TRACE ELEMENT GEOCHEMISTRY OF COMPOSITIONALLY LAYERED IMPACT SPHERULES.
S. M. Hibbard[1] and A. K. Davatzes[2], [1]Department of Earth and Environmental Science, Temple University (1901 N. 13th St., Room 326, Philadelphia, PA. 19122. shibbard@temple.edu), [2]Department of Earth and Environmental Science, Temple University (1901 N. 13th St. Philadelphia, PA. 19046. alix@temple.edu).

Introduction: At least 12 Archean impact are preserved as spherule beds within the Kaapvaal and Pilbara cratons [1,2]. Large impacts vaporize bolide and target material, which rises into the atmosphere as a hot vapor plume [3,4]. Vaporized material condenses into melt droplets that crystallize and quench before being deposited globally [3,4]; however, details regarding how spherules nucleate, grow, crystallize, and interact with each other and their surroundings are still a source of controversy [5,6,7]. This study of Archean impact spherules from the S3 spherule layer in the Barberton Greenstone Belt (BGB) in the Kaapvaal Craton may provide insight into complex spherule formational mechanisms.

Type 4b spherules [8] are layered phyllosilicate spherules with discrete differences in texture and composition between the inner and outer layer, even after alteration (Fig. 1). Many contain a boundary of Ti-oxides (primarily anatase with some rutile) between the two layers [8], or have radial Ti-oxides in the outer layer. Microprobe analyses of the inner and outer layers of type 4b spherules show elemental differences of major elements, indicating two different primary compositions during formation, which have subsequently been altered during diagenesis [6]. In this study, compositionally layered phyllosilicate spherules were analyzed using Energy Dispersive X-ray Spectroscopy (EDS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) to measure major, trace, and rare earth element (REE) concentrations to infer original melt composition and further elucidate the process of spherule formation. This study consequently provides implications for understanding vapor plume dynamics.

Imaging and major element geochemistry: Compositionally layered spherules comprise approximately 15% of the S3 spherule layer [8]. Forty type 4b spherules were analyzed using the Oxford Aztec Energy Advanced Xmax 50 EDS System to identify and collect semi-quantitative major elemental data of the inner and outer layers in preparation for the LA-ICP-MS.

Backscatter Electron (BSE) images (Fig. 1) and elemental X-ray maps (Fig. 2) are used show differences in elemental concentrations. BSE data are displayed as greyscale images where brightness is related to the mean atomic weight (Fig. 1). Major element concentrations differ between the inner and outer layers of most spherules sampled. A few spherules do not have a noticeable change in brightness, but still contain a rim or radial texture of Ti-oxides that marks the boundary between the two layers.

X-ray maps provide a spatial distribution of a given element within a region of interest (Fig. 2). Mg and Fe are commonly greater in the core, with Al, Ti, and K greater in the outer layer (e.g., Fig. 2). 88% of the spherules have an outer layer enriched in Ti-oxides.

Both BSE and X-ray maps have revealed textural differences in type 4b spherules not observed petrographically. For example, in the spherules, anatase tends to look opaque petrographically due to small grain size [8]; however, it appears bright and is easily distinguished in the SEM images due to its higher atomic weight (Fig. 2).

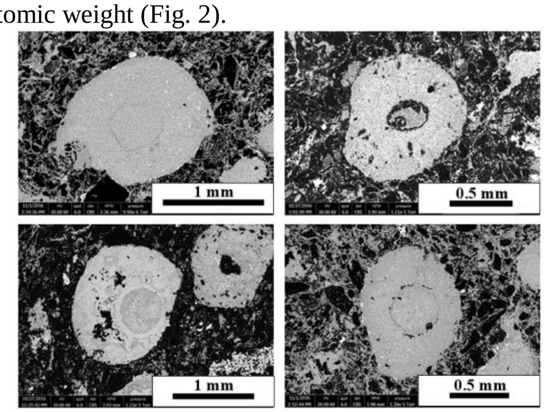

Figure 1: *BSE images of BGB type 4b compositionally layered phyllosilicate spherules with varying textures and sizes.*

Trace element geochemistry: Fifteen spherules were selected for trace and REE analysis using LA-ICP-MS. At least 3 spot analyses within the core and 3 in the outer layer of each spherule were collected. All data are standardized to 50 wt% SiO_2, which is lower than the bulk S3 average, but more consistent with phyllosilicate abundances [8]. Incompatible elements (Nb, Ta, Zr, Hf), immobile elements (Ti, Al, Sc), and Cr have been shown to be unaffected by diagenesis and are therefore representative of the primary composition [8,9].

Spidergrams normalized to CI chondrite are used to compare the inner and outer layers with the bulk S3 average deteremined previously by [8] using ICP-MS (Fig. 3). Ga is used as a proxy for Al. The majority of REE plots have nearly flat patterns, with little to no LREE/HREE fractionation; however, the outer layers tend to have higher concentrations, averaging about 10x chondritic, whereas the interiors are at or below chondritic levels. Zr is consistently lower in the interior compared to the outer layers of these spherules. The REE and spidergram patterns of the type 4b spherules are consistent with a more mafic inner layer and a more intermediate outer layer.

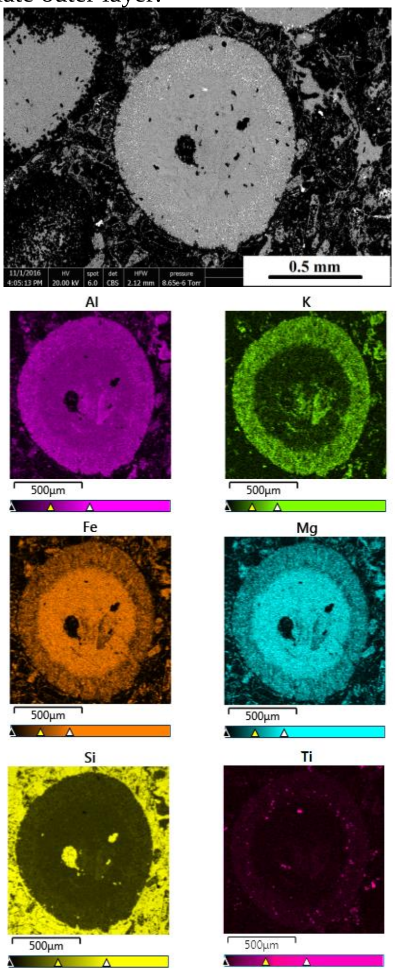

Figure 2: *BSE image of a type 4b spherule, SAF380-4A-N13 (top), and X-ray maps of Al, K, Fe, Mg, Si, and Ti (bottom). X-ray maps show depleted Al, K, Si, and Ti and enriched Fe and Mg in the core compared to the outer layer.*

Compositional grading occurs within fall-deposited sections of the S3 spherule layer [5]. Both petrologic and geochemical signatures of the spherules grade from the base to the top of the bed, with the base comprising a more chondritic signature and the top comprising a more basaltic signature, based on bulk analyses [5]. Type 4b spherules are found in the middle of pure fall-out sequences of the S3 spherule layer [5]. This study supports the idea of vapor and melt fractionation in the plume and suggests two possible methods of formation: (1) Type 4b spherules may form by the accretion of less mafic material from the plume onto existing melt droplets as the plume continues to fractionate [5], or (2) Type 4b spherules may form by the collision of melt droplets of different viscosities, as a function of compositional fractionation [6].

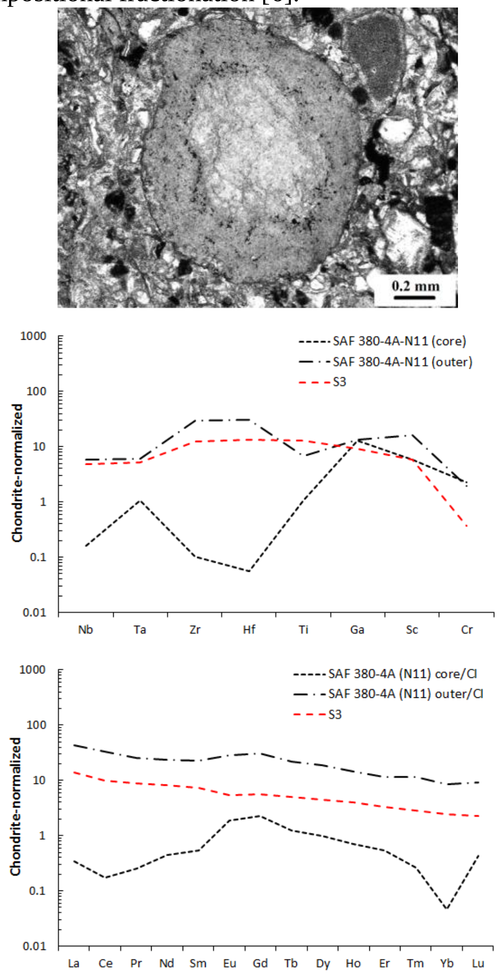

Figure 3: *Plane polarized light image of a type 4b spherule, SAF380-4A-N11 (top), trace element plot (middle), and REE plot of the core and outer layer (bottom). Ga is used as a proxy for Al; bulk S3 uses Al. Plots are normalized to CI chondrite.*

References: [1] Glass B. P. and Simonson B. M. (2012) *Elements*. [2] Lowe et al. (2014) *Geology*. [3] Lowe et al. (2003) *Astrobiology*. [4] Simonson B. M. and Glass B. P. (2004) *AREPS*. [5] Krull-Davatzes A. E. et al. (2006) *EPSL*. [6] Krull-Davatzes A. E. and Byerly G. R. (2012) *LPSC, XLIII,* Abstract #2093. [7] Johnson B. C. and Melosh H. J. (2012) *ICARUS*. [8] Krull-Davatzes A. E. et al. (2012) *Precambrian Research*. [9] Krull-Davatzes et al. (2014) *Geology*.

Additional Information: The authors would like to thank Dr. Richard Ash at the University of Maryland for use and assistance with the LA-ICP-MS and Dr. Dmitriy Dikin at Temple University for use and assistance with the SEM. This research is funded by NSF grant 1352095 to A. K. Davatzes.