LOCATION AND SPECIATION OF GERMANIUM IN THE BUTLER AND NORTHWEST AFRICA 859 UNGROUPED IRON METEORITES. Laurence A.J. Garvie[1,2], Chi Ma[3], and Axel Wittmann[4]; [1]Center for Meteorite Studies, [2]School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA (lgarvie@asu.edu); [3]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, USA. [4]Eyring Materials Center, Arizona State University, Tempe, AZ 85287, USA.

Introduction: Butler is a Ni-rich (~16 wt%) ungrouped iron meteorite with the highest recorded bulk Ge near 0.2 wt% [1]. It has an anomalous structure dominated by long pointed kamacite lamellae (termed α sparks) dispersed in a plessitic (α+γ) matrix [2]. Northwest Africa (NWA) 859 (aka Taza) is structurally and compositionally similar to Butler. The elemental data (J.T. Wasson, priv. comm.) for these two irons are remarkably similar across a range of elements including Cr, Co, Ni, Ga, Ge, As, W, Ir, Pt, and Au. Germanium is an unusual element as it displays siderophile, chalcophile, and lithophile tendencies. As such, its partitioning and mineralogical associations can provide insights into early Solar System processes. Here, we explore the location and speciation of Ge in these irons, and in the process, describe a new and common Ge-rich Ni-P mineral.

Materials and methods: Pieces of Butler and NWA 859 were cut so they fit into a 1-inch SEM holder. The samples were polished and nital etched. SEM and WDS analyses were performed with the JEOL JXA-8530F electron microprobe in the Eyring Materials Center at ASU, and the CAMECA SX100 electron microprobe in the Michael J. Drake Electron Microprobe lab at the UofA. Electron backscatter diffraction (EBSD) analysis was undertaken using an HKL EBSD system on a ZEISS 1550VP Field-Emission SEM, operated at 20 kV and 6 nA in focused beam mode with a 70º tilted stage and in a variable pressure mode (25 Pa) at the California Institute of Technology. The structure was determined and cell constants obtained by matching experimental EBSD patterns with Ni-Ge-P, Ni-Si-P, and Ni-P phases.

Results: WDS data show Ge to ~0.6 wt% in the tetrataenite (Tt) adjacent to the kamacite (Fig. 1). The Ge and Ni concentrations roughly parallel each other, with lower concentrations in the kamacite, increasing sharply in the tetrataenite and then decreasing towards the plessite. Ge and Ni are spatially variable in the plessite: in general, Ge is partitioned to the Ni-rich γ phase. Iron (and Co, not shown) concentrations anticorrelate with Ni and Ge. The composition of the tetrataenite with the maximum Ge is $Fe_{58.1}Ni_{41.2}Ge_{0.4}Co_{0.3}$. A typical analysis from kamacite free of precipitates has the composition $Fe_{93.32}Ni_{5.10}Ge_{0.15}Co_{1.43}$. The elemental line profile for Ge (Fig. 1) shows concentration spikes within the kamacite: these spikes correlate with the locations of precipitates.

Preliminary TEM studies revealed Ge-rich submicron Ni-Fe-P precipitates in Butler [3]. These precipitates were characterized on extraction replicas. As such, the location of the precipitates with specific metal structures proved challenging. In contrast, the high-spatial-resolution SEM imaging clearly reveals an abundance of high-Z precipitates in the kamacite (Fig. 2). Few precipitates were found in the surrounding plessite. They are typically submicron sized and show platy euhedral and equant morphologies, with some kamacite containing hundreds of nanoparticles per 100 μm^2 (Fig. 2). WDS maps and EDS analyses show that most precipitates are rich in Ni, Ge, and P. In contrast, Ge was not detected by EDS in the coarser grained schreibersite and nickelphosphide precipitates. EDS data from the precipitates embedded in the kamacite shows high, but variable Fe, with lesser Ni, P, and with Ge to 1.5 wt%. In order to better constrain the compositions of the precipitates, they were separated from the metal and deposited onto a C planchette (Fig. 3).

A new Ni-Ge-P mineral. EDS spectra from the majority of the sub-micron-sized precipitates extracted from Taza show high x-ray counts for Ni, Ge, and P. Preliminary standardless EDS analyses show these particles contain ~8 to 10 wt% Ge, Fe typically < 1 wt%, and metal to P ratio near 4. A subset of particles contained measurable (by EDS) quantities of Ga±Pd±As±S. The EBSD patterns from the Ni-Ge-P precipitates were matched to the P-1 triclinic structure of synthetic $Ni_4Ge_{0.33}P_{1.17}$ [4], with a mean angular deviation of 0.35º to 0.40º, providing the following cell parameters: triclinic, a = 6.613 Å, b =6.70 Å, c = 6.80 Å, α = 98.7°, β = 102.7°, γ = 119.1°, space group: P-1, V = 244.75 Å^3, and Z = 4. The density (calc.) is 8.01 g·cm^{-3} using the formula $Ni_4Ge_{0.33}P_{1.17}$. These data are consistent with the discovery of a new mineral.

Conclusions: The partitioning of Ge with tetrataenite is consistent with earlier studies [5], showing the strong affinity of Ge with Ni. Here, we show a further strong partitioning of Ge into a new and common Fe-free Ni-phosphides in the kamacite of Butler and NWA 859, with Ge as a structurally essential constituent.

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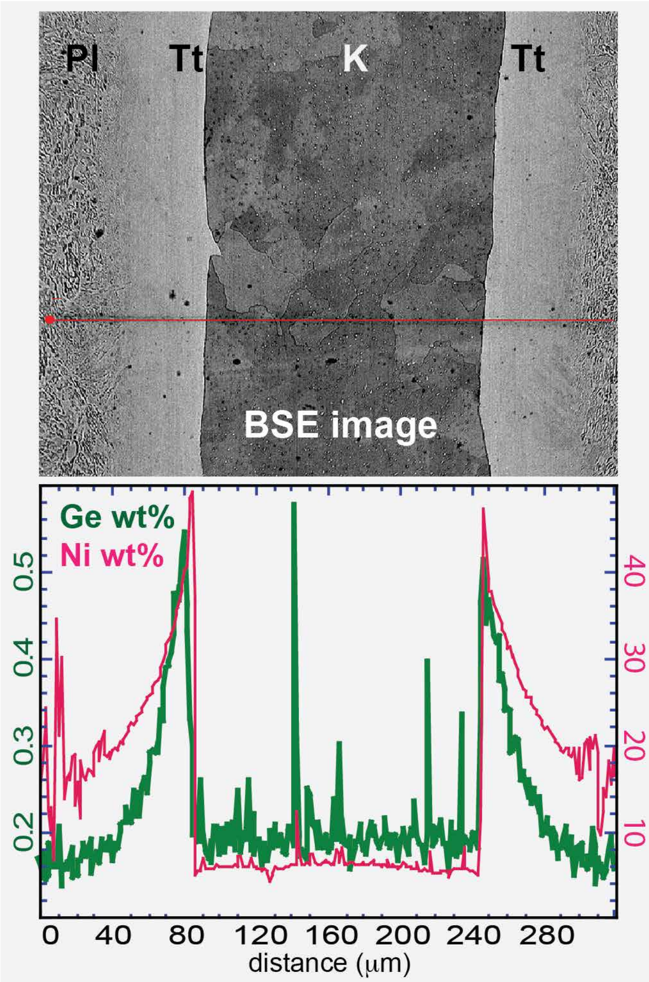

Figure 1 (above). Backscattered SEM image of a kamacite spark (K) from Butler, bordered by tetrataenite (Tt) and plessite (Pl). The red line shows the location of the elemental line profiles for Ge and Ni. Ge and Ni concentrations peak in the tetrateanite. The high Ge spikes in the kamacite correspond to the location of nanoprecipitates. **Figure 2 (right)**. SEI SEM image (top) from a representative kamacite spark from Taza and corresponding elemental maps for Ni, Ge, and P. Each of the nanoprecipitates in the SEI image shows high x-ray counts (white in the images) for Ni, Ge, and P. **Figure 3 (below)**. SEI SEM image of a cluster of nanoparticles extracted from Taza and deposited onto a C planchette. EDS shows these particles to be dominted by Ni, Ge, and P, with minor Fe.