Fe-Ni Sulfides in Kool Grains from Comets: Support for High Temperature Igneous Origins. D. J. Joswiak[1], D. E. Brownlee[1], Z. Gainsforth[2] and A. J. Westphal[2]. [1]University of Washington, Dept. of Astronomy, Seattle, WA 98195, [2]Space Sciences Laboratory, University of California, Berkeley, CA USA 94720. email: joswiak@ astro.washington.edu.

Introduction: Our investigations of samples from comet Wild 2 and a giant cluster interplanetary dust particle (IDP) have shown that Fe-Ni sulfides – Ni-rich pyrrhotite/monosulfide solid solution (MSS), pentlandite and sometimes NiS – are often associated with Kool grains, assemblages of FeO-rich olivines+Na,Cr-rich augite+albitic feldspar or Na,Al silicate glass+/-Mg,Al-rich chromite which likely have high temperature origins [1]. Kool grains appear to have been formed by igneous and/or metamorphic processes and are observed in nearly all bulbous Stardust (SD) tracks and a large number of particles from a giant cluster IDP (GCP) and add to the number of high temperature materials observed in comet samples including CAIs, AOAs and chondrules. Unlike refractory objects and chondrules, however, Kool grains have not been observed in chondrites. Because Kool grains are abundant in comet samples, understanding their origin(s) is important toward improved understanding of comets.

Proposed origins for Fe-Ni sulfides in chondrites, IDPs, and other ET materials include 1) sulfurization of Fe-Ni metal in the solar nebula [2,3], 2) aqueous alteration on parent bodies [4] and 3) liquid immiscibility and exsolution of MSS during cooling of high temperature Fe-Ni-S melts [5]. Here we discuss the presence of Fe-Ni sulfides in Kool grains and suggest that these minerals formed contemporaneously with Kool grains and therefore they also likely formed by igneous processes at high temperatures.

Samples and Analytical Techniques: Studied samples include comet Wild 2 fragments extracted from silica aerogel tracks from the SD spacecraft and a giant cluster IDP collected in Earth's stratosphere. The giant cluster IDP is a large particle consisting of thousands of submicron to 40 µm size fragments and has numerous properties that suggest it was derived from a comet including unequilibrated mineralogy, fragile porous morphology, high abundance of presolar silicates and uncorrelated Mn/Fe ratios in olivines similar to olivines from Wild 2 [6, and references therein].

Ultramicotome sections of Kool grain particles from both comet Wild 2 and the giant cluster IDP were produced from potted butts embedded in acrylic or epoxy and studied at the University of Washington with a Tecnai TF20 STEM. Standard bright- and dark-field imaging, EDX analyses, electron diffraction and compositional mapping techniques were employed.

Results: A Fe-Ni-S ternary diagram of sulfides from more than 15 Kool grains from Wild 2 and the giant cluster IDP is shown in Fig. 1. Ni abundances in the sulfides vary widely, ranging from 0.2-64 wt% and include, pyrrhotite, Ni-rich MSS, pentlandite and NiS. A typical sulfide-bearing Kool grain P6-13 from GCP is shown in Fig. 2. The 10 µm Kool grain consists of Fo_{67-69} olivine, Na,Cr-rich augite, Al silicate glass, Mg,Al chromite (inclusions), Ni-rich pyrrhotite and pentlandite. Distinct grain boundary contacts between the sulfides and olivine or Al silicate glass are visible.

In general, most Kool grains contain at least one sulfide and some contain up to four sometimes with widely different Fe/Ni ratios. Although not observed in all Kool grains, Ni abundances in some sulfides appear to vary inversely with size. This is observed, for instance, in Kool grain P5-1 where three distinct sulfides with widely different Fe/Ni ratios have sizes (expressed as silicate/sulfide area ratios) that vary inversely with Ni concentration (Fig.3).

At least 11 Kool grains (5 from Wild 2 and 6 from GCP) contain pentlandite and sometimes NiS (probably millerite). Measurements of the apparent sizes of 9 of these Ni-rich sulfides show a size variation from 66–820 nm (ave.: 350 nm). At least two pentlandites have rounded or globular shapes (Fig. 4). Low Ni pyrrhotites, however, are often conspicuously larger with apparent sizes varying from ~1.2–6 µm (ave.: 2. 9 µm). Thus, volumes of the pyrrhotites are on average >500x larger than the pentlandites (or NiS).

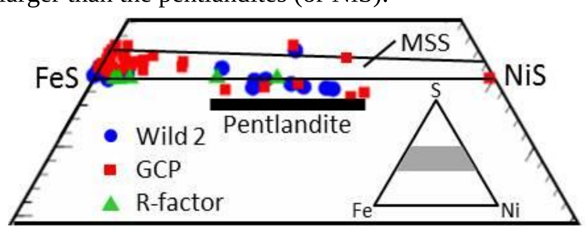

Fig. 1: Fe-Ni-S ternary diagram (atom%) showing sulfide compositions from Kool grains in >15 particles from Wild 2 and the giant cluster IDP (GCP). Sulfides range from low-Ni pyrrhotite to Ni-rich MSS, pentlandite and NiS. Green triangles show calculated immiscible MSS crystallizing (increasing Ni/Fe) from average Wild 2 pyrrhotite melt for S losses of 0, 20, 50, 90 and 95%.

Discussion. It is widely accepted that most Fe-Ni sulfides (most often pyrrhotite and pentlandite) in terrestrial basalts, komatiites and other igneous rocks form by liquid immiscibility. During cooling, S-bearing silicate melts will reach S saturation enabling sulfide immiscibility and formation of pyrrhotite. Later subsolidus cooling can exsolve Ni-rich sulfides such as pentlandite. Globular-shaped sulfides (troilite) observed in the interiors of some chondrules likely formed in a similar manner [5].

Most Kool grain sulfides are Ni-bearing pyrrhotites and pentlandites which often display solid grain boundary contacts with silicates (Fig. 2) indicating contemporaneous formation. MELTS [7] modelling of CI compositions produces FeO-rich olivine+clinopyroxene+Mg,Al chromite+Na-rich feldspar showing Kool grain minerals are consistent with formation from igneous melts. If Kool grains formed from CI-like high temperature liquids then sulfide immiscibility would be expected, even with significant S loss, due to the high abundance of S in a CI bulk composition.

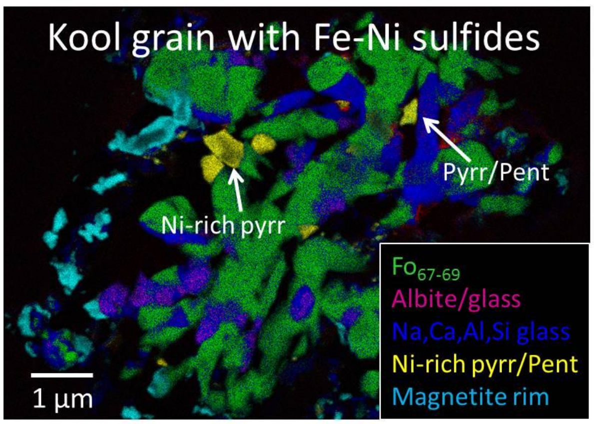

Fig. 2: Compositional map of a microtome slice of Kool grain P6-13 from the giant cluster IDP. Phases include FeO-rich olivine (green), albitic or Na-Ca-Al silicate glass or feldspar (red, blue) and Ni-rich pyrrhotite and pentlandite. Mg,Al chromite is also present.

How can the high variability of Fe/Ni ratios be explained in sulfides from Kool grains (Figs. 1 and 3)? In terrestrial ore petrology studies the concept of the R-factor (=bulk silicate/sulfide ratio), where sulfides become more Ni-rich at higher silicate/sulfide ratios, convincingly explains the formation of Ni-rich sulfides in large silicate bodies that formed from cooling magmas. We employ a similar concept here to explain the Ni-rich sulfides in Kool grains. If Kool grains form from cooling of CI-like liquids, then sulfides with higher Ni/Fe ratios can form as volatile S is variably lost from the particles. Because of the high partition coefficients for Ni in sulfides, Ni will preferentially partition into an immiscible sulfide melt over silicates such as olivine. Thus, as S is lost during cooling, Ni will become enriched into the remaining sulfide liquid and produce Ni-rich sulfides contemporaneously with silicates. Thus, smaller sulfides should become more Ni-rich, on average. Simple modelling shows that the Fe/(Ni+Fe) ratios of MSS decrease from 0.95 to 0.54 as the silicate/sulfide ratio (R-factor) changes from 1.9 to 46 corresponding to sulfide Ni increases from 3.1 to 27 wt% (green triangles, Fig. 1). This mechanism can explain some of the variability of sulfide Fe/Ni ratios in Kool grains and other particles in the comet samples believed to have igneous origins. We note that sulfide Ni enrichment is observed in immiscible sulfide droplets in partially melted fusion crusts in stony meteorites due to S loss during atmospheric entry[8].

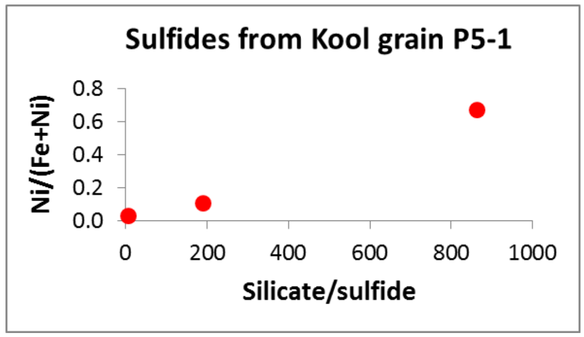

Fig 3: Correlation between Ni contents of 3 sulfides from a Kool grain from GCP and silicate/sulfide ratios. Diagram indicates that smaller sulfides in the Kool grain are more Ni-rich.

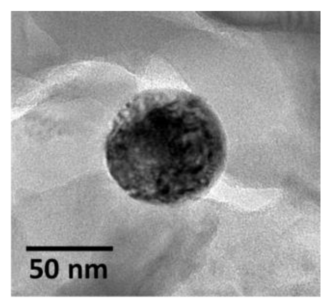

Fig. 4:Bright-field image of 60nm spherical pentlandite in a Kool grain from SD track 191. Globular Fe,Ni sulfides that formed from immiscible sulfide melts are observed in chondrules [5] and terrestrial basalts [9].

Conclusions: Textural, mineralogical and chemical data and modelling suggest that many Fe-Ni sulfides in Kool grains from comet samples formed from immiscible silicate/sulfide melts, possibly from bulk CI source materials. The large range of Fe-Ni sulfides in Kool grains may result from variable S loss which has the effect of enriching Ni in remaining sulfide liquids.

References: [1] Joswiak et al. (2009) *MAPS* 44: 1561-1588. [2] Lauretta et al. (1997) *Science* 277: 358-360. [3] Zolensky and Thomas (1995) *GCA* 59: 4707-4712. [4] Bullock et al. (2005) *GCA* 69: 2687-2700. [5] Marrocchi and Libourel (2013) *GCA* 119: 117-136. [6] Joswiak et al. *MAPS* (2017) 52: 1612-1648. [7] Ghiorso and Sack (1995) *CMP* 119: 197-212. [8]Genge and Grady (1999), *MAPS* 34: 341-356. [9] Czamanske and Moore (1977) *GSAB* 88: 587-599.