earlier in the mission (figure 1). Furthermore, there is a clear correlation between the HF detected by the TLS and the HCl detected by EGA (figure 2).

Of the post-DU runs, only two samples have evidence of oxychlorine compounds such as perchlorate or chlorate (the Rock Hall and Edinburgh samples, TID 25505 and 25572, respectively). Therefore, chloride salts are the most likely candidates for the source of the increased HCl seen in recent samples. The HF could be from fluorite, fluorapatite, or other F-bearing minerals associated with chlorides, an area still under investigation.

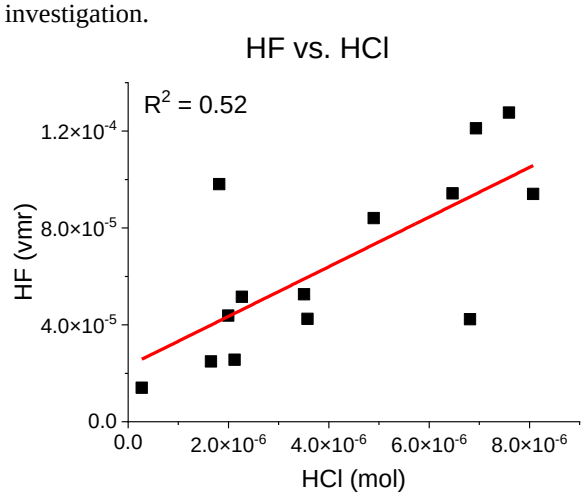

Fig 2 – plot of HF vmr from TLS vs. mol HCl from EGA for Duluth through Zechstein samples (black) with a linear fit (red) that has an R^2 value of 0.52.

Interpretation: The detection of increasing HCl and HF are interesting for at least two reasons. First, they confirm the increasing detections of Cl-bearing compounds by ChemCam [2, 3] and APXS [4] in the same region and the detection of halite in the Quela (and potentially a more recent) sample by the CheMin X-ray

diffraction instrument on MSL [5]. While SAM and CheMin analyze different portions of the same drilled sample, SAM has lower detection limits and these data show that the halite detected by CheMin in drilled samples is likely present in many other samples, but below CheMin detection limits. Furthermore, since drill locations have been selected to be vein-free bedrock, the Cl-bearing salts detected by SAM could be in the bedrock fabric, not in later-stage veins formed by subsequent aqueous alteration (however, drilling through small veins is fairly common so veins cannot be ruled out as a potential salt source).

Second, the correlation of HCl and HF seen in SAM data is an interesting observation that could provide insight into evaporite composition. Terrestrial data indicate that while Cl and Br covary across a wide range, Cl and F only correlate at elevated Cl concentration [6]. Fluorite and fluorapatite have also been detected previously by ChemCam and CheMin [7, 8]. To investigate the source of the HCl/HF detected by SAM, we have run halite and fluorapatite samples in SAM-like EGA instruments. Thus far, we have seen HCl releases from halite consistent with SAM results, but have not detected HF, which is not surprising because our EGA instruments are much less sensitive to HF than the TLS due to interferences with H_2O fragments in the mass spectrometer.

Conclusion: These data indicate increasing amounts of Cl and F-bearing salts as MSL traverses up Mt. Sharp. This is consistent with current models for sediment deposition in Gale Crater where higher elevations experience more drying events. These drying events lead to salts either precipitating out in pore spaces before or during lithification, or the formation of evaporites which were later reworked by subsequent aqueous alteration, and the salts would have been concentrated in veins that are ubiquitous throughout the Mt. Sharp sequence explored to date. SAM data are suggestive of Cl and F salts in the bedrock, consistent with previous data from ChemCam that support salts in both the bedrock and veins, so this is further evidence that both are likely in Mt. Sharp strata.

References: [1] Milliken R. E. et al. (2010) *Geophysical Research Letters, 37*. [2] Meslin P. Y. et al. (2022) *LPS LIII, this conference.* [3] Thomas N. H. et al. (2019) *Geophysical Research Letters, 46*, 10754-10763. [4] Gellert R. et al. (2022) *LPS LIII, this conference.* [5] Achilles C. N. et al. (2020) *Journal of Geophysical Research: Planets, 125*, 8, e2019JE006295. [6] Worden R. H. (1996) *Mineralogical Magazine, 60*, 259-274. [7] Forni O. et al. (2021) *LPS LII,* Abstract #1503. [8] Nachon M. et al. (2017) *Icarus, 281*, 121-136.