Fe-Mg-Mn SYSTEMATICS OF KOOL GRAINS FROM COMETS: UNIQUE SOLAR SYSTEM MATERIALS.

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Introduction. Our studies of comet Wild 2 samples and a giant cluster interplanetary dust particle (GCP) with a probable cometary origin [1] have revealed an abundance of polymineralic assemblages composed of FeO-rich olivine, Na,Cr-rich clinopyroxene, albite (or Al+/-Na silicate glass)+/-chromite+/-Ni-rich Fe sulfides [2]. We have observed these assemblages, which we call Kool grains (**ko**smochloric high-Ca pyroxene+**ol**ivine), in every bulbous track that we have studied from the Stardust collector, in ~15% of fragments from GCP and in at least six individual stratospheric IDPs (Fig. 1). Our studies of these enigmatic grains suggest they may have igneous and/or metamorphic origins and likely formed in high temperature environments in the early Solar System (SS) [2].

Although Kool grains have only been observed in comet samples, they have some mineralogical resemblances to type II chondrules as well as some silicate inclusions which are found in primitive achondrites and irons [3]. However, Kool grains differ from these materials because they are significantly smaller (submicron to ~10 µm), lack Fe,Ni metal, contain Ni-rich sulfides and do not have orthopyroxenes. Also, compared to chondrules Kool grain clinopyroxenes are Na- and Cr-rich. It is intriguing that silicate inclusions from achondrites contain kosmochloric diopside, Na-rich feldspar +/- FeO-rich olivine [3], the signature phases of Kool grains, but they are also typically rich in metal+/-troilite+/-graphite which are not observed in Kool grains. Thus, Kool grains are mineralogically unique even when compared to the most similar ET materials.

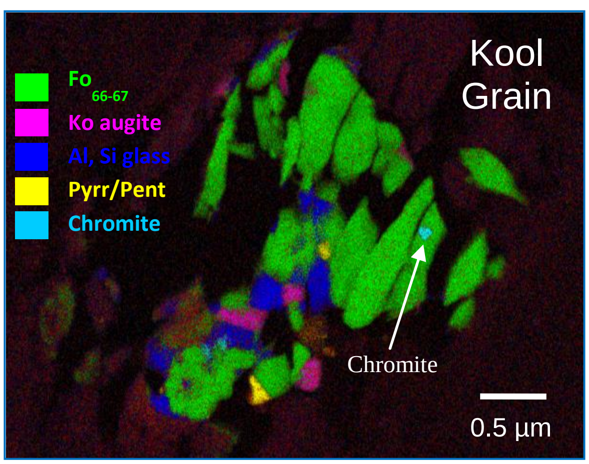

Fig. 1: Element map of Kool grain from Stardust track 141 (Coki) showing FeO-rich olivine (Fo_{66-67}), kosmochloric augite, Al-Si glass, Ni-rich pyrrhotite and pentlandite and Al-Mg chromite inclusion.

Recently we have begun a bulk composition study of Kool grains to improve our understanding of their origins and their possible relationships to other SS materials. In particular, we have begun looking at the Fe-Mg-Mn system because relationships between these elements in chondrites and primitive achondrites have provided important insights into identifying major processes that occurred in the early SS [4]. Our results from this study suggest that Kool grains are very primitive but also experienced a major metal-silicate fractionation similar to most chondrite groups.

Sample Preparation and Analytical Methods. Five Kool grains from comet Wild 2 and three from the giant cluster IDP were selected for bulk chemical analyses. The Wild 2 grains were extracted from tracks in either irregular-shaped aerogel fragments or cut keystones [5] which were flattened between clean glass slides. Particles from GCP were individually extracted and washed in hexane to remove adhering Si oil The giant cluster IDP is a large particle that was collected in the stratosphere on a U2 aircraft collector flag and consists of many thousands of grains up to ~40 µm and has chemical and physical properties which suggest it may have originated from a comet [1].

Ultramicrotome sections (<70nm) of the comet particles were cut from potted butts after embedding in either acrylic or epoxy resins. The samples were then mounted on standard Cu TEM grids and studied with a Tecnai TF20 STEM located at the University of Washington. EDX analyses were obtained using a thin window EDAX X-ray detector and quantified with Genesis software using mineral and NIST standards and Cliff–Lorimer correction factors. Bright- and dark-field imaging, electron diffraction and compositional mapping were also employed to study the grains.

Bulk compositions from the 8 Kool grains were obtained by one of two methods: 1) direct measurement of microtome sections using irregular rasters conformable to the particle outline or 2) EDX analyses of olivines and co-existing kosmochloric high-Ca pyroxenes combined with modal abundances measured with ImageJ software. Although the latter technique does not provide compositions of all the major and minor elements in the Kool grains, it does provide the necessary bulk Fe, Mg and Mn compositions for this study as these elements are either absent or only minimally present in the other Kool grain phases.

Results. Following the work of [4], bulk compositions of 8 Kool grains from comet Wild 2 (solid black circles) and the giant cluster IDP (solid black triangles) are plotted in the Fe/Mg vs Fe/Mn diagram in

Fig. 2. Also plotted in the figure are bulk compositions from the 13 chondrite groups, fields for primitive achondrites (gray shaded region), IAB silicate inclusions from winonaites (solid oval) and evolved achondrites (dashed oval) [4]. The figure shows that all Kool grains have solar Mg/Mn ratios but are strongly depleted in Fe relative to CI.

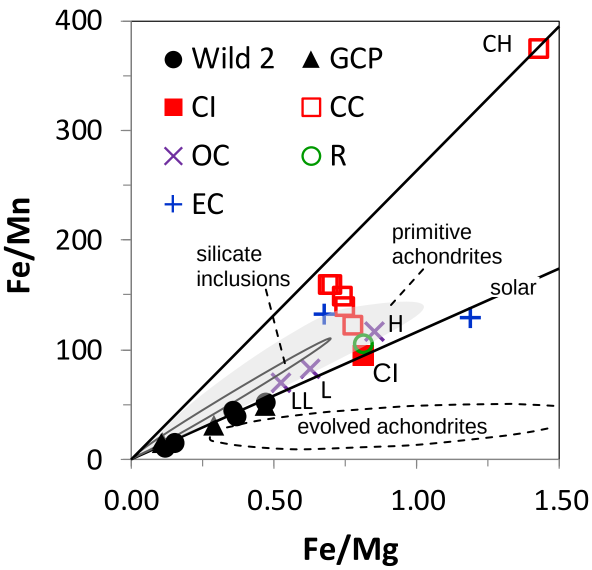

Fig. 2. Fe/Mg vs Fe/Mn diagram showing relationships between bulk Kool grains from comet samples Wild 2 and GCP and meteorite groups (bulk). GCP=giant cluster particle. Silicate inclusion field from winonaites [4].

Discussion. The important properties of Fig. 2 that are useful to apply toward Kool grains are: 1) Lines passing through the origin represent constant Mg/Mn ratios and therefore points along these lines solely represent Fe addition or loss relative to other points on the line. The H, L and LL ordinary chondrite (OC) groups (purple X's) exhibit this behavior. 2) Vertical trends represent Mn fractionation. The carbonaceous chondrites (CC) (open red squares) trending away from CI (solid red square) demonstrate that all CCs have lost Mn (relative to CI), a process believed to be nebular in origin [6]. 3) Horizontal trends in the diagram represent variable Fe/Mg ratios without Fe-Mn fractionation and signify igneous processes such as fractional crystallization or accumulation from melts. Evolved achondrites (dashed oval) which likely formed on parent bodies are consistent with these igneous processes [4]. Bulk type II chondrules display ~horizontal trends (not shown) which cut across the solar line [7].

Bulk Kool grains plot at low Fe/Mg ratios **on the solar line** suggesting that these materials formed from CI-like compositions that experienced significant Fe loss but maintained their solar Mg/Mn ratios. This suggests that if Kool grains formed in the solar nebula then they experienced a major metal-silicate fractionation(s) like most chondrite and primitive achondrite groups [4]. The Fe depletions in the meteorite groups are widely believed to be a result of loss of metal alloys from silicates which likely occurred in the solar protoplanetary disk [8].

Unlike most chondrite and primitive achondrite groups whose Mg/Mn slopes are greater than CI, Kool grains fall on the CI line and therefore have the most primitive Mg/Mn ratios of all meteorite groups (except CI). Additionally, because Kool grains do not fall along a horizontal trend they are not formed by fractional crystallization processes that likely produced the evolved achondrites [4]. However, because Kool grain textures and mineral assemblages and other properties are consistent with igneous/metamorphic processes and that they contain volatile phases including sulfides, albite and glass, Kool grains must have formed in short time spans if they formed at high temperatures. Thus, if Kool grains formed in the nebula then they formed in rapid heating/cooling events and from unfractionated or only slightly fractionated melts after a major loss of Fe metal. When compared to chondrites, their oxidized Fe contents, degree of Fe depletion and constant Mg/Mn ratio are most consistent with ordinary chondrites. Oxygen isotopic analyses obtained from a Kool grain from track 77 [9] plot above the terrestrial fractionation line similar to OCs (not shown here). We give credit to the prediction of Goodrich and Delaney [4] that materials with Fe/Mg vs Fe/Mn patterns like OCs were common in the early SS. Kool grains may represent some of these materials.

Conclusions. Fe-Mg-Mn systematics demonstrate that Kool grains are unique ET materials with low Fe abundances and chondritic Mg/Mn ratios, properties which are unlike any other SS material. Kool grains appear to have formed from a primitive nebular material that experienced metal-silicate fractionation without Mn-Mg disturbance. These findings add to the likelihood that Kool grains formed in environments similar to those that produced chondrules. Their sole presence in comets suggests Kool grains were likely destroyed in other SS bodies but kept intact in comets where high temperature processing was minimal or non-existent.

References: [1] Joswiak et al. (2017) *MAPS* 52: 1612-1648. [2] Joswiak et al. (2009) *MAPS* 44: 1561-1588. [3] Mittlefehldt et al. (1998) *Rev. in Min.*, vol. 36, 4-1 to 4-195. [4] Goodrich and Delaney (2000) *GCA* 64: 149-160. [5] Westphal et al. (2004) *MAPS* 39: 1375-1386. [6] Larimer and Wasson (1988) *Meteorites and the Early Solar System*, 416-435. [7] Berlin et al. (2011) *MAPS* 46: 513-533. [8] Anders (1971) *Ann. Rev. of Astro. and Astrophysics* 9: 1-34. [9] Nakashima et al. (2012) *EPSL* 357-358: 355-365.