SPHERULES IN THE MARTIAN POLYMICT BRECCIAS. I: ORIGIN AND INTERNAL CHEMICAL ZONING. S. Sillitoe-Kukas[1], M. Humayun[1], R. H. Hewins[2,3], B. Zanda[2,4], D. E. Moser[5], G. Arcuri[5], A. J. Irving[6] and J.-P. Lorand[7], [1]Florida State University, Tallahassee, FL 32310, USA (sms17w@my.fsu.edu); [2]IMPMC, Sorbonne Université, MNHN-UPMC, 75005 Paris, France; [3]Rutgers University, Piscataway, NJ 08854, USA; [4]IMCCE, Observatoire de Paris - CNRS UMR 8028, 75014 Paris, France; [5]University of Western Ontario, London, Ontario N6A 5B7, Canada; [6]University of Washington, Seattle, WA 99123, USA; [7]CNRS 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 Fo_{74-48} 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.

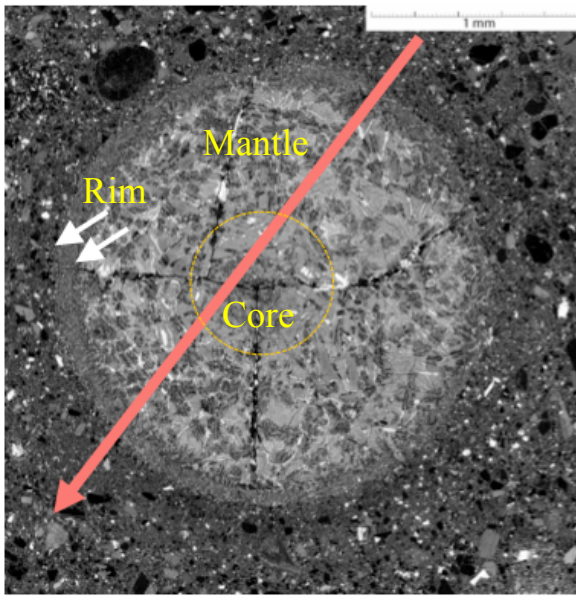

Fig. 1: BSE image of vitrophyric spherule NWA 7533 SP5. White arrows mark rim; yellow circle marks core; red arrow marks laser trace. Scale bar is 1 mm.

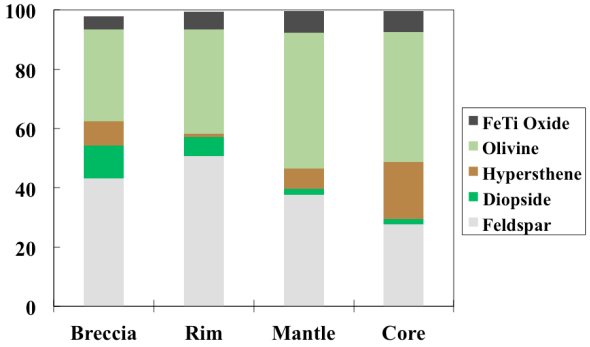

Fig. 2: Normative composition of spherule SP5 compared with the bulk NWA 7533 breccia composition.

The major element zoning for spherule SP5 are summarized by a plot of normative mineralogy (Fig. 2). CIPW norms were calculated using $Fe^{+3}/\Sigma Fe$ of 0.1, except where the resulting composition was too silica-undersaturated. Then the $Fe^{+3}/\Sigma Fe$ ratio (0.1-0.3) was

adjusted to avoid the formation of nepheline in the norm. Accordingly, the ratio of olivine to hypersthene obtained is dependent on the $Fe^{+3}/\Sigma Fe$ 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_2O_5 abundances, but higher Ti, Fe, Ni and Co abundances. Chemical zoning of MgO and Al_2O_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.

Volatile element depletion. Many elements (alkalis, P, Mn, Zn, Tl, Pb, U) may be affected by volatile losses but interpretation of the abundances of these elements is complicated by competing processes. Gallium and Al form a powerful pair of elements to examine volatility, since neither element is soluble under conditions of weathering and sedimentation, but Ga is volatile during impact melting while Al is not. Fig. 4 shows a plot of Ga vs. Al_2O_3 for the spherules compared with martian igneous meteorites and the bulk breccia. Martian igneous meteorites define a planetary trend of Ga vs. Al, but the spherules plot systematically below the planetary trend by as much as a factor of three (Fig. 4). Spherules with low bulk Ga are also zoned with the lowest Ga/Al in the interior and higher Ga/Al in the rim. Volatilization may also have lowered the abundances of alkalis, P, Mn, Zn, etc.

Origin of the internal zoning. The radial chemical variation is interpreted as the result of accretion of droplets onto the surface of a molten spherule from the impact plume [6]. The composition of the core and mantle may differ due to chemical exchange between the molten droplet and the vapor of the impact plume. Small droplets, potentially formed in an undercooled vapor, are the likely source of rim material. The clot-aureole structures in clast-laden melt rocks from NWA 7533 [7] may be precursors to spherules. In these structures, a fine-grained plagioclase-pyroxene rim surrounds a core of pyroxene and magnetite [7].

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.

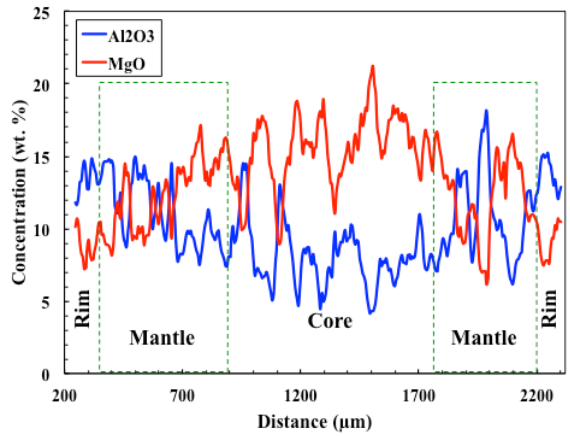

Fig. 3: Chemical zoning of MgO and Al_2O_3 in SP5. Presence of crystals results in anticorrelated peaks.

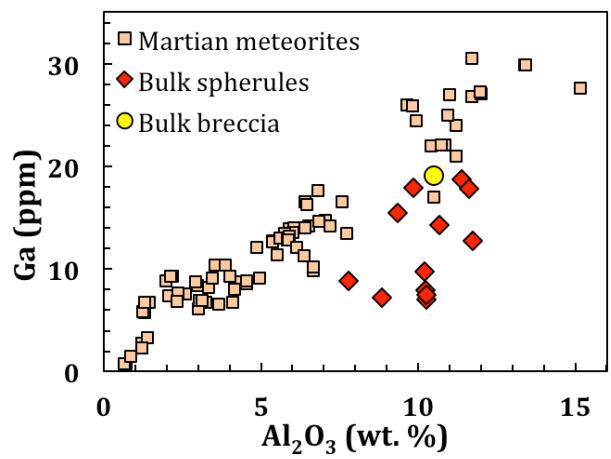

Fig. 4: Ga vs. Al_2O_3 for martian igneous meteorites, bulk breccia and bulk spherules. Martian igneous meteorites define the planetary Ga/Al ratio.

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

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