VOLATILE ELEMENT EVOLUTION IN THE MARTIAN CRUST. COMMUNICATIONS WITH THE MARTIAN SURFACE AND ATMOSPHERE? M. Neuman[1], A. Gargano[2], C.K. Shearer[2,3,4], K. Wang[1], Z. Sharp[3], K. Ziegler[2], J. Simon[5]. [1]Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University in St. Louis, St. Louis, MO 63130; [2]Dept. of Earth and Planetary Science, University of New Mexico, Albuquerque, NM 87131; [3] Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131; [4]Lunar and Planetary Institute, Houston TX 77058; [5]NASA Johnson Space Center, Houston, TX 20771. (mdneuman@wustl.edu, cshearer@unm.edu)

Introduction: A variety of features, "pods" or "pockets" and veins of impact produced "glasses" are observed in martian meteorites (e.g., EETA79001, Tissint, LAR 06319). Lithology C from EETA79001 has been examined by many previous studies and the origin of this glassy lithology has been long debated [e.g., 1-11]. Lithology C is an assemblage of individual pods and thin, interconnecting, veins [6], and consists of finely intermingled dark brown to black glassy and cryptocrystalline materials. The cryptocrystalline component consists of quench textures (e.g., pyroxene), mixtures of partially melted relict grains and post-melting reaction products [4,9-11].

Lithology C contains high concentrations of rare gasses and has rare gas ratios (e.g.,$^{84}Kr/^{132}Xe$, $^{40}Ar/^{36}Ar$, $^{129}Xe/^{132}Xe$) similar to those measured by the Viking spacecraft on Mars [12,13]. The I_{Sr} in lithology C is heterogeneous [14]. Excess ^{36}Ar and ^{80}Kr has been attributed to high neutron irradiation of Cl- and Br-rich martian soil that has been incorporated into EETA79001 by impact processes [4].

Here, we explore the variation in halogens (Cl, F, Br, I), moderately volatile elements (K, Cu, Zn), and their isotopic ratios (Cl, K, Cu, Zn) in lithology C. These data are used to test models for the origin of this lithology: (a) impact melting of martian soil [e.g., 1-5], (b) impact melting of host rock lithology A,B [e.g.,6-8], or (c) impact melting of partially weathered portions of the host rock [9]. Most of these elements and isotopes have been measured on lithology A and B. Lithology C should be different if it contains remobilized martian soil. If this lithology represents a martial soil fraction the stable isotope compositions provide a view of interactions between the martian atmosphere and crust and potentially soil-forming processes on the martian surface (e.g., 4, 12,13, 15-19). Additionally, this work tests the models for Cl isotope reservoirs proposed by [5,15,18 20-22] and models for the stability of ClO_4, ClO_3, and NO_3 on the martian surface and their effect on Cl isotope fractionation [5,15,18]. Results also have implications for the Cl isotopic composition of the Solar System [21].

Analytical Approaches: Sample EETA 79001,764 represents a "glassy" lithology C sample collected from a newly exposed face of martian meteorite EETA 79001 (Fig. 1). It is adjacent to olivine-bearing lithology A. The sample had a mass of 452 mg and was split among different labs at the University of New Mexico, Washington University in St. Louis, and the Johnson Space Center for analysis. Analytical approaches follow that of [23] for major and trace elements, [24] for halogens, [20,21] for Cl isotopes, [e.g., 25] for triple O isotopes, and [23, 26-28] for the isotopes of K, Cu, Zn.

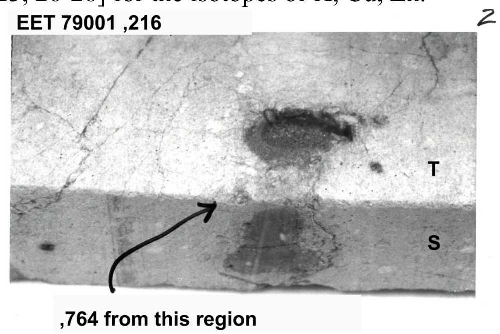

Fig. 1. Location of sample EET 79001,764 (from JSC Antarctic Meteorite Curation 2021).

Results: *Bulk rock analyses*: Much like previous analyses of lithology C, the bulk rock analysis of this sample has many characteristics of lithology A. For example, it has a Mg#, Ni, Co, that overlaps with previous lithology A analyses. However, it does have a higher normative plagioclase abundance than A. The REE pattern parallels that for lithology A and B although at slightly lower concentrations. In addition, the pattern has a slight positive Eu anomaly suggesting that it has an excess plagioclase component compared to lithologies *A,B.*

Halogens: Fluorine, Cl, Br, and I were analyzed. The values for the water soluble component (WSC) are F= 0.9 ppm, Cl= 40.0 ppm, Br= 0.017 ppm, and I=0.011 ppm. The values for the solid bulk component (SBC) are F= 117 ppm, Cl= 131 ppm, Br= 0.153 ppm, and I=0.175 ppm. Based on previously published analyses of lithology A and B, ratios such as Cl/Br, F/Cl, and Br/I for lithology C are distinct.

Oxygen isotopes: Triple oxygen isotope measurements were made on three sample splits. The $\delta'^{18}O$ (‰ V-SMOW) is plotted against $\delta'^{17}O$ (‰ V-SMOW) in Fig. 2. These lithology C data plot within the field of most martian meteorites. The exception is NWA 7034, reputed to represent a lithology that partially evolved on the martian surface. NWA 7034 is displaced from all other martian meteorites.

Chlorine isotopes: The SBC Cl concentration measured is 131 ppm with a $\delta^{37}Cl_{SMOW}$ of +0.86 ‰. This value is compared to martian meteorites in Fig. 3 and is distinct from lithology A.

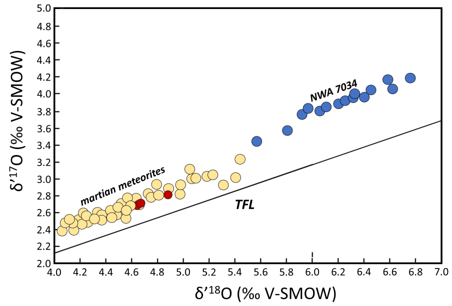

Fig. 2. Plot of δ'^{18}O (‰ V-SMOW) against δ'^{17}O (‰ V-SMOW) for EETA79001 lithology C (in red). Other martian meteorites are plotted in yellow, whereas unique martian meteorite NWA 7034 is plotted in blue. The terrestrial fractionation line (TFL) is shown. NWA7034 data and shergottite compilation from [17].

Potassium isotopes: The K concentration measured was 280 ppm with a $\delta^{41}K_{SRM\ 3141a}$ of –0.81‰. A comparison to other martian meteorites is in Fig. 4. It is significantly different from EETA 79001A and other martian meteorites previously measured [26].

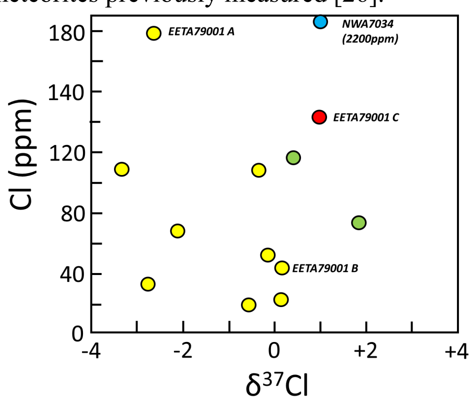

Fig. 3. δ^{37}Cl versus Cl ppm for the three EETA79001 lithologies, shergottites (yellow), Nakhlites (green) and surface breccia NWA 7034 (blue) [20-22].

Copper isotopes: The Cu concentration measured was 10.3 ppm with a $\delta^{65}Cu_{SRM\ 976}$ of –0.15‰. To our knowledge, this is the first Cu isotope measurement made on a martian meteorite.

Zinc isotopes: The Zn concentration measured was 53.5 ppm with an isotopic composition of $\delta^{66}Zn_{JMC\ Lyon}$ = +0.34‰, $\delta^{67}Zn_{JMC\ Lyon}$ = +0.51‰. and $\delta^{68}Zn_{JMC\ Lyon}$ = +0.69‰. These values are compared to other martian meteorites in Fig. 5, and they are nearly identical to those of EETA 79001A [28].

Discussion: Most of the major and trace element abundances of the studied glass pod are very similar to the host lithology A and therefore do not require the involvement of a soil component. The possible S [6-8] and plagioclase component excesses in lithology C are best explained by the preferential mobilization of Fe-sulfide and plagioclase from the host-lithology during impact. This is consistent with Zn isotope data which illustrates similarity between lithologies A and C. However, this relatively simple model does not account for the K and Cl isotope data, the halogens, and previously measured δD [29]. These differences between A and C imply the addition of a water-soluble surface component added to lithology A that was partitioned into the lithology C melts during its formation through impact melting.

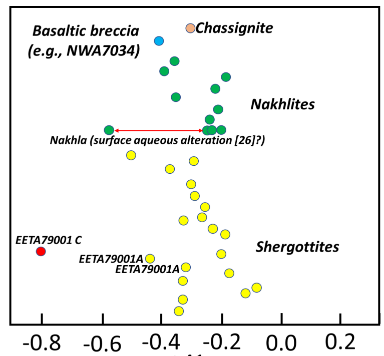

Fig. 4. δ^{41}K for EETA79001 C compared to other martian meteorites [26]. Variation observed in Nakhla had been attributed to surface alteration by [26].

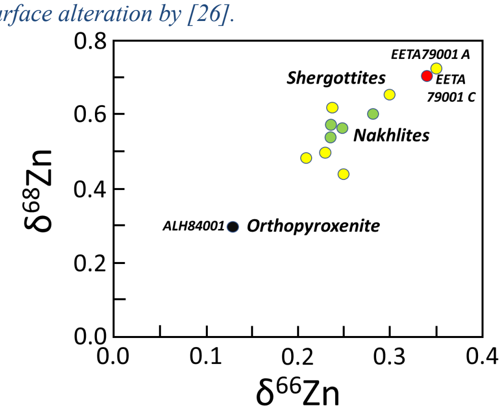

Fig. 5. δ^{66}Zn and δ^{68}Zn for EETA79001 C compared to other martian meteorites [27].

References: [1] Gooding et al., (1986) *GCA*, 50, 1049-1059; [2] Gooding et al., (1991) *LPSC XXII*, 461-462; [3] Wentworth and Gooding (1986) *Meteoritics*, 21, 536-537; [4] Rao et al., (1999) *GRL*, 26, 3265-3268; [5] Kounaves et al., (2014) *Icarus*, 229, 206-213; [6] Walton et al, (2010) *GCA*, 74, 4829-4843; [7] Schrader et al., (2011) *42nd LPSC*, abst.# 1608; [8] Barret et al., (2014) *GCA*, 125, 23-33. [9] Chennaoui Aoudjehane et al. (2012) *Science*, 338, 785-788; [10] Gooding and Muenow (1986) *GCA*, 50, 1049-1059; [11] Martinez and Gooding (1986) *Antarctic Meteorite Newsletter*, 9 (1), 23. JSC Curator's Office, Houston; [12] Bogard and Johnson (1983) *Science*, 221, 651-654; [13] Bogard et al. (1984) *GCA*, 48, 1723-1739; [14] Nyquist et al. (1986) *LPSC XVII*, 624-625; [15] Franz et al., (2014) *Nature*, 506 (74960, 364-368; [16] Glaven et al.(2013) *JGR Planets* 118, 1955-1973; [17] Agee et al., (2013) *Science*, 339 (6121), 780-785; [18] Farley et al. (2016) *EPSL* 438, 14-24; [19] Wu et al. (2018) *EPSL* 504, 94-105; [20] Williams et al. (2016) *MAPS*, 51, 2092-2110; [21] Sharp et al. (2016) *MAPS*, 51, 2111-2126; [22] Shearer et al. (2018) *GCA*, 234, 24-36; [23] Neuman et al. (2022) *GCA*, 316, 1-20; [24] Gargano et al. (2020) *PNAS*, 117, 23418-23425; [25] Sharp and Wostbrock (2021) *RiMG*, 86,179-196; [26] Tian et al. (2021) *PNAS,* 118, e2101155118; [27] Paniello et al. (2012) *Nature,* 490, 376-379; [28] Day et al. (2019) *GCA,* 266, 131-143; [29] Liu et al. (2018) *EPSL*, 490, 206-215.