TRANSMISSION ELECTRON MICROSCOPE STUDY OF PLATINUM GROUP ELEMENT-RICH MICRONUGGETS FROM TWO SPHERULE LAYER INTERSECTIONS, BARBERTON GREENSTONE BELT, SOUTH AFRICA.

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Introduction: Archean spherule layers (SL) in the Barberton Greenstone Belt (BGB) are amongst the oldest known impact deposits on Earth. Spherules could either represent molten impact ejecta, condensation products from impact plumes or crater ejecta melted during atmospheric reentry. Barberton SL were originally identified by their excessive PGE contents. The search for phases hosting this extraterrestrial PGE signature lead to discovery of sub-µm PGE phases [1], whose formation is still controversial. Primary meteoritic particles from the impacting body, the product of impact melting, or a scenario of condensation in the impact plume have all been proposed as origin of these alloys. Here, we report the results of a first transmission electron microscopy (TEM) study of three submicrometer sized, primary PGE metal nuggets. Samples are from the BARB5 ICDP drill core from the barite valley Syncline, central BGB, and from the CT3 exploration core, northwestern BGB.

Methodology: Following SEM and EMPA characterization, FIB foils from three PGE grains were prepared for TEM. Specifically, one cluster of platinum-group minerals (PGMs) in a sample from the BARB5 drill core at 511.36 m depth from the central part of the BGB and two PGE micronuggets (PGM-1; PGM-13) in a CT3 core sample at 69.35 m depth were analyzed. Bright and dark field TEM, high-resolution TEM, and electron diffraction methods were applied to determine the nature, textural characteristics, microstructure, and orientation with respect to the Ni-Cr spinel host crystals for these PGE particles. Additionally, nano-scale analytics (EDX) including spot analysis and line profiling in PGE micronuggets and host spinel were carried out to obtain detailed information about the composition, chemical zoning, and possible diffusion at host-nugget interfaces.

Results: Bright field TEM and HAADF mode imaging of a 600 nm PGE-bearing metal particle from the BARB5 drill core show that this micronugget is composed of several 50-200 nm, platelet-shaped crystals, sometimes exhibiting hexagonal morphologies. The crystals are randomly oriented and have no apparent preferred crystallographic orientation to the host. Selected area electron diffraction (SAED) patterns of individual grains revealed that they form a heterogeneous agglomeration of platy, 4-20 nm sized particles. TEM EDX spot analysis of selected crystals showed that individual nanocrystals are Ni and Fe rich and contain varying amounts of different refractory metals, such as Ir, Pt, Ru, Os, and Rh. In general, Fe, Ni, and Pt are enriched in the center of PGMs changing to lower concentrations at the rims (but chemical analysis is often hindered by the internal polycrystallinity of individual PGM grains).

Micronugget PGM-1 in drill core CT3 is a homogeneous monocrystal of 600 nm size, enclosed by Ni-Cr spinel. No structural relation between PGE micronugget and host phase was found. PGM-1 does not contain any Fe and is composed of non-refractory Ni alloyed with Ir, Pt, Ru and Os. A line profil across the host-nugget boundary of PGM-1 demonstrates a distinct interface zone with abrupt change of Ni and PGE abundances with a nearly complete decrease of Ru and Ir and rapidly changing Ni abundance. PGM-13 is a ca. 800 nm PGE micronugget likely composed of 3 individual subgrains. SAED pattern of one of the three subgrains indicates a hexagonal closest packing (hcp) crystal structure without apparent crystallographic orientation relationships to the Ni-Cr spinel host. Subgrains in PGM-13 feature individual chemical PGE compositions (different Ni/Ru and Ni/Pt ratios).

Discussion: High resolution TEM analysis of PGMs in Ni-Cr spinel from Archean SL samples from the BGB has so far indicated that there is no structural or chemical relation between primary PGE micronuggets and Ni-Cr spinel. PGE metal phases are composed of individual single crystals of varied chemical compositions, that are foreign to the host. At the boundary between Ni-Cr spinel and PGE phases a distinct, narrow interface zone with rapidly changing PGE abundances is observed. SAED patterns in PGM-13 are consistent with hcp crystal structure, which is thought to be the stable form for such alloys at high temperature [2]. Random orientation of PGE crystals, missing crystallographic orientation of PGE crystals with respect to the host, individual chemical compositions of PGE phases, and their internal chemical zoning all argue against their formation by exsolution from the Ni-Cr spinel. More microstructural and compositional data are necessary to precisely constrain the nature of PGE phases and, thus, the formation process of these submicrometer PGE micronuggets.

References: [1] Mohr-Westheide T. et al. 2015. *Geology 43:*299-302. [2] Harries D. 2012. *Meteorit. Planet. Sci., 47:*2148-2159.