SPHERULE-MATRIX COMPLEMENTARITY IN AN ARCHEAN IMPACT SPHERULE DEPOSIT FROM BARBERTON, SOUTH AFRICA. Toni Schulz[1] and Christian Koeberl[1], [1]Department of Lithospheric Research, University of Vienna, Josef-Holaubek-Platz 2, A-1090 Vienna, Austria (toni.schulz@univie.ac.at, christian.koeberl@univie.ac.at).

Introduction: Collisions and impact processes have been important throughout the history of the Earth. The earliest preserved impact record dates to about half a billion years after the first preserved rock record on Earth, in the form of (distal?) ejecta layers. Several such spherule horizons in the Barberton Greenstone belt, South Africa, and in Australia, with ages between about 3.5 and 3.2 Ga, have been proposed as being of impact origin. The spherules are mostly spherical particles, up to a few mm across, of quenched melt droplets that supposedly formed by condensation from vapor clouds. The spherule layers are coarse-grained and interpreted to have been deposited in quiet water environments. The original mineralogical and chemical composition of the spherules has been almost completely changed by alteration. The stratigraphic positions of these layers at different geographic locations are difficult to correlate and the possibility exists that some of the layers represent duplication. Unlike modern impact ejecta deposits, these spherule layers show extreme enrichments in the platinum group elements (PGEs), in some cases exceeding the chondritic concentrations. The present study focuses on a spherule horizon from the 760-m-long ICDP core BARB5 from the Barite Valley Syncline, Barberton Greenstone Belt, South Africa. Previous work on samples from the BARB5 spherule layers is described by Schulz et al. [1]. The reported geochemical and isotopic studies, especially concentrations and interelement ratios of samples from the BARB5 spherule layer section, are distinct from sedimentary country rocks of the Fig Tree Group and point towards signatures comparable to compositional ranges for known chondrite groups (even though the amounts of meteoritic components vary significantly between the different spherule layers). Here we report on further, more detailed, analyses of spherules and matrix in these samples.

Samples and Methods: A chip of spherule-bearing strata was cut from a slice of the BARB5 drill core using diamond wire saw and subsequently cleaned in an ultrasonic bath in 1 M HCl for 20 min. After gently crushing the sample in an agate mortar into various grain size fractions (to achieve optimal spherule separation), three ~80 mg separates were obtained via handpicking under a binocular, comprising spherule and groundmass (carbonaceous shale) fractions. Due to the small size and often irregular shapes of the spherules (dumbbell, ovoid, or broken), no perfect separation of spherules from groundmass was achieved. Instead, a highly spherule-enriched fraction (> ~95% spherules) and a highly spherule-depleted groundmass fraction (< ~5% spherules) were obtained. These were termed spherule sample and matrix fraction. A mixed fraction (called mix), containing spherules and groundmass in roughly equal proportions, was also analyzed.

After powdering these separates, the homogenized sample powders were spiked with a tracer composed of mixed ^{185}Re–^{190}Os–^{191}Ir–^{194}Pt isotopes and digested in 7 mL of inverse aqua regia acid mixture at 250°C and 100-130 bars in an Anton-Paar high pressure asher for 4 hours. Separation of Os from the other HSE was achieved by $CHCl_3$/HBr liquid extraction procedures and further purification by H_2SO_4/H_2CrO_4 micro-distillation technique. The Os isotope ratio- and Os concentration measurements were carried out in negative mode, using a Finnigan TRITON thermal ionization mass spectrometer (TIMS). After ion chromatography, all other highly siderophile elements (HSE) were measured using a Thermo Element XR SF-ICP-MS in single collector mode. Total blanks for this study (n = 1) were ~0.7 pg for Os, ~7 pg for Re, ~1 pg for Ir, and ~23 pg for Pt. All reported sample concentrations were blank corrected. For further details describing the method, see Schulz et al. [1]. Some aspects of the work were described in [2].

Results: Rhenium concentrations range from 2.3 (spherule sample) to 18.14 ppb (mix) with the matrix fraction (nearly spherule-free shale sample) exhibiting 3.7 ppb. For all PGEs, the highest concentrations are always measured in the matrix fraction, the lowest in the spherule sample, with consistently intermediate values in the mixed sample. Peak concentrations are 171 ppb for Os, 206 ppb for Ir and 5950 ppb for Pt, and minimum concentrations are 84 ppb for Os, 70 ppb for Ir, and 185 ppb for Pt). All PGE concentrations are comparable to spherule-groundmass assemblages (bulk samples) measured from the same BARB5 drill core section (Schulz et al. [1]; see Fig. 1). Measured $^{187}Os/^{188}Os$ ratios of the three samples are all very similar and range from 0.106 (spherule sample and mix) to 0.108 (matrix fraction), again comparable to the least radiogenic values measured by Schulz et al. [1].

Discussion and Conclusions: Preliminary studies on Archean impact spherule deposits revealed enormous meteoritic admixtures of up to 100% (and more) of a meteoritic component (e.g., [1, 3 – 6]). This is in contrast to the usually only a few percent or even fractions of a percent of meteoritic components in other impactites (e.g., Koeberl [7] and references therein). The reasons for the magnitudes of extraterrestrial (ET) admixtures in some Archean impact spherules were debated (e.g., [3], [4], [8]), but conditions during spherule condensation within an impact plume (probably favoring such large enrichments in comparison to melt generated impactites), as well as possible secondary enrichments related to metamorphism, ore formation, or post-depositional remobilization, may play a role (e.g., Glass and Simonson [9] and references therein). However, our results demonstrate that, even though highly supercrustal PGE concentrations and chondritic $^{187}Os/^{188}Os$ signatures are a common feature of all three analyzed fractions, the carrier phase of the extraterrestrial (ET) component is not solely, if at all, restricted to the spherules. Instead, high concentrations of carrier phase(s) must reside in the matrix (groundmass). Notably, our results confirm petrographic studies and element mapping by Mohr-Westheide et al. [10] and Fritz et al. [11], who revealed that ET admixtures can be found in both reservoirs (spherules and groundmass). Mohr-Westheide et al. [10] identified common occurrences of Ni-rich Cr-spinels as the suspected primary constituents and carrier phases of the projectile component in spherule layers of the BARB5 drill core section. Thus, our study is novel in that it shows that such carrier phase/s (i) seem to be distributed unequally between spherules and groundmass and (ii) that higher concentrations can be found in the matrix.

In contrast to the PGE abundances between the spherule and matrix separate, the nearly constant and chondritic $^{187}Os/^{188}Os$ ratios in all analyzed samples may indicate that ^{187}Os in the separates is predominantly of meteoritic origin, ruling out any terrestrially sourced secondary enrichments of the PGEs during post-impact mobilization.

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References: [1] Schulz T. et al. (2017) *Geochim. Cosmochim. Acta*, ***211***, 322-340. [2] Heldwein O. (2017) BSc thesis, University of Vienna, 37 pp. [3] Koeberl C. et al. (1993) *Earth Planet. Sci. Lett., 119*, 441-452. [4] Reimold W.U. et al. (2000) In: Impacts and the Early Earth (eds. I Gilmour and C. Koeberl), Lecture Notes in Earth Sciences 91, Springer, Heidelberg, pp. 117–180. [5] Glikson A. and Allen C. (2004) *Earth Planet. Sci. Lett. 220*, 247-264. [6] Simonson B.M. and Glass, B.P. (2004) *Ann. Rev. Earth Planet. Sci., 32*, 329–361. [7] Koeberl C. (2014) In: Davis A.M., ed., Treatise on Geochemistry, Volume 2 (2nd ed.): Amsterdam, Elsevier, p. 73–118. [8] Hofmann A. et al. (2006) In: Reimold W.U. and Gibson R.L. (eds.), Processes on the Early Earth: *Geol. Soc. Amer. Special Paper 405*, pp. 33–56. [9] Glass B.P. and Simonson B.M. (2013) Distal Impact Ejecta Layers: Impact Studies: Berlin, Springer, 716 p. [10] Mohr-Westheide T. et al. (2015) *Geology*, *43*, 299-302. [11] Fritz J. et al. (2016) *Meteoritics Planet. Sci.*, *51*, 2441-2458. [12] Siebert C. et al. (2005). *Geochim. Cosmochim. Acta*, *69*, 1787-1801. [13] Tagle R. and Berlin J. (2008) *Meteoritics Planet. Sci.*, *43*, 541-559.

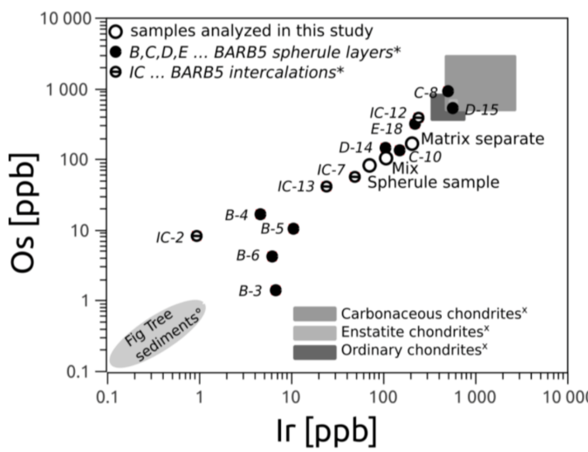

Fig. 1.: Osmium vs. Ir contents in the spherule-enriched strata of the BARB5 drill core, modified after [1]. Data from this study are included and show significant admixtures of an ET component in all three samples and complementarities between spherule-enriched and spherule-depleted reservoirs. This argues for higher ET carrier phase enrichments in the groundmass compared to spherules. Data for Fig Tree Group sediments reflect the background (country rock) PGE abundances and are from Siebert et al. [12]. Chondrite data are from Tagle and Berlin [13].