TEM, HR FE-SEM/EDX AND TKD ANALYSIS OF PLATINUM GROUP ELEMENT-RICH MICRONUGGETS IN BARBERTON SPHERULE LAYER SAMPLES.

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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 be molten impact ejecta and condensation products from impact plumes, or ejecta from impact craters that were 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 unresolved. Primary particles from the projectile, product of impact melting, or condensation in the plume have been proposed. We report results of a recent TEM study of six sub-µm platinum group-mineral (PGM) phases and a compositional FE-SEM/EDX study of additional eight PGMs, all hosted by Ni-Cr spinel. In addition, first results of a noval approach by transmission Kikuchi diffraction (TKD) analysis [2] tested on four PGE metal particles will be presented. Samples are from the BARB5 ICDP drill core (Barite Valley Syncline, central BGB), and from the CT3 exploration core (NE BGB).

Methodology: Following SEM and EMPA characterization, FIB foils from ten PGM grains were prepared for TEM and TKD analysis. Bright and dark field TEM, high-resolution TEM, and electron diffraction methods were applied to determine the textural characteristics, microstructure, and orientation with respect to the Ni-Cr spinel host crystals for these PGE particles. In addition, nano-scale TEM-EDX 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 evidence for diffusion at host-nugget interfaces. FE-SEM-EDX hyperspectal data were acquired at 6 kV and 77 pA on bulk samples. Quantification was performed with pure element reference samples (L- and M-line families of Ru, Rh, Pd, Re, Os, Ir, Pt: ~2-3 keV; Ni-L, Fe Cu-L: <1 keV) [4]. TKD in the scanning electron microscope (SEM) using electron-transparent, focused ion beam (FIB) samples was applied to analyze the crystal orientation of PGM grains at 10 nanometer resolution. EDS for phase identification was performed simultaneously with TKD.

Results: TEM imaging of sub-µm PGE-bearing metal particles shows for some micronuggets that they contain randomly oriented crystals, have no apparent preferred crystallographic orientation to the host, and are sometimes composed of 4-20 nm sized subgrains. These nanocrystals are Ni- and sometimes Fe-rich, and contain varying amounts of Ir, Pt, Ru, Os, and Rh. For one micronugget (*PGM-6* from the CT3 core), a distinct exsolution pattern of parallel lamellae is apparent throughout the particle, and needle-like exsolutions were observed in the Ni-Cr spinel host. One PGE metal nugget (*PGM-9b)* shows droplet morphology characteristic for precipitation from a (siliceous) melt [compare 3]. Quantification of maps with 4x4 binning of ~5 nm pixels and area spectra shows the presence of Ir, Pt, Ru, Rh, Os, Ni in highly variable chemical zonation patterns. For one specimen (CT3_71-82-chrm2-PGM2) an internal PGE zonation pattern according to the normal sequence of PGE condensation temperatures [5] was observed, with highly refractory metals in the central part, and lower refractory metals in the outer part of the particle.

First TKD analysis of four metal particles confirmed the compositional results from FE-SEM/EDX. For CT3_71-82-chrm2-PGM2, TKD and EDS identified a Ru-Ir-Os phase with hexagonal symmetry in the center of the grain and a Ni-Pt phase in pseudo-cubic crystal structure in the outer part. No preferred crystallographic orientations of PGE crystals with respect to the host phase were observed by TKD.

Conclusions: TEM analysis provides sometimes evidence for either the formation of such PGMs by exsolution from the spinel host phase, precipitation from a melt phase, or condensation from a gas phase (of the impact vapor plume) [3]. The quantification results for eight PGE phases from core CT3 by low kV FE-SEM/EDX, and the first TKD analyses of metal particles showed no consistent chemical zonation trend that could support a specific formation mechanism. However, for one PGM sample a PGE zonation pattern was found that is compatible with a condensation origin. In summary, compositional data and microstructural results indicate that several mechanisms may have been involved in the formation of PGM associated with Ni-Cr spinel in Archean SL. Further analytical efforts must be made to enlarge the statistical database. Our non-destructive low voltage FE-SEM/EDX with sub-µm spatial resolution will stimulate new approaches to earth and planetary sciences, and can be used as a reconnaissance method before selection and preparation for other, complementary analytical techniques (TEM, EBSD, and NanoSIMS).

References: [1] Mohr-Westheide T. et al. 2015. *Geology 43:*299-302. [2] Daly et al., 2017 *GCA* 216:42-60. [3] Mohr-Westheide et al. 2018. *MAPS*, accepted for publication 28 March 2018 [4] Salge T. et al. 2017 (abstract) *80th Ann. Meet. of The Met. Soc.*, Santa Fe, USA, July 2017. [5] Lodders K. 2003. *Astrophys. Jour., 591*:1220-1247.