GERMANIUM ELEMENTAL AND ISOTOPIC TRACING OF CA. 3.2 GA IMPACT SPHERULE LAYERS FROM THE BARBERTON GREENSTONE BELT (SOUTH AFRICA).

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Introduction: Planet formation resulted from complex processes of collision-accretion during Solar System history. Migration of giant planets and energetic collisions of planetary bodies with telluric planets are thought to be at the origin of an intense bombardment during the first 1.5 Ga as testified by the lunar crater record [1]. There is no record of ancient impact craters as old as ~ 3 Ga on Earth. However, evidence of early bombardment comes from the identification of impact spherules that were molten or condensed from vaporized target and impactor material. The 3.47-3.24 Ga spherule layers from the Barberton Greenstone Belt (BGB) constitute some of the oldest traces of heavy bombardment on Earth [2]. Spherule layers with high platinum group metal (PGE) contents display Cr isotopic anomalies indicating a carbonaceous chondrite like projectile [3]. Impacts include high-temperature processes that may lead to the loss of volatile elements with light isotopes escaping in the vapour phase. Germanium is a siderophile and volatile element that may record evaporation or condensation processes [4], and the nature of an impactor. Here we present a Ge elemental and isotopic study of 3.23 Ga spherule layer intersections that were acquired recently in the BARB5 drill core from Barberton (ICDP 2012-2013, Fig Tree Group, Barite Valley syncline). Drilling intercepted well preserved spherule layers that alternate with shale and chert layers from 510 to 512 m depth [5].

Samples and methods: A 22 cm long sample from 511.31 to 511.51 m depth in the BARB 5 core exhibits 4 spherule layers each about 4 cm thick that are intercalated with 1.5 cm-thick shale layers *(Figure 1)* [5]. The section was carefully cut into 22 sub-samples according to lithologies, after close examination under the binocular microscope to ensure the absence of spherules in the shale sub-samples and *vice versa*. These small 0,2g to 1g sub-samples were powdered in an agate mortar, and analyzed for major (ICP-OES) and trace elements (ICP-MS) at the SARM facility (CRPG-Nancy), and for Ge isotopic compositions by using chemistry and MC-ICPMS techniques (Neptune*Plus,* ThermoScientific) developed at CRPG ($\delta^{74/70}Ge_{NIST3120a} \pm 0.2‰$, 2σ SD) [4,6].

Results and discussion: The chemical profiles *(Figure 1)* show contrasting compositions between spherule and shale layers, as well as between the lower layer 1 with distinct populations of spherules, and heterogeneous composition, and the more homogeneous upper layers 2 to 4. Ge contents are higher in spherule layers (3-7 ppm) compared to shale layers (2-3 ppm), the latter having Ge concentrations typical of terrestrial shale. The Ge enrichment pattern is mirrored by major (SiO_2, Al_2O_3, K_2O, Na_2O, TiO_2) and trace element contents, irrespective of their geochemical affinity, i.e., whether volatile or refractory (Ti, Nb, Zr), siderophile or lithophile. The exception are the LREEs (La, Ce, Nd) that are preferentially enriched in shale layers. The shale layers are also characterized by very high Fe_2O_3 (≈30%), LOI (≈20%), MgO and MnO, and to a lesser extent CaO contents, indicative of being siderite-rich.

A "Ge signal" of about 4 ppm characterizes the spherule layers. A heterogeneous Ge distribution up to 7 ppm in some deformed sub-samples in layer 1 does not allow to rule out fluid-induced remobilization.

First Ge isotopic measurements indicate a lighter Ge isotopic composition for the spherule layer 3 ($\delta^{74/70}Ge_{NIST3120a} < -0.9‰$) compared to any terrestrial crustal or meteoritic Ge isotopic compositions [4,6]. This signature agrees with an evaporation-condensation mechanism following the impact, also resulting in enrichment of volatile Ge in the condensed phase.

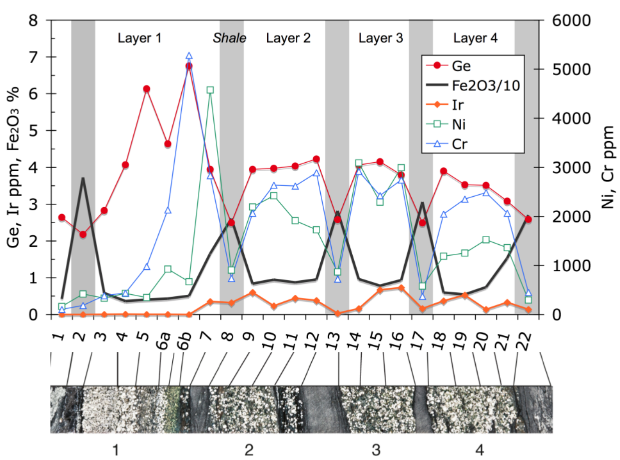

Figure 1: Chemical profiles of Fe_2O_3, and Ge, Ni, Cr and Ir across the 4 spherule layers and intercalated shales from BARB5 drill core. Ir data by INAA from [5].

References: [1] Fritz J. et al. 2014. *Planetary and Space Science* 98:254–267. [2] Hofmann A. et al. 2006. *Geological Society of America, Special Paper* 405:35-56. [3] Kyte F. T. et al. 2003. *Geology* 31:283-286. [4] Luais B. 2007. *Earth and Planetary Science Letters* 262:21-36. [5] Mohr-Westheide T. et al. 2015. *Geology* 43:299-302. [6] Luais B. 2012. *Chemical Geology* 334:295-311.