PLATINUM GROUP ELEMENT-RICH MICRONUGGETS FROM ARCHEAN SPHERULE LAYERS IN THE BARBERTON GREENSTONE BELT, SOUTH AFRICA: TEM AND HR FE-SEM/EDX ANALYSIS.

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Introduction: Archean spherule layers (SL) in the Barberton Greenstone Belt (BGB) are amongst the oldest known impact deposits on Earth that were originally identified by their excessive PGE contents. The search for phases hosting this extraterrestrial PGE component lead to discovery of sub-µm PGE phases [1], whose formation process(es) is (are) still controversial: primary particles from the projectile, the product of impact melting, or condensation from the impact plume have all been proposed as possible origin for these alloys. We here report results of a TEM study of six sub-µm PGE metal nuggets and a FE-SEM/EDX study of additional eight PGE metal particles. Samples are from the BARB5 ICDP drill core and from the CT3 exploration core.

Results: TEM imaging of a 600 nm PGE-bearing metal particle from BARB5 shows that this micronugget (*BARB-PGM-1*) is composed of several 50-200 nm, platelet-shaped crystals, in part of hexagonal morphology. Crystals are randomly oriented, have no apparent preferred crystallographic orientation to the host, and are composed of 4-20 nm subgrains. These nanocrystals are Ni and Fe rich and contain varying amounts of Ir, Pt, Ru, Os, and Rh. Micronugget *PGM-1* from core CT3 is a homogeneous, 600 nm monocrystal, without structural relation to the spinel host. *PGM-1* does not contain any Fe and is composed of non-refractory Ni alloyed with Ir, Pt, Ru and Os. Sample *PGM-13* (CT3) is a 800 nm micronugget seemingly composed of 3 individual subgrains. Electron diffration indicates a hexagonal closest packing (hcp) crystal structure, without apparent crystallographic orientation relationship to the Ni-Cr spinel host. Subgrains in *PGM-13* feature different Ni/Ru and Ni/Pt ratios. *PGM-6* (CT3) is a 800 nm PGE metal alloy with well developed crystal faces. A distinct exsolution pattern of parallel lamellae is apparent throughout the particle and needle-like exsolutions were observed in the surrounding Ni-Cr spinel. Electron diffraction revealed a preferred crystallographic host-nugget relation. *PGM-9a* (CT3) is a 2 µm PGE-bearing Pt-Ni alloy with cubic crystal structure, a lamellar eutectic microstructure, and no preferred structural orientation to the host. *PGM-9b* from the same host spinel is a 2.4 µm micronugget composed of 3 subcrystals composed of varying amounts of Pt, Os, Ni and secondary Sb, As, and S. *PGM-9b* shows morphologies characteristic for exsolution from a (siliceous) melt, i.e., droplet morphology. All PGMs investigated in this study have distinct interface zones across the host-nugget boundary with near-complete decrease of Ni and PGE abundances, as revealed by EDX line profiling.

FE-SEM-EDX analysis of eight PGM nuggets from CT3 was carried out at 6 kV accelerating voltage and only 75 pA probe current [2]. Quantitative analysis of maps and area spectra show that the PGMs contain different amounts of Ni alloyed variably with Ir, Pt, Ru, and Rh in highly variable chemical zonation patterns.

Conclusion: High resolution TEM analysis of six PGMs in Ni-Cr spinel from four Archean spherule layer samples in the BGB indicates that there is no structural or chemical relation between primary PGE-rich micronuggets and Ni-Cr spinel - for five of the six PGM particles analysed. For one PGM particle (*PGM-6*), formation by exsolution from the Ni-Cr spinel is strongly supported by an exsolution pattern and a preferred crystallographic host-nugget relationship. Chemical zonation patterns of PGEs in PGMs in *BARB-PGM-1*, *PGM-1* and *PGM-13* sometimes match expectations in terms of an origin by direct equilibrium condensation but for some elements (e.g., Pt in central areas of such particles) they are contrary to the accepted condensation sequence. This could be due to control by the local composition of a PGM formation region in the impact vapor plume. Formation of PGMs by exsolution from a melt seems to be most likely for *PGMs 9a* and *9b*, as indicated by droplet shaped morphology, but appears unlikely for all other PGMs investigated here. The quantification results of eight additional PGE phases from core CT3, by low voltage FE-SEM/EDX, show no consistent chemical zonation trend that could be taken as support for one specific formation mechanism.

In summary, TEM analysis in this study provides evidence for the formation of such PGMs by exsolution from the spinel host phase, exsolution/precipitation from a melt phase, and condensation from a gas phase (of the impact vapor plume). Low voltage FE-SEM/EDX with sub-micrometer spatial resolution has successfully demonstrated that this method can be used to characterise and pre-select samples for further planned TEM investigations that are necessary to better constrain the nature of PGE phases and decipher their formation history.

References: [1] Mohr-Westheide T. et al. 2015. *Geology 43:*299-302. [2] Salge T. et al. (abstract, submitted) *80th Annual Meeting of The Meteoritical Societ*, Santa Fe, USA, July 2017.