PETROLOGY AND GEOCHEMISTRY OF ARCHEAN SPHERULE LAYER OCCURRENCES IN THE BARB 5 ICDP DRILL CORE, BARBERTON GREENSTONE BELT. T. Mohr-Westheide[1], J. Fritz[1], A. Hofmann[2], R. Tagle[3], C. Koeberl[4,5], W.U. Reimold[1,6], D. Mader[4], T. Schulz[4], and D. Höhnel[1] [1]Museum für Naturkunde Berlin, Invalidenstrasse 43, 10115 Berlin, Germany. [2]Department of Geology, University of Johannesburg, Johannesburg, South Africa. [3]Bruker Nano GmbH, Am Studio 2, 12489 Berlin, Germany. [4]University of Vienna, 1090 Wien, Austria. [5]Natural History Museum, 1010 Vienna, Austria. [6]Humboldt-Universität zu Berlin, Unter den Linden 6, 10099 Berlin, Germany. E-mail: tanja.mohr-westheide@mfn-berlin.de;

Introduction: In the Barberton Greenstone Belt (BGB), four distinct spherule horizons (S1-S4) with ages between about 3.5 and 3.2 Ga have been considered amongst the oldest remnants of large bolide impacts onto Earth [1,2] and allow to investigate the early Archean impact record on Earth. Spherules in these layers are interpreted as molten impact ejecta and condensation products from impact plumes or ejecta that were melted during atmospheric re-entry [2,3]. Primary signatures preserved in the spherule layers may provide insights regarding the impact event(s) and the projectiles involved. However, the spherule layers were extensively modified by sedimentary, diagenetic, and metamorphic processes [4], leaving, for example, questions regarding the number of individual spherule layers or the nature of primary versus secondary spinel and primary versus secondary projectile signatures [5].

In order to discriminate between primary and secondary (alteration) geochemical characteristics of the spherule layers, a comprehensive study of sedimentary, petrographic, mineralogical, and geochemical characteristics from a set of new samples of spherule layers discovered between 510 and 512 m depth in the 760-m-long ICDP drill core BARB 5 from the Barite Valley Syncline of the BGB has been carried out.

Analytical methods: All samples were studied by transmitted and reflected light microcopy, scanning electron microscopy (SEM), with the Bruker M4 Tornado micro-XRF scanner, and by instrumental neutron activation analysis (INAA). The Bruker M4 Tornado is a micro X-ray fluorescence spectrometer (μ-XRF) with a focused X-ray beam from a Rh-anode operated at 50 kV for non-invasive high spatial resolution (<25 μm) scans. A continuous section of the depth interval from 511.31 to 511.51 m was cut into 22 individual subsamples, which were each divided into two parts. Each sample was analyzed at the University of Vienna for trace element contents by instrumental neutron activation analysis (INAA) and the Os isotopic composition by isotope dilution-thermal ionization mass spectrometry.

Results: In a 20 cm thick core interval (511.31-511.51 m) in BARB 5 (Fig. 1) 0.3 to 2 mm sized spherules occur densely packed in four layers each about 4 cm thick (Fig. 1). A further, 4 cm thick, intersection of a spherule layer occurs at 512.30 m depth, results for which will be disussed elsewhere. Layers 1-4 are separated by <1.5 cm thick shale beds. Cross-lamination is observed in the interval between layers 1 and 2. This spherule-layer-bearing interval correlates either with spherule layer S2 or S3 [6] or represents a different unit. Spherules on top of layer 1 (Fig. 1) are strongly sheared, in stark contrast to the generally un- or slightly deformed spherules in layers 2-4. In general, all spherule beds are comprehensively altered to assemblages of quartz, phyllosilicates, K-feldspar, Mg-siderite, barite, and calcite. The spherule layers in BARB 5 core show sulfide mineralization increasing from layer 1 to layer 4, with main ore minerals being pyrite, chalcopyrite, and gersdorffite. Sulfide mineralization often affects both matrix and spherules; some spherules are totally replaced by sulfides. Statistical analysis of spherule size did not show sorting of the individual spherule beds, but a slight increase of average spherule size from top to bottom was observed.

The bottom layer 1 displays a comparatively low Cr abundance in the matrix and even less in the spherules, as shown by the X-ray elemental map (Fig. 1). Chromium is highly concentrated in the sheared spherule zone (Fig. 1) enriched in chlorite and colored green. Nickel does not correlate with chromium and is only abundant in the zone straddling the transition from the green layer into the shale interbed above. Ni abundances in spherule layers may or may not be correlated with S and As contents. Chromite grains are well visible in a few undeformed sperules on top of the sheared zone. In contrast to layer 1, layers 2-4 contain zircon and nickel-rich chrome-spinel. Such Ni-rich chromites have been reported from both layers S2 and S3 [5,6]. Scanning electron microscopy indicates that spinel in BARB 5 has distinct multiple types of zonation, mainly reflected in their Fe, Ni, Zn, and Cr contents. A major spinel type involves cores rich in NiO (up to 19 wt%), changing to rims rich in ZnO (up to 7.9 wt%) (Fig. 2). Another main type is characterized by moderate NiO (up to 7.5 wt%) and relatively high Cr_2O_3 (up to 50 wt%) contents without zonation. The contents of Cr_2O_3 and NiO display, in general, a negative correlation. Where abundant, Co correlates well with nickel. In some cases V is abundant (up to >3.1 wt%). Highest Zn concentrations are often observed around the rims of Ni-rich spinels. Internally broken spinel frequently shows marginal Zn-enrichment on all fragments, indicating that this is likely secondary alteration late in the evolution of these materials.

The trace element analyses by INAA showed distinctly elevated contents of the siderophile elements, such as Ni, Co, Ir, and Os, but also of Cr and Au, over the whole sample section. The lowest contents were found right at the top of the section, with about 0.3 to 10 ppb Ir, 7 to 22 ppm Co, and 120 to 470 ppm Ni. The highest amounts were found at the bottom of spherule layer 3 (Fig. 1) with about 600 ppb Ir, 250 ppm Co, and 3800 ppm Ni, as well as at the bottom of spherule layer 2 with 730 ppb Ir, 530 ppm Co, and 5400 ppm Ni. In other parts of the section, the siderophile element contents were lower, with Ir in the 150-400 ppb range.

Conclusions: The presence of four closely spaced spherule beds with intermittent thin sedimentary layers is suggestive of aquatic deposition after a single impact event, with multiphase currents affecting sedimentation. However, grain size statistics do not significantly indicate regular decrease of spherule sizes from layers 1 to 4, which one would expect to occur with deposition under waning current activity. Our preliminary petrographic and geochemical findings indicate strong hydrothermal overprint for all lithologies in the studied section of the BARB 5 core. Primary characteristics include spherule size and shapes, and presence of Ni-rich chromite (projectile related formation), as well as zircon (terrestrial source) – both of which are, however, noticeably absent in layer 1. Sulfide mineralization, (e.g., pyrite, gersdorffite, and other sulfides) is of secondary origin and may be related to chemical alteration and metamorphism. High Zn concentrations frequently observed along cataclased spinel grains likely relate to late overprint. High abundances of the siderophile elements (Ni, Co, Ir, Os, Cr, and Au) are thought to reflect extraterrestrial components. However, as already observed by [7], these abundances are on the same level, or even exceeding, the contents of these elements in chondritic meteorites, which remains puzzling. The Os isotopic compositions are currently being analyzed and will hopefully shed additional light on the nature of the siderophile element enrichment.

References: [1] Lowe D. R. et al. (1989) *Science*, 245, 959-962. [2] Lowe D. R. et al. (2003) *Astrobiology*, 3, 7-47. [3] Johnson B. C. and Melosh H. J. (2014) *Icarus,* 228, 347-363. [4] Hofmann A. et al. (2006) *Geol. Soc. Amer. Spec. Pap. 405, 33-56.2* [5] Reimold W. U. et al. (2000) In: *Impacts and the Early Earth*, 117-180. [6] Byerly G. R. and Lowe D. R. (1994) *Geochim. Cosmochim. Acta*, 58, 3469-3486. [7] Koeberl C. and Reimold W. U. (1995) *Precambrian Research,* 74, 1-33.

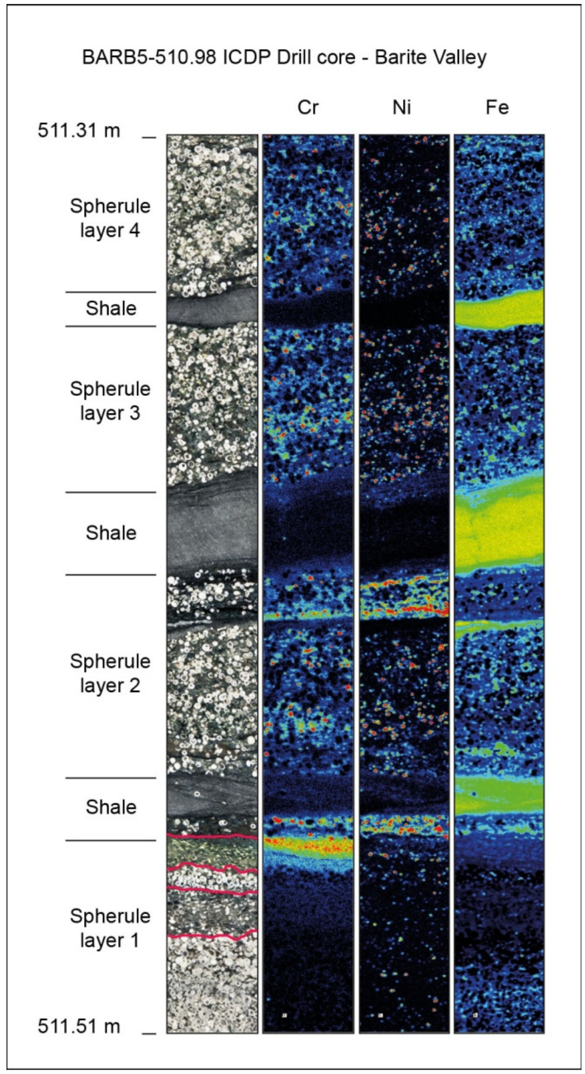

Fig. 1: Archean spherule layers (1-4) from the BARB5 drill core. The core interval hosts 4 spherule layers separated by shale beds. Elemental scans on the right (Bruker M4 Tornado micro-XRF scanner) show the distribution of Cr, Ni, and Fe.

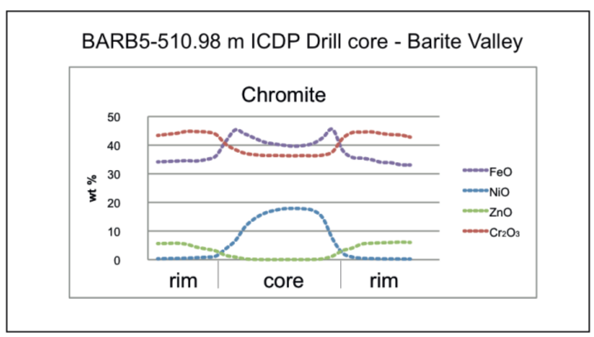

Fig. 2: Main spinel type occurring in the BARB5-510.98 core. Note zonation from cores rich in NiO (up to 19 wt%) changing to rims rich in ZnO (up to 7.9 wt%).