SPHERULES IN THE MARTIAN POLYMICT BRECCIAS. I: ORIGIN AND INTERNAL CHEMICAL ZONING. S. Silliteo-Kukas1, M. Humayun1, R. H. Hewins2,3, B. Zanda2,4, D. E. Moser5, G. Arcuri6, A. J. Irving6 and J.-P. Lorand1, 1Florida State University, Tallahassee, FL 32310, USA (sms17w@my.fsu.edu); 2IMPMC, Sorbonne Université, MNHN-UPMC, 75005 Paris, France; 3Rutgers University, Piscataway, NJ 08854, USA; 4MCCE, 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, 44322 Nantes Cédex 3, France.

Introduction: Early Mars experienced a period of intense crustal growth, aqueous alteration, weathering and sedimentation. Noachian Mars was also subjected to intense meteoritic bombardment, so that early aqueous sediments and igneous rocks would be brecciated and impact melted [1], however we have little knowledge of the physical record of these processes. Terrestrial Archean rocks contain spherule beds of impact melted sediments [2]. Analogous spherule beds must have existed on Mars. The only known martian meteoritic breccia available for study [3-4] contains an abundance of impact-melt clasts, vitrophyric spherules, clast-laden melt rocks, and other products of early bombardment [5-7]. The vitrophyric spherules are 0.5-10 mm diameter objects that are generally well rounded, and appear to be internally zoned [6-7]. Compositionally, the spherules are basaltic, with only three known examples that contain FeO-rich olivine blades [3, 5, 7] that are exceptionally rich in Ni [5]. This high-Ni composition is the basis of their interpretation of these spherules as impact melts [5].

Here, we report detailed chemical studies by LA-ICP-MS of vitrophyric spherules from NWA 7034, NWA 7475, NWA 7533, NWA 8171 and Rabt Sbayta 003, all paired stones of a single martian polymict breccia, to investigate in more detail the internal chemical zoning with implications for the genesis of spherules. In a companion report, we consider the provenance of the material that formed the spherules.

Samples and Analytical Methodology: Spherules exposed on polished sections or polished slabs of NWA 7034 (3A-1), NWA 7475, NWA 7533 (SP2, SP5, SP7) and Rabt Sbayta 003 were imaged by BSE. No BSE imaging was available for a polished slab of NWA 8171. The spherules were analyzed by LA-ICP-MS using an ESI™ New Wave™ UP193FX laser ablation system coupled to a Thermo Element XR™ at the Plasma Analytical Facility at FSU. Spot sizes of 25-50 µm were used for line scans across the spherules. For the larger spherules, 100 µm spot analyses were performed to improve detection limits. Laser repetition rate was 50 Hz in all analyses. A multielement method detailed previously was applied [8].

Results: A BSE image of a zoned spherule, NWA 7533 SP5, is shown in Fig. 1. For the large spherules studied, such as SP5, many exhibited a three-tier zoning pattern consisting of a feldspathic rim, a mantle and a core.

The major element zoning for spherule SP5 is summarized by a plot of normative mineralogy (Fig. 2). CIPW norms were calculated using Fe3+/ΣFe of 0.1, except where the resulting composition was too silica-undersaturated. Then the Fe3+/ΣFe ratio (0.1-0.3) was

![Fig. 1: BSE image of vitrophyric spherule NWA 7533 SP5. White arrows mark rim; yellow circle marks core; red arrow marks laser trace. Scale bar is 1 mm.](image1.png)

![Fig. 2: Normative composition of spherule SP5 compared with the bulk NWA 7533 breccia composition.](image2.png)
adjusted to avoid the formation of nepheline in the norm. Accordingly, the ratio of olivine to hypersthene obtained is dependent on the Fe$^{2+}$/Fe ratio used. The rim is more feldspathic than the mantle or core. For bulk spherules, the feldspar component is dominated by plagioclase and comprised ~40% of the normative abundances, with some exceptions having 30–45% feldspar. The mafic component was dominated by olivine ± hypersthene, with diopside forming 0–20% of the norm. The most abundant compositional variety of spherule is strikingly similar to the composition of the bulk breccia composition, with lower P$_{2}$O$_{5}$ abundances, but higher Ti, Fe, Ni and Co abundances. Chemical zoning of MgO and Al$_{2}$O$_{3}$ in SP5 (Fig. 3) show that the core is more magnesian, the rim is more feldspathic and the mantle is more ferroan.

**Discussion:** The spherules exhibited a number of interesting compositional features that revealed important clues to their origin as impact melts.

*Siderophile elements.* In the spherules, the abundances of Re, Os and Ir fall below detection limits of ~0.1 ppb, while Os and Ir are detected at levels of tens of ppb in the breccia matrix. However, Pt and Ru are present in chondritic ratios at levels similar to those in the breccia. The low Re-Os-Ir is suspected to be due to volatilization of the spherules under oxidizing conditions. There is no correlation between Ni-Co contents and Ru-Pt abundances, so that the high Ni-Co abundances are not due to direct meteoritic contamination of impact melts.

![Fig. 3: Chemical zoning of MgO and Al$_{2}$O$_{3}$ in SP5. Presence of crystals results in anticorrelated peaks.](image)

**Acknowledgements:** We are extremely grateful to Mendy Ouzillou (NWA 8171) and Ben Hoenagels (Rabt Sbayta 003) for their generous loans of polished slabs containing multiple spherules.