TRANSMISSION ELECTRON MICROSCOPE STUDIES OF PLATINUM GROUP ELEMENT-RICH MICRONUGGETS IN BARBERTON SPHERULE LAYER SAMPLES. T. Mohr-Westheide[1,2], A. Greshake[1], R.Wirth[3], W.U. Reimold[1,4]; [1]Museum für Naturkunde, Leibniz-Institut für Evolutions- und Biodiversitätsforschung, Invalidenstrasse 43, 10115 Berlin, Germany. [2] Freie Universität Berlin (FU Berlin), Institut für Geologische Wissenschaften, Malteserstrasse 74-100, D-12249 Berlin, Germany, [3]Helmholtz-Zentrum Potsdam, Deutsches GeoForschungsZentrum (GFZ), Sektion 4.3, Telegrafenberg, D-14473 Potsdam, Germany. [3]Humboldt Universität zu Berlin, Unter den Linden 6, 10099 Berlin, Germany. E-mail: tanja.mohr-westheide@mfn-berlin.de.

Introduction: The oldest known remnants of large bolide impacts onto Earth are ca. 3.47-3.2 Ga old Archean spherule layers of the Barberton Greenstone Belt (BGB) in South Africa and the Pilbara craton in West Australia. Spherules in these layers are interpreted as molten impact ejecta and condensation products from impact plumes or ejecta that were melted during atmospheric reentry. Barberton spherule layers were identified by their excessive PGE contents. The search for phases hosting the extraterrestrial PGE signature in BGB spherule layer samples lead to the discovery of sub-µm PGE micronuggets [1]. The formation of these PGE alloys 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.

Methods: 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 CT3 core sample at 69.35 m depth from the north-eastern part of the BGB were analyzed. The foils are 15 × 10 × 0.1 µm in dimension and were studied using a FEI Tecnai™ G2 F20 X-Twin operated at 200 kV with a field emission gun electron source at GFZ Potsdam. The microscope is equipped with an EDAX ultra-thin window EDX system, a Fishione high-angle annular dark-field (HAADF) detector, and a post-column Gatan imaging filter (GIF Tridiem). Bright and dark field TEM, high-resolution TEM and electron diffraction methods were applied to these PGE micronuggets to determine their nature, their textural characteristics, their microstructure, and their orientation with respect to the spinel host crystals. Additionally, nanoscale analytics (EDX) including spot analysis and line profiling in PGE micronuggets and Ni-Cr spinel were carried out to obtain detailed information about the composition, chemical zoning, and possible diffusion at host-nugget interfaces.

Results: A 600 nm sized PGE-bearing metal particle from the BARB5 drill core sample, hosted by Ni-Cr spinel, was analyzed by TEM. Bright field TEM and HAADF mode imaging (Fig. 1) 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 spinel. Selected area electron diffraction (SAED) patterns of individual grains revealed that they form a heterogeneous agglomeration of platy, 4-20 nm sized particles.

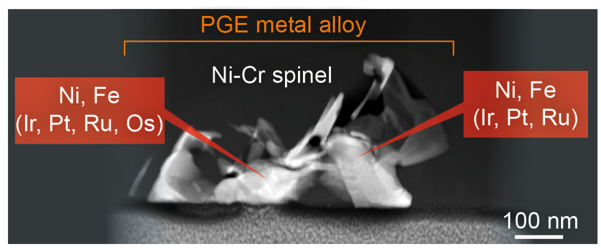

Fig. 1: HAADF image of a PGE rich micronugget, composed of randomly oriented single crystals of different sizes, hosted by Ni-Cr spinel. Individual crystals feature different elemental compositions.

TEM EDX spot analysis of selected crystals of the cluster showed that individual nanocrystals are in general Ni and Fe based and contain varying amounts of different refractory metals, such as Ir, Pt, Ru, Os, and Rh. While most of the grains are enriched in Ir, Pt and Ru, few grains also contain significant amounts of the highly refractory siderophile element Os (Fig. 1). Individual internal chemical zonation of platy crystals is commonly observed in the PGM cluster, by changes in Ru, Pt, Fe, and Ni abundances. 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 (Fig. 2) in drill core CT3 is a homogeneous monocrystal with a diameter of 600 nm enclosed by Ni-Cr spinel. No structural relation between PGE micronugget and host phase has been found. PGM-1 does not contain any Fe and is composed of nonrefractory Ni (40 at%) alloyed with Ir, Pt, Ru and Os. A line profil across the host-nugget boundary of PGM-1 (Fig. 2) 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. Further PGE phase identification by TEM nano-scale EDX spot analysis in PGM-1 revealed nearly complete absence of Os and Pt in the outer parts of the crystal, whereas a significant amount of highly refractory Os and lower refractory Pt can be detected in the center of the nugget.

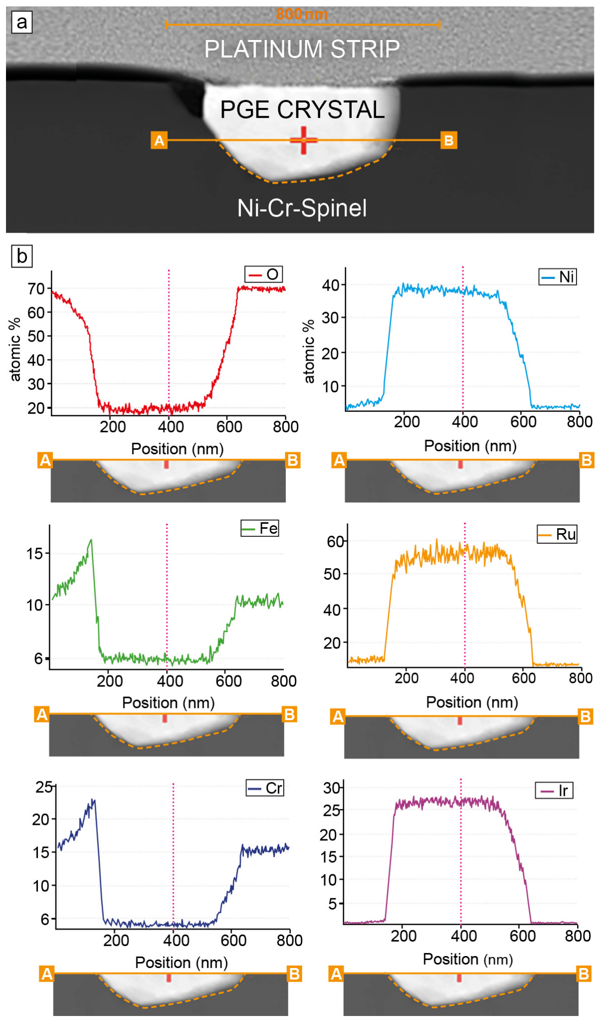

Fig. 2: (a) PGE-rich monocrystal PGM-1 in association with Ni-Cr spinel in HAADF mode documenting a 800 nm EDX line profil with a step size of 2 nm across the host-nugget boundary, plotted in b. (b) EDX line profil demonstrating rapidly changing PGE abundances at the Ni-Cr spinel/PGE micronugget interface.

PGM-13 is a ca. 800 nm sized PGE micronugget possibly composed of 3 individual subgrains. A SAED pattern of one of the three subgrains indicates a hexagonal closest packing (hcp) crystal structure without apparent crystallographic orientation relationships to the surrounding Ni-Cr spinel. Subgrains in PGM-13 feature individual chemical compositions re. PGEs. Varied compositions re. Ni/Ru and Ni/Pt has been found.

Discussion: High resolution TEM analysis of PGMs in Ni-Cr spinel from Archean spherule layer 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. Two SAED patterns in PGM-13 are consistent with hexagonal closest packing structure (hcp), 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.

A further process for generation of PGMs could be precipitation from impact melt but our observations do neither show any features typical of melting (e.g., droplet shape) nor a consistent trend for precipitation of PGMs from a melt phase (e.g., expected crystallization products along a profile from center to rim). Platy agglomeration of irregularly shaped PGM nanophases (4-20 nm) in Ni-Cr spinel as observed in the BARB 5 sample would rather suggest a formation of PGMs from a gasphase. Regarding the formation of PGM alloys in Ni-Cr spinel by condensation it is to note that refractory metals would condense in the order Re, Os, Ir and Ru, followed by the less refractory metals Pt, Rh, Fe and Ni [3]. However, in our TEM study the chemical elemental compositions of individual PGMs sometimes feature internal variations that are compatible with a condensation origin but not consistently - at least not all elements behave concordant with the predicted condensation sequence (e.g., Pt that is often enriched in the center of PGMs).

Concerning the hypothesis that PGE phases could represent remnants of the meteoritic projectile, it is to note that this scenario is very unlikely, as it would require a very exotic projectile, and to date no meteorite is known to contain major amounts of PGE nuggets. So far, it has thus not been possible to unambiguously pinpoint whether PGE phases either represent remnants of the meteoritic projectile, formed by condensation in the impact vapor plume, or are crystallization products from impact melt. 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. [3] Lodders K. (2003) *Astrophys. Jour., 591,* 2, 1220-1247.