ANCIENT MARTIAN POLYMICT BRECCIAS: THE ORIGIN OF THE SPHERULES WITHIN. S. Sillitoe-Kukas,1 M. Humayun,1 R. H. Hewins2,3, B. Zanda2,4, D. E. Moser3, G. Arcuri3, A. J. Irving6 and J.-P. Lorand2, 1Florida State University, Tallahassee, FL 32310, USA (sms17w@my fsu edu); 2IMPMC, Sor- bonne Université, MNHN-UPMC, 75005 Paris, France; 3Rutgers University, Piscataway, NJ 08854, USA; 4IMCCE, Observatoire de Paris - CNRS UMR 8028, 75014 Paris, France; 5University of Western Ontario, London, Ontario N6A 5B7, Canada; 6University of Washington, Seattle, WA 99123, USA; 7CNRS UMR 6112, Université de Nantes, 44222 Nantes Cédex 3, France.

Introduction: Ancient Mars underwent many geological processes, such as crustal growth, sedimentation, and meteoritic bombardments [1]. Many of these processes no longer take place on Mars, but the deformation they caused still scar the Martian surface. Until recently, the only method in which to study these ancient processes was to send rovers and satellites to Mars and study SNC’s here on Earth. However, the SNC’s igneous composition restricted scientists from studying the surface processes of Mars. It wasn’t until 2012 when the meteorite, now known as the Martian Polymict Breccia, was discovered in North West Africa that scientists were able to study the ancient Martian surface processes in fully equipped laboratories here on Earth [2,3]. Vitrophyric spherules formed by impact melting of Martian protolith were observed within the breccia [2,3]. 14 vitrophyric spherules were found within paired stones of the single large breccia. In addition to these 14 spherules, 8 mini-spherules found within the spherule on the face of NWA 7475; these mini-spherules have been named after the cast of the popular TV series, The Big Bang Theory. The vitrophyric spherules range from 0.5 – 7 mm in diameter and appear to be well rounded and internally zoned. In this study, we review the composition of the spherules and mini-spherules analyzed by LA-ICP-MS [4].

Results: Figure 1 shows a BSE image of NWA 7533 SP5 exhibiting internal zoning. This three-tier zoning pattern shows a fractionation of Mg when moving from the Mg-rich core to the ferroan mantle and to the feldspathic crust. This zoning pattern is common in many of the large spherules, with smaller spherules showing only two-tier zoning. Anomalies in Zr, Hf, Nb and Ta ratios are shown in Figure 2. The spherules showed enrichments in some volatile elements and depletions in others (Figure 3A and 3B), including the deviation from the planetary Ga/Al2O3 ratio, as seen in Figure 3C. ZAP1, like the other large spherules, also shows three-tier zoning (Figure 4) and loss of volatile elements; however, it also includes what appear to be smaller accreted spherules [5] (Figure 3). Chemical analysis indicates 3 distinct species of “mini-spherules”: normative feldspar-rich (Bernadette, Amy and Sheldon-FSP), normative mafic-rich (Sheldon, Leonard, Penny and Stuart), and spherule-like (Howard and Mrs. Hofstadter). Relative to the spherules and bulk breccia, the mini-spherules are depleted in REE, P, and Th and show enrichments in Sr and Ba.

Discussion: The spherules exhibited a number of interesting compositional features that revealed important clues to their origin. The mini-spherules also showed variations in their chemical composition both distinguishing them from the spherules and from each other.

Spherules: Zoning. Origin of the internal zoning is inferred to be the result of accretion around a molten core that was ejected into an impact plume [5]. The refractory elements in the individual spherule zones were analyzed. Figure 2 shows a negative anomaly in the rim for Zr, Hf, Nb and Ta relative to other refractory elements. We take this to represent heavy mineral sorting among two different lithologies in the target rock. This sort of separation would not have taken place in the impact plume or the spherule itself. In terrestrial environments, density sorting is accomplished most efficiently in aqueous deposition environments.
Within the spherules show both enrichments of planetary Ga/Al ratio and depletions (P, Ga, and U). Weathering and alteration of protolith can lead to the loss of volatile elements; however, Figure 2 shows two insoluble elements – Ga (volatile) and Al2O3 (refractory). Due to their characteristics, we can infer that we have lost and alteration were not responsible for the loss of Ga but instead volatility being the most likely cause. This relationship is also exhibited in other volatile elements that correlate with Ga, such as Zn and B. Phosphorous differs from Ga as such that it was depleted from the spherule precursors. This is shown in Figure 3C where P2O5 exhibits no correlation with Ga, indicating that P2O5 was not lost in volatilization.

**Mini-Spherules: Origin.** Amy, Bernadette and Sheldon-FSP (a small feldspathic grain within Sheldon) are K-Ba-feldspars (albite-hyalophane) [6] and closely resemble veins cross-cutting several of the spherules. Sheldon, Leonard, Penny and Stuart are mafic mini-spherules whose REE composition sits between those of the feldspar-rich and ZAP1-like mini-spherules. Based on their chemical compositions, we examine two alternative explanations for their formation: (i) hydrothermal infillings, and (ii) alteration products. Based on their chemical composition, it is likely hydrothermal material filled cavities formed during the degassing of ZAP1 resulting in Amy, Bernadette and Sheldon-FSP. The P-Th-REE depletions in Sheldon, Leonard, Penny, and Stuart can explained by acid-leaching of phosphates effectively removing these elements while leaving Ti-Nb-Ta at original concentrations [7]. The mini-spherules are unique from the breccia in that they have undergone low-temperature processes not seen in other components of the breccia.

**Conclusion:** The spherules are significant because they represent multiple lithologies as a result of Martian sedimentary processes acting on the spherules precursors. The loss of volatile elements during the impact is best captured by Ga and correlating elements which allow us to constrain the abundances of other volatile elements (Zn, B, etc.). The mini-spherules represent materials distinct from the bulk breccia, spherules, and ZAP1 and were likely formed by hydrothermal infilling or post-impact alteration of devitrified glass.