CORRELATED H2O–δD SYSTEMATICS AND IRON AND CHROMIUM VALENCES OF NOMINALLY ANHYDROUS MINERALS IN THE LUNAR BASALTIC BRECCIA METEORITE ELEPHANT MORAINE (EET) 87521.

A. G. Distel[1], J. Davidson[1,2], M. Wadhwa[1], R. L. Hervig[1], S. R. Sutton[3,4], and A. Lanzirotti[4], [1]School of Earth and Space Exploration (SESE), Arizona State University (ASU), USA (agdistel@asu.edu). [2]Buseck Center for Meteorite Studies, SESE, Arizona State University, USA. [3]Department of the Geophysical Sciences and [4]Center for Advanced Radiation Sources (CARS), University of Chicago, Chicago, IL 60637, USA.

Introduction: The H_2O–δD systematics of planetary materials can be indicative of the origin of their volatile components, and the primary magmatic and/or secondary alteration processes they have experienced ([1–6] and references therein). Since the discovery of water in lunar volcanic glasses [7], studies of water in lunar samples have primarily focused on melt inclusions in nominally anhydrous minerals (NAMs), and volatile-rich minerals, such as apatite [e.g., 2,8]. However, since apatite is a late-forming phase in these samples, it does not preserve the original characteristics of the magmatic water. Thus, we are studying NAMs in the lunar basalts as they are some of the earliest-formed minerals, and so are more likely to preserve the original characteristics of lunar magmatic water.

Deciphering a mineral's H_2O–δD systematics is complicated by numerous processes (both primary and secondary) that can affect the H isotope signatures and water contents [e.g. 1,2]. Thus, a combination of hydrogen isotope composition and other geochemical parameters that are influenced by various magmatic and secondary alteration processes are required to understand a sample's petrogenesis [e.g., 9].

Here we report H isotope compositions (δD in per mil), water concentrations (H_2O in μg/g), and Fe and Cr valences of nominally anhydrous minerals (pyroxene and olivine) in the lunar basaltic breccia meteorite Elephant Moraine (EET) 87521 to further constrain its petrogenesis. EET 87521 is a very low-Ti (VLT) lunar basaltic breccia and was selected for this study as it has a relatively low cosmic ray exposure age of <10–50 Ma [10,11], thereby requiring minimal correction for spallation production of cosmogenic D. It also has a low weathering grade [12], potentially limiting the effects of terrestrial weathering.

Methods: An interior chip of EET 87521 was anhydrously prepared [3,4,5] and co-mounted with terrestrial standards in indium metal in a one-inch aluminum disc. Element mapping, high-resolution secondary electron (SE) and backscattered electron (BSE) imaging, and determination of mineral major element compositions were performed on a JEOL JXA-8530F electron probe microanalyzer (EPMA) at ASU. The water concentrations and hydrogen isotope compositions were determined via secondary ion mass spectrometry (SIMS) with the Cameca IMS-6f at ASU using analytical protocols similar to those of [4,5]. The H_2O concentrations were determined using a $H^-/^{16}O^-$ vs. H_2O (μg/g) calibration curve for terrestrial standards (PMR 53 pyroxene, KBH-1 [13,14]). Using the same pyroxene standards, we monitored the instrumental mass fractionation and instrumental H background (11 μg/g H_2O on dehydrated PMR 53) throughout the analytical session. They were corrected for using the methods of [8, 15].

The Fe and Cr valences of the olivine and pyroxene grains were analyzed in areas adjacent to the SIMS pits. Following the methods of [16,17], the valences were determined using station 13-ID-E at the GSECARS X-ray microprobe at the Advanced Photon Source at Argonne National Laboratory. The "Lasso" (least absolute shrinkage and selection operator) method was used for Fe and is detailed in [18]. The Fe valence is reported here as "2 + ($Fe^{3+}/\Sigma Fe$)" with a precision of ± 0.016 (2σ). The Cr valence is reported here as "2 + ($Cr^{3+}/\Sigma Cr$)" with a precision of ± 0.02 (2σ).

Results: Thirteen pyroxenes were analyzed that ranged in major element compositions ($Wo_{11–34}En_{13–61}Fs_{20–65}$; Fig. 1). The H_2O contents ranged from 19 ± 4 to 118 ± 25 μg/g. Once corrected for cosmic ray exposure (CRE) using the D production rate of [19], the hydrogen isotope compositions of the pyroxenes ranged from δD = –526 ± 90 ‰ to –1 ± 67 ‰. The Fe valence for these thirteen pyroxenes ranges from 2.04 to 2.12 and the Cr valence ranges from 2.58 to 2.80.

We also analyzed five olivines that ranged in composition from Fo_3 to Fo_{60}. Two olivines did not contain detectable H_2O. The water contents for the other three olivines ranged from 19 ± 4 to 63 ± 13 μg/g. The CRE-corrected H isotope compositions ranged from δD = –293 ± 94 ‰ to –146 ± 51 ‰. The Fe valence for these three olivines ranges from 2.00 to 2.01 and the Cr valence ranges from 2.48 to 2.87.

Discussion: There is no apparent relationship between the water concentrations and H isotope compositions of NAMs in EET 87521 (Fig. 2 in [20]). The EET 87521 pyroxene grains are generally isotopically lighter than the range inferred for indigenous lunar water (δD from –200 to +200 ‰ [2]), and those we analyzed in the potentially paired lunar basaltic breccia EET 96008 [21]. This may be due to

various primary magmatic and secondary alteration processes that could alter the original H₂O–δD systematics of the lunar NAMs.
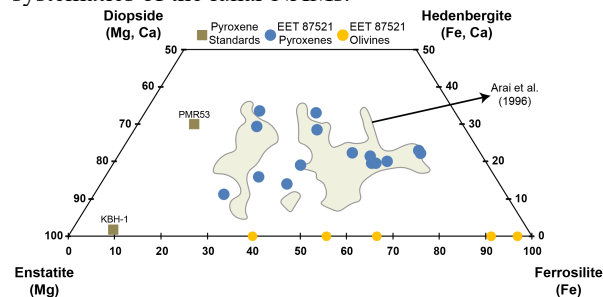

Figure 1. *Pyroxene compositions in EET 87521. The shaded field represents the range of pyroxene compositional data measured in EET 87521 by [22].*

As in our previous studies of EET 96008 [9, 23], the Fe and Cr valences of NAMs in EET 87521 are well-correlated with each other. Given the low water concentrations of the NAMs and the meteorite's low weathering grade, these observations suggest that terrestrial alteration did not significantly alter the H₂O–δD systematics of EET 87521.

Magma degassing, a common primary magmatic process on the Moon, can alter H₂O–δD systematics and Fe and Cr valences, generally reflected by a negative correlation between D/H ratios and water concentrations, and also between Fe valence and water concentrations [2,9]. Since such correlations are not observed, it is unlikely that magma degassing played a significant role in the petrogenesis of EET 87521.

Although the effects of shock in pyroxenes are not well understood, shock processes are known to increase δD in other phases [1]. Cosmic ray exposure (CRE) can also increase δD by introducing cosmogenic D through spallation reactions [2]. Since the H isotope compositions of EET 87521 NAMs are relatively light, shock and CRE are not likely to have had significant effect on the H₂O–δD systematics.

The implantation of isotopically light solar wind into lunar regolith can also affect the primary H isotope signature by decreasing δD [2,24]. The mixing of solar wind-rich lunar regolith with a 'fresh' basalt has been documented [2,24], and could potentially explain the isotopically light δD seen in NAMs from EET 87521.

When considering the H isotope compositions and Fe valences of pyroxenes in EET 87521, two distinct pyroxene groups become apparent (Fig. 2). Group 1 is characterized by more Mg-rich pyroxenes that are less oxidized and have heavier H isotope compositions (δD of –1 to –184 ‰; Fig. 1,2). Group 2 pyroxenes are more Fe-rich, isotopically light (δD of –237 to –526 ‰) and are generally more oxidized (Fig. 1,2).
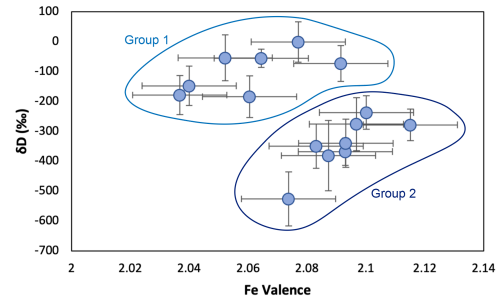

Figure 2. *Plot of δD (‰) vs. Fe valence for pyroxenes in EET 87521. Errors are 2σ.*

Conclusions: Since EET 87521 is a breccia, the two pyroxene groups (Fig. 2) could potentially record two separate sources or alteration histories. The isotopically lightest H isotope compositions (Group 2) could potentially be explained by mixing of the parent magma with solar wind-rich lunar regolith. To further investigate, we will perform future analyses on NAMs in Apollo basalts, which are presumably not affected by terrestrial alteration and some of which are also thought to have been affected by solar wind incorporation [25].

References: [1] Hallis L. J. (2017) *Phil. Trans. R. Soc. A, 375,* 20150390. [2] Stephant A. et al. (2020) *GCA, 284,* 196–221. [3] Davidson J. et al. (2020) *EPSL, 552,* 116597. [4] Davidson J. et al. (2021) *LPS LII*, #2103. [5] Davidson J. et al. (2022) *LPS LIII*, #1546. [6] Stephant A. et al. (2021) *GCA, 297,* 203–219. [7] Saal A. E. et al. (2008) *Nature* 454:192–195. [8] Barnes J. J. et al. (2013) *Chem. Geol., 337–338*, 48–55. [9] Wadhwa M. et al. (2023) *MetSoc,* #6051. [10] Vogt S. et al. (1993) *GCA, 57,* 3793–3799. [11] Eugster O. et al. (1996) *MAPS, 31*, 299–304. [12] Grossman J. N. (1994) *Met. Bull. 76, Meteoritics, 29,* 100–143. [13] Bell D. R. et al. (1995) *Am. Min., 80,* 465–474. [14] Bell D. R. and Ihinger P. D. (2000) *GCA, 64,* 2109–2118. [15] Mosenfelder J. L et al. (2011) *Am. Min., 96,* 1725–1741. [16] Sutton S. R. et al. (2017) *GCA* 204:313–330. [17] Sutton S. R. et al. (2020) *Chem. Geol.* 531:119305. [18] Dyar D. et al. (2016) *Am. Min.* 101:1171–1189. [19] Merlivat L. et al. (1976) *LPS VII,* 649–658. [20] Distel A. G. et al. (2023) *LPS LIV*, #1754. [21] Distel A. G. et al. (2022) *MetSoc,* #6120. [22] Arai T. et al. (1996) *MAPS* 31, 877–892. [23] Wadhwa M. et al. (2022) *MetSoc,* #6501 [24] Treiman A. H. et al. (2016) *Am. Min., 101,* 1596–1603. [25] Taylor L. A. et al. (2004) *Am. Min.* 89, 1617–1624.