HYDROTHERMAL INFILLING OF A UNIQUE, LAYERED SPHERULE WITHIN THE MARTIAN POLYMICT BRECCIA NORTHWEST AFRICA 7475. S. Sillitoe-Kukas[1], M. Humayun[1], D. E. Moser[2], G. Arcuri[5] and A. J. Irving[3], [1]Florida State University, Tallahassee, FL 32310, USA (sms17w@my.fsu.edu); [2]University of Western Ontario, London, Ontario N6A 5B7, Canada; [3]University of Washington, Seattle, WA 99123, USA.

Introduction: The ancient martian polymict breccia Northwest Africa (NWA) 7475 and its paired meteorites [1-3], contain large (mm-sized) vitrophyric spherules [3-5]. These spherules formed by impact melting of hydrothermally altered and weathered rocks of basaltic composition, some or all of the target rocks being sediments [6-7]. All the spherules have fractures in their cores that appear to be cooling and contraction features. In some of the spherules, these fractures are filled with albite-hyalophane (K, Ba-feldspar)-magnetite-sulfide veins [5]. A unique, 4.5 mm layered spherule was described by [3] from NWA 7475. This spherule contains numerous smaller minispherules that were described as "captured, glassy spherules" inferred to have been accreted to the large spherule [3]. This unique spherule was studied thoroughly at the Zircon & Accessory Phases Laboratory (ZAP Lab) at Western University, and has been nicknamed ZAP1. In a LA-ICP-MS study of numerous spherules from the breccia [6-7], it seemed desirable to include ZAP1 since the minispherules within it could provide more detailed information about processes in the impact plumes that formed these spherules.

In this study, we report detailed chemical studies by LA-ICP-MS of the complex, layered spherule ZAP1 from NWA 7475 and provide critical data towards a different interpretation of the origin of the mini-spherules as hydrothermal infilling similar to the veins described by [5].

Samples and Analytical Methodology: A chemical map of polished slab NWA 7475 was imaged by SEM-BSE and EDS. When one's world is limited to a single spherule, one's thoughts turn cosmological. Accordingly, we named the various mini-spherules within ZAP1 after the characters of the popular TV series, *The Big Bang Theory*. LA-ICP-MS using an ESI™ New Wave™ UP193FX laser ablation system coupled to the Thermo Element XR™ at the Plasma Analytical Facility at FSU was performed following methods detailed elsewhere [6-7]. Most hydrothermal infillings were analyzed using lines with 25-50 µm spot sizes. Three mini-spherules were analyzed using spots of 25-100 µm spot sizes. All analyses were conducted using 50 Hz laser repetition rate.

Results: ZAP1 consists of three compositional zones: an inner Mg-rich core, an Fe-rich mantle with numerous layered Fe-oxides, and a thin Na-rich rim (Fig. 1). Many of the mini-spherules are present in the Fe-rich mantle consistent with accretionary capture (Fig. 1). The largest of the mini-spherules, *Sheldon*, consisted of a grain of feldspar at the margin, and a mafic core. Some provided analyses of feldspars only perhaps due to how the mini-spherules intersected the plane of the polished section. Others offered a vitrophyric infilling of unique composition described in more detail below.

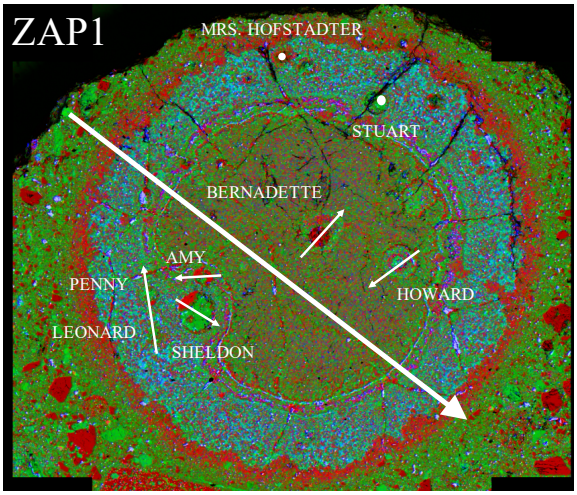

Fig. 1: EDS image of ZAP1 in NWA 7475 showing mini-spherules and main LA-ICP-MS track. LA-ICP-MS traces: arrows and spots on mini-spherules. Red: Na, Blue: Fe, Green: Mg.

Sheldon: This minispherule consists of a mafic body with a feldspathic grain on its margin present within an embayment of Fe-rich mantle material into the core of ZAP1. The mafic region is enriched in Zn, has U (~1 ppm), but is spectacularly depleted in Th, Ti, Na, P, K and REE. It is also the only mini-spherule studied thus far that lacks an enrichment in Ba (Fig. 2).

Sheldon-Fsp, Amy, Bernadette: The chemical analysis for the feldspathic grain in *Sheldon* (Fig. 1), and for the entirety of *Amy* and *Bernadette*, showed enrichments in K-Ba-Sr and large depletions in Th, U, Nb, Ta, Ti, P and REE. These grains are dominated by hyalophane feldspar as reported in veins from spherules in NWA 7533 [5].

Mrs. Hofstadter: Although a distinct Na-rich area was observed in the chemical map of ZAP1, named *Mrs. Hofstadter*, the chemical composition found in *Mrs. Hofstadter* is most similar to that of ZAP1. *Mrs. Hofstadter* lacks the depletions in Th, Ti and P of the

other mini-spherules studied but is enriched in Zn relative to ZAP1.

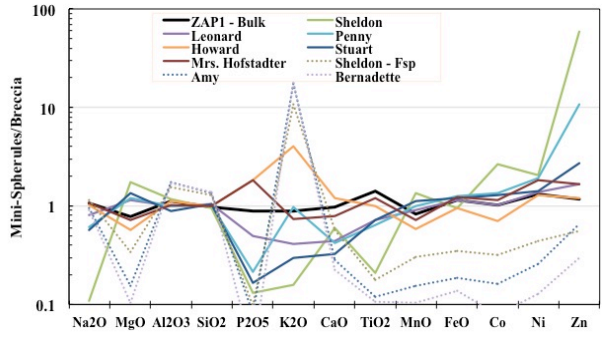

Fig. 2: Elemental compositions of various mini-spherules from ZAP1 normalized to bulk NWA 7533 breccia.

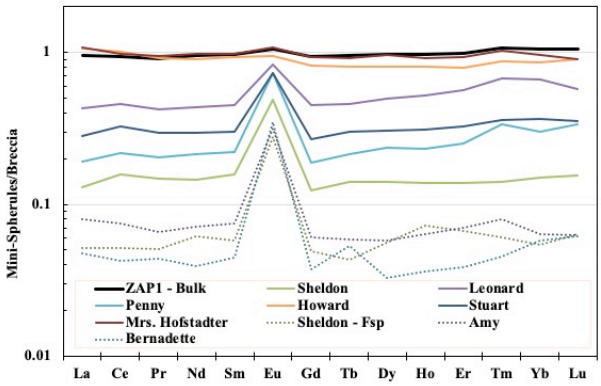

Fig. 3: REE abundances normalized to bulk NWA 7533 breccia for mini-spherules from ZAP1.

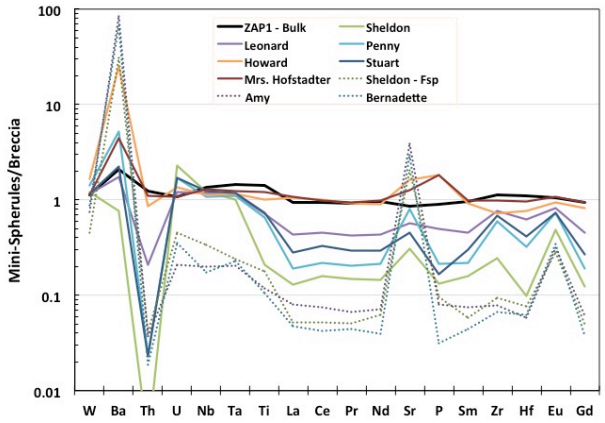

Fig. 4: Refractory incompatible element abundances in the mini-spherules from ZAP1 normalized to bulk NWA 7533 breccia.

Howard: This is a double-ringed mini-spherule within the Mg-rich core of ZAP1. The two concentric rings are composed of Fe-oxides and Fe-sulfide. Chemical composition is similar to spherule material [6-7]. The strongest Ba and Sr signatures of the non-feldpathic group are found in Howard. *Howard* is also high in K and P and depleted in Co, Mg and Mn.

Penny, Leonard and Stuart: Penny, Leonard, and Stuart are depleted in REE. Penny is depleted in Th but has a strong Ba and Zn enrichment. Leonard has a depletion of Ba compared to ZAP1 and a less pronounced Th depletion. Stuart is compositionally intermediate between Leonard and Penny in REE.

Discussion: Hydrothermal infillings within NWA 7475 ZAP1 appear at first glance to be microspherules that were captured and incorporated into ZAP1. Wittman et al. [3] state this sort of spherule capture is common in impact clouds where accretion takes place. Only two of the objects studied here are possibly captured spherules: *Mrs. Hofstadter* and *Howard*. Three were K-Ba-feldspars: Sheldon-Fsp, Amy and Bernadette, similar to vein material [5]. Sheldon, Penny, Leonard and Stuart are mafic materials, depleted in Ti, Th, P and REE with positive Eu anomalies. The depletions of high field strength elements and similarities to veins from other spherules implies hydrothermal transport of material into pre-existing cavities. ZAP1 likely had vesicles formed by degassing of accreted mantle layers, that filled with hydrothermal material after ZAP1 landed in a spherule bed. Fractures in other spherules were similarly filled with hydrothermal veins that provided induration to the spherules preventing them from falling apart. Given the low density of spherules within the breccia, its is conceivable that those spherules now found in the breccia were weathered or remobilized from other spherule bed(s), then mixed with regolith materials prior to compaction. This would explain why none of the other lithologies is infused with similar hydrothermal material, and no veins of similar composition are found in the breccia.

Veins in NWA 7533 SP7 [5] were too thin to obtain a chemical analysis by LA-ICP-MS free of the surrounding spherule. The mini-spherules in ZAP1 have provided a conveniently detailed chemical composition for the hydrothermal material that filled fractures and vesicles within the spherules, possibly immediately after deposition. The lack of P and Th could be related to residual monazite that prevented Th transport by the hydrothermal fluids.

References: [1] Agee C. B. et al. (2013) *Science 339*, 780-785. [2] Humayun M. et al. (2013) Nature 503, 513-516. [3] Wittmann A. et al. (2015) *MaPS 50*, 326-352. [4] Udry A. et al. (2014) *GCA 141*, 281-293. [5] Hewins R. H. et al. (2017) *MaPS 52*, 89-124. [6] Sillitoe-Kukas S. et al. (2019) *LPS L*, Abstract# 1354. [7] Humayun M. et al. (2019) *LPS L*, Abstract# 2154.