GERMANIUM- AND GALLIUM-RICH NICKEL PHOSPHIDE "Ni_3P" NANOPRECIPITATES FROM THE ODESSA (IAB-MG) IRON METEORITE Laurence A.J. Garvie[1,2], [1]Center for Meteorite Studies, [2]School of Earth and Space Exploration, Arizona State University, 781 East Terrace Rd., Tempe, AZ 85287-6004 (lgarvie@asu.edu).

Introduction: Measurements of Ge and Ga in iron meteorites have been central in their chemical classification, e.g., [1, 2]. In iron meteorites, Ga concentrations typically range from 0.1 to 200 ppm and Ge to ~500 ppm [2, 3], and to ~2000 ppm Ge in Butler [4, 5] and the Taza iron (NWA 859).

Several studies have sought to understand the geochemical behavior of Ge and Ga during the evolution of iron bodies. Key is understanding the distribution of these elements during Widmanstätten formation and between the precipitating phases. Goldstein [4] measured <40 ppm Ge in schreibersite, troilite, and cohenite from a range of irons, regardless of the bulk Ge content. Similarly, Ge in the Brenham pallasite ranges from 56 ppm in the metal, silicate-oxide 0.85 ppm, and troilite 17.3 ppm [6]. These data suggest that Ge partitions to the metals during evolution of the irons. Micropobe measurements show correlations between Ni and Ge, showing that Ge favors taenite relative to kamacite. The ratio of Ge in the taenite relative to the bulk is near 2 [4]. For example, Odessa taenite contains 460 ppm Ge and 180-305 ppm in the kamacite [4]. The Ge environment in Canyon Diablo kamacite was studied by EXAFS: the data suggest that Ge (and Ga) is surrounded by bcc Fe [7]. Yet, despite these studies, the hosts for Ge and Ga in iron meteorites are poorly constrained.

Here are described abundant Ni-rich, Fe-poor M_3P nanoprecipitates with wt% levels of Ge and Ga from the Odessa iron meteorite. Schreibersite $(Fe,Ni)_3P$ is abundant in a range of iron meteorites [10]. In general, large skeletal and swathing rims precipitated directly from the taenite and have low Ni contents (to 15%), whereas smaller grains precipitated later along α- α, α -γ and inside plessite can have Ni to 50% [10]. The Ni-analogue of schreibersite with Ni/Fe>1 called nicklephosphide, contains up to ~54 wt% in Butler and ~57 wt% in Vicenice [11, 12]. To date, "Ni_3P" with minor Fe has not been described from meteorites.

Methods: Precipitates from a 1 x 1 cm representative piece of Odessa dominated by kamacite were extracted onto amorphous carbon (aC) films [8] and examined with a 100 kV transmission electron microscopy (TEM) and compositions measured by energy-dispersive x-ray spectroscopy (EDX).

Occurrence and Chemistry: A range of sub-micron-sized precipitates were extracted onto aC films, including Mo-rich Cr-N, PGE-rich nuggets, and most commonly Ni-rich, Fe-poor phosphides. The majority of the phosphides have the empirical formula M_3P, and a subset close to $M_{2.5}P$. The latter may correspond to Ni_8P_3 or $Ni_{12}P_5$ [9]. This contribution focusses on the M_3P nanoprecipitates.

The Ni-rich, Fe-poor M_3P nanoprecipitates contain up to 4.05 wt% Ge and 1.4 wt% Ga (Table 1). The avaerage Ge/Ga = 3.9, is close to that for bulk Odessa (Ga 75 ppm, Ge 285 ppm, Ge/Ga=3.8, [2]). In addition, several of the particles contain EDX-measurable Zn, Pd, and Sn (Table 1). Three morphologies are dominant: euhedral (Fig. 1A), needle (Fig. 1B), and nuggets (Fig. 1C,D). Micron-sized schreibersites with Fe>Ni do not contain EDX-measurable Ge or Ga (data not shown). The Pd and Sn was restricted to the <100-nm-sized nuggets. EDX spectra acquired from the aC film, through a hole in the film, and from the Cu supporting grid show intense Cu K lines from the supporting grid and small peaks for Fe and Si. No peaks were seen for Ge, Ga, Pd, Sn, or Zn showing that these elements are indigenous to the M_3P particles.

Discussion: Nanoprecipitates in steels can harbor the bulk of selected trace elements, e.g., [13]. However, till now, such trace-element-bearing nanoprecipitates have not been described from iron meteorites. The formation of the Ni_3P nanoprecipitates in the kamacite differs from the typical large schreibersite. While the large schreibersite in Odessa formed at high temperatures (~900°C) from the $\gamma \rightarrow \gamma$+Ph nucleation path, the Ni_3P nanoprecipitates formed below 500°C via $\alpha \rightarrow \alpha$+Ph. At the low temperatures, the growing Ni_3P preferentially incorporate trace elements such as Ge, Ga, Pd, and Sn from the surrounding kamacite. The thin taenite rims contain higher Ge than the bulk kamacite [4], with the Ge likely a component of the Ni-Fe lattice. However, the taenite rims constitute only a small areal% of the Odessa, and thus the bulk of the Ge budget is present in the Ni_3P nanoprecipitates in the kamacite. The high areal density of the Ni_3P particles implies that they are a significant reservoir for Ge and Ga in Odessa.

Conclusion: The discovery of abundant Ge-Ga-rich Ni_3P implies that significant Ge and Ga in kamacite is bound to nanoprecipitates and not within the metal structure as suggested by [7]. The discovery of Ge in distinct chemical environments, i.e., taenite versus phosphide, may have implications for understanding the Ge isotopic fractionation between metal and phosphides e.g., [14, 15] in iron meteorites.

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Table 1: Composition (wt%) of the M_3P phosphide nanoprecipitates.

				Element (wt%)							
#	**Ni**	**Fe**	**Zn**	**Ge**	**Ga**	**Pd**	**Sn**	**P**	**Si**	**Ge/Ga**	**Σ****
4	75.86	5.46	-	2.66	0.86	-	-	14.50	0.66	3.1	2.94
5	80.52	3.27	-	1.32	0.25	-	-	14.16	0.48	5.3	3.06
8	79.34	1.42	-	3.03	1.40	-	-	14.36	0.44	2.2	3.00
9	80.87	2.37	-	1.54	0.60	-	-	13.97	0.66	2.6	3.05
13	81.34	1.79	-	1.55	0.42	-	-	14.52	0.34	3.7	3.02
15	79.80	0.71	0.58	3.17	0.78	t	-	14.44	0.53	4.1	2.94
16*	75.89	1.42	1.68	3.08	0.60	1.67	0.74	14.18	0.74	5.1	2.92
17	81.34	1.50	-	1.97	0.48	-	-	14.28	0.42	4.1	3.04
18	79.28	1.12	-	3.49	0.87	-	0.66	14.26	0.36	4.0	3.03
19	78.90	1.36	-	4.05	0.89	-	-	14.35	0.44	4.6	3.01
mean	79.31	2.04	-	2.59	0.72	-	-	14.30	0.51	3.9	3.00

- Particle number: **4** – euhedral, **5** – euhedral, particle Fig. 1A, **8** – needle, **9** – euhedral, **13** – needle, particle Fig. 1B, **15** – nugget, particle Fig. 1C, **16** – nugget, particle in Fig. 1C, **17** – subhedral, particle Fig. 1C, **18** – nugget, particle Fig. 1D, **19** – euhedral. t – trace amount. * - other 4d transition elements also present but at low concentrations. ** - sum of cations relative to an empirical formula with P+Si=1.

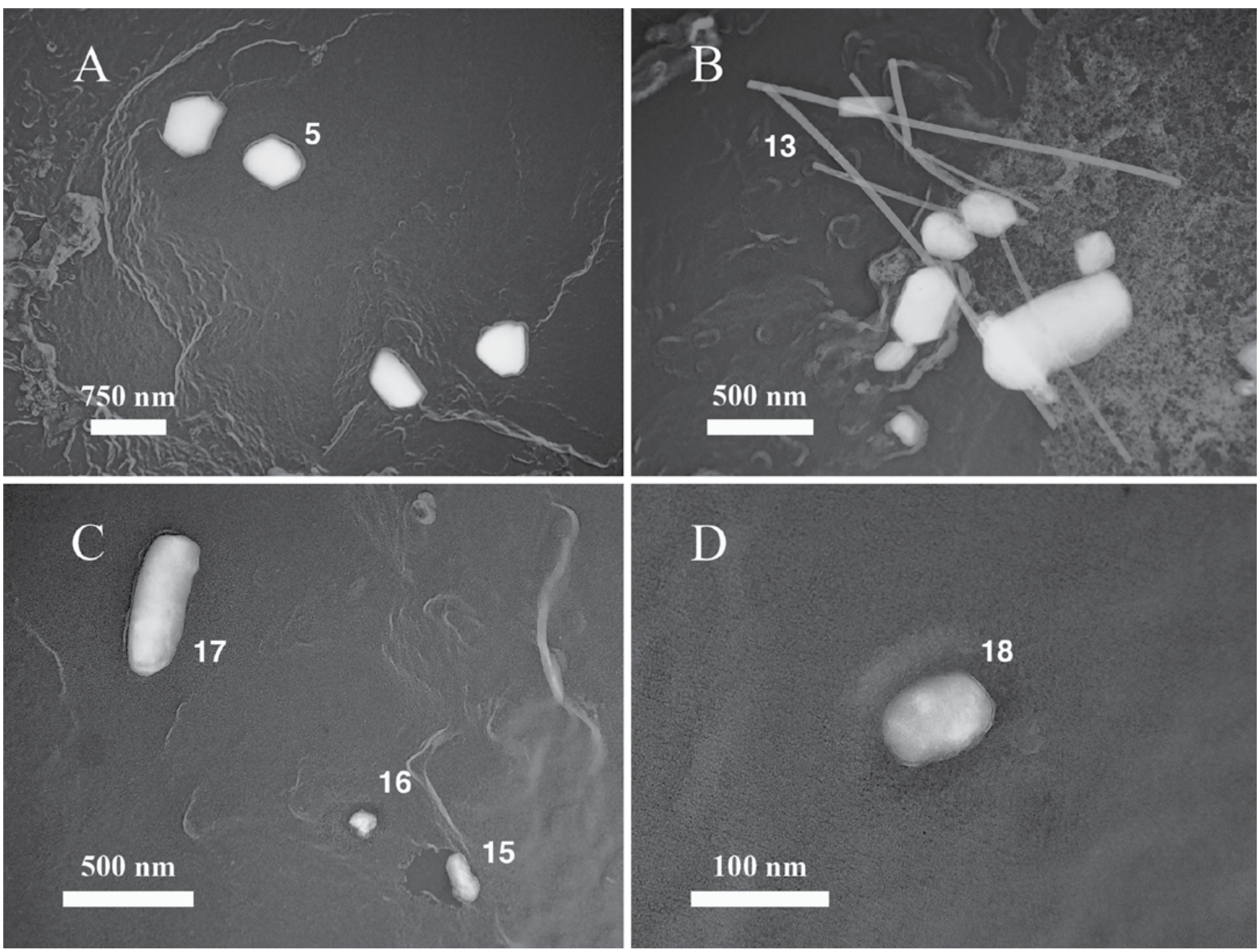

Figure 1. **A** through **D** - TEM images of "Ni_3P" particles from the Odessa iron supported on aC film. Number next to the particles corresponds to the analysis number in Table 1.