AMINO ACIDS IN THE ASTEROIDAL WATER-BEARING SALT CRYSTALS HOSTED IN THE ZAG METEORITE.
Q. H. S. Chan[1], M. E. Zolensky[1], A. S. Burton[1], and D. R. Locke[2]. [1]NASA Johnson Space Center, Houston, TX, USA. E-mail: hschan@nasa.gov. [2]HX5 – Jacobs JETS contract, NASA Johnson Space Center, Houston, TX, USA.

Introduction: Solid evidence of liquid water in primitive meteorites is given by the ordinary chondrites H5 Monahans (1998) and H3-6 Zag. Aqueous fluid inclusion-bearing halite (NaCl) crystals were shown to be common in Zag [1, 2]. These striking blue/purple crystals (Figure 1), which gained the coloration from electron-trapping in the Cl-vacancies through exposure to ionizing radiation, were determined to be over 4.0-4.7 billion years old by I-Xe dating [3]. The halite grains are present as discrete grains within an H-chondrite matrix with no evidence for aqueous alteration that indicates a xenogenic source, possibly ancient cryovolcanism [4]. They were proposed to be formed from the cryovolcanic plumes on icy C-type asteroids (possibly Ceres), and were transferred and incorporated into the H chondrite parent asteroid following the eruption event(s) [5].

A unique aspect of these halites is that they contain abundant solid inclusions hosted within the halites alongside the water inclusions. The solid inclusions were suggested to be entrained within the fluid erupted from the cryovolcanic event(s), and were shown to be comprised of abundant organics. Spectrofluorometric study and Raman imaging of the halites have identified macromolecular carbon and aliphatic carbon compounds [6]. In order to investigate the type of organics present in Zag and in particular within the fluid-bearing halites, we studied for the first time the amino acid contents of a selected mineral (halite) phase in a meteorite sample.

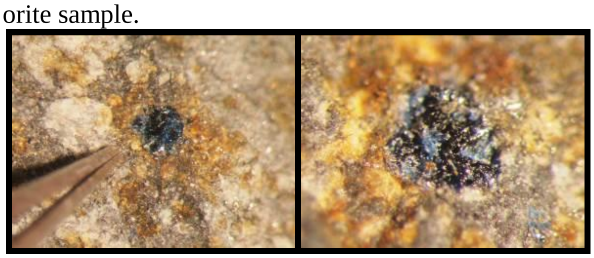

Figure 1. A blue halite hosted in Zag (JSC) with tips of tweezer for scale. Size of the crystal is ~2 μm.

Samples and Analytical Techniques: We analyzed two samples of the Zag meteorite provided by E. Thompson [Zag (JSC): 87 mg] and the Natural History Museum of London, UK [Zag (NHM): 67 mg]. Zag (JSC) was sent to M. Zolensky directly after its recovery in Morocco, and was stored in a nitrogen-filled cabinet thereafter. Halite crystals were subsampled from the meteorite samples [Zag halite (JSC): 3 mg; Zag halite (NHM): 2 mg] with pre-sterilized tools in a Class 10 clean lab at NASA JSC. Crystals from the meteorite sample surfaces were not used in this study, to avoid terrestrial contamination.

The HCl-hydrolyzed hot-water extracts of the samples were derivatized with *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC) [7]. The amino acid abundances and distributions were measured by ultra performance liquid chromatography fluorescence detection and quadrupole time of flight hybrid mass spectrometry (UPLC-FD/QToF-MS) at NASA JSC. The non-hydrolyzed portions of the samples (i.e. free amino acids only) were also analyzed but will not be discussed here. Sterilized (500°C, 24 h) laboratory halite and alumina samples were subjected to the same procedures and analyzed as procedural blanks.

Results and Discussion: Amino acids in the samples were identified by comparing the retention time and measured mass to an amino acid standard mixture analyzed on the same day. The UPLC is coupled with both a fluorescence detector and a mass spectrometer so it is capable of performing both fluorescence and mass spectrometry measurments from a single sample injection. The UV fluorescence traces of the samples are presented in Figure 2. The fluorescence intensities of the samples are presented as relative intensities, which indicates a low procedural blank level, indicating that minimal contamination accrued during the amino acid extraction procedures in the laboratory.

Zag (JSC) and Zag (NHM) show different fluorescence patterns. The amino acids in Zag (NHM) are generally higher in abundances than Zag (JSC), except for α-AIB (peak 16, Figure 3), suggesting either sample heterogeneity as Zag contains different lithologies (H3–4 matrix, H4–5 light-colored metamorphic clast, H5–6 silicate-darkened clast, impact-melt clast [2], and carbonaceous clast [8]), and/or different curation conditions (JSC: nitrogen cabinet; NHM: atm air in dessicator). The amino acids in Zag (NHM) are predominantly proteic amino acids (e.g. glycine, aspartic acid, serine), and the low ratios between their L- and D-enantiomers (D/L ratios) suggest that they are terrestrial contaminants. The most abundant amino acids in Zag (JSC) are glycine and β-alanine. Only β-alanine and γ-ABA were present in Zag halite (JSC) above blank level. The high abundances of these amino acids are consistent with what has been previously observed for thermally altered meteorites [9, 10], though terrestrial contamination cannot be completely ruled out.

Although low D/L ratios were observed for the common proteic amino acids such as glutamic acid, the presence of amino acids that are rare or absent in terrestrial biology (e.g. β-ABA, α-AIB) in the meteorite bulk samples indicates that they are likely indigenous to the meteorite.

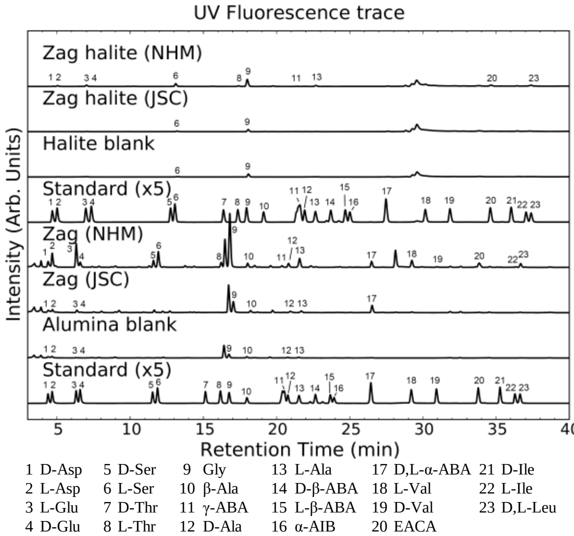

Figure 2. The 3-40 min region of the LC-FD chromatograms of the OPA/NAC derivatives of acid-hydrolyzed amino acid extracts of Zag, subsampled halite grains, procedural blank and 10^{-6} M amino acid standard mixture (250 pmol in column, scaled). Abbreviations: Asp=aspartic acid; Glu=glutamic acid; Ser=serine; Thr=threonine; Gly=glycine; Ala=alanine; ABA=amino-*n*-butyric acid; AIB=aminoisobutyric acid; Val=valine; EACA=ε-amino-*n*-caproic acid; Ile=isoleucine and Leu=leucine.

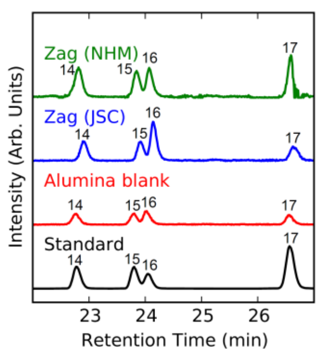

Figure 3. Representative LC-MS chromatograms for selected 4-carbon amino acids of the bulk samples.

Amino acid analyses of ordinary chondrites have only been reported for the LL3 chondrites Bishunpur and Chainpur, LL5 Antarctic meteorites LaPaz Icefield (LAP) 03573, LAP 03624 and LAP 03637, and the L6 chondrites Shişr 031 and Shişr 035 [11-13]. While Shişr 031 and Shişr 035 were comprised of mostly proteic amino acids like glycine and glutamic acid [13], Bishunpur and Chainpur contain a significant amount of γ-ABA and β-alanine. α-AIB is also present in these LL3 chondrites but only at a very low abundance [12]. Likewise, only glycine, β-alanine, and γ-ABA were found in the three LL5 LAP samples [11]. Some LL3 and all L6 meteorites have undergone extensive thermal metamorphism at temperatures of >500°C [2], but the presence of indigenous amino acids in the LL3 chondrites suggests that amino acids may be formed through Fischer-Tropsch type (FTT) gas-grain reactions after the meteorite parent body cooled to lower temperatures. β-alanine, which is a *n*-ω-amino acid [9], is also one of the most abundant amino acids in Zag, and its presence is consistent with its production through FTT reactions as the Zag parent body cooled down from the metamorphism (600−950°C). α-AIB, although present at low concentration, can also be synthesized under the FTT conditions [14]. Contrastingly, the rarity of vapor bubbles in Zag's fluid inclusions within the halite crystals suggests a low formation temperature for the fluids (≤100°C; probably 25−50°C) [15], and the continued presence of the fluid inclusions indicates that the incorporation of the halites into the H chondrite asteroid postdate the metamorphic epoch. The halites are essentially free of amino acids, which suggest that the origin of the halites (e.g. cryovolcanic plumes on icy C-type asteroids) is also low in amino acid abundance, and limited amino acids were produced and adsorbed on the halite grains after their incorporation onto the Zag parent body.

References: [1] Whitby J. *et al.* (2000) *Science*, *288*, 1819-1821. [2] Rubin A.E. *et al.* (2002) *MAPS*, *37*, 125-141. [3] Bogard D.D. *et al.* (2001) *MAPS*, *36*, 107-122. [4] Wilson L. and Keil K. (1996) *EPSL*, *140*, 191-200. [5] Fries M. *et al.* (2013) 76th Annual Meeting of the Meteoritical Society,5266. [6] Fries M. *et al.* (2011) *MAPS Supplement*, *74*, 5390. [7] Glavin D.P. *et al.* (2006) *MAPS*, *41*, 889-902. [8] Zolensky M. *et al.* (2003) *MAPS Supplement*, *38*, 5216. [9] Burton A.S. *et al.* (2012) *MAPS*, *47*, 374-386. [10] Burton A.S. *et al.* (2015) *MAPS*, *50*, 470-482. [11] Botta O. *et al.* (2008) *MAPS*, *43*, 1465-1480. [12] Chan H.S. *et al.* (2012) *MAPS*, *47*, 1502-1516. [13] Martins Z. *et al.* (2007) *MAPS*, *42*, 1581-1595. [14] Pizzarello S. (2012) *MAPS*, *47*, 1291-1296. [15] Zolensky M.E. *et al.* (1999) *Science*, *285*, 1377-1379.

Acknowledgements: We thank Edwin Thompson and the National History Museum London for the Zag samples. QHSC acknowledges support from the NASA Postdoctoral Program at the JSC, administered by Universities Space Research Association through a contract with NASA. MZ was supported by the NASA Cosmochemistry Program. ASB acknowledges support from the NASA Exobiology and Early Career programs.