POSSIBLE GEMS AND ULTRA-FINE GRAINED POLYPHASE UNITS IN COMET WILD 2. Z. Gainsforth^{1,†}, A. L. Butterworth¹, C. E. Jilly-Rehak¹, A. J. Westphal¹, D. E. Brownlee², D. Joswiak², R. C. Ogliore³, M. E. Zolensky⁴, H. A. Bechtel⁵, D. S. Ebel⁶, G. R. Huss⁷, S. A. Sandford⁸, A. J. White⁶, ¹Space Sciences Laboratory, University of California, Berkeley, CA 94720, ²Dept. of Astronomy, University of Washington, Seattle, WA 98195, ³Laboratory for Space Sciences, University in St. Louis, St. Louis, MO, 63117, ⁴ARES, NASA Johnson Space Center, Houston, TX 77058, ⁵Advanced Light Source, Lawrence Berkeley Laboratory, Berkeley, CA 94720, ⁶Dept. Earth Planet. Sci., American Museum Natural History, NY, NY 10024, ⁷University of Hawai'i at Manoa, Honolulu, HI 96822, ⁸NASA Ames Research Center, Moffett Field, CA 94035, [†]e-mail: zackg@ssl.berkeley.edu.

Introduction: GEMS and ultra-fine grained polyphase units (UFG-PU) in anhydrous IDPs are probably some of the most primitive materials in the solar system. UFG-PUs contain nanocrystalline silicates, oxides, metals and sulfides. GEMS are rounded, ≈ 100 nm across amorphous silicates containing embedded Fe-Ni metal grains and sulfides. GEMS are one of the most abundant constituents in some anhydrous CP-IDPs, often accounting for half the material or more[1]. When NASA's Stardust mission returned with samples from comet Wild 2 in 2006, it was thought that UFG-PUs and GEMS would be among the most abundant materials found. However, possibly because of heating during the capture process in aerogel[2], neither GEMS nor UFG-PUs have been clearly found.

Experimental: Track C2086,22,191 is one of the largest tracks in the Stardust collection. As a consortium we are studying it with optical, X-ray, electron, and ion microscopies. Andromeda is a 15 μ m diameter terminal particle and consists of a large nC pyrrhotite crystal shielding fine grained material (FGM) in its wake, similar to Febo[3, 4]. However, Andromeda is >2x the diameter of Febo and some nanophases appear intact, including an object consistent with GEMS in anhydrous IDPs.

After keystoning[5], we embedded Andromeda into epoxy, microtomed, and then examined it using Transmission Electron Microscopy (TEM) at the National Center for Electron Microscopy (NCEM) at the Lawrence Berkeley National Laboratory. We used an FEI Titan TEM with a 0.6 sr EDS detector for imaging, electron diffraction and EDS analysis. We used beam voltages between 80-200 keV to optimize imaging and EDS. We kept the current < 0.5 nA in STEM mode in order to minimize beam damage, and we used sequential mapping to track the loss of volatile elements such as Na[6].

Observations: Andromeda's FGM contains sulfides, crystalline silicates and amorphous silicates. Many of the silicates are nanocrystalline with well defined shapes, i.e. circular, euhedral, and blocky. The embedding epoxy permeated the FGM to make contact with the primary sulfide, which means the FGM is highly porous. In many regions, the silicate nanoparticles are surrounded completely by epoxy and are not connected to neighboring silicates. Often, ultramicrotomy will cut silicate material into shards which can shuffle during the sample preparation, and malleable material can have a weblike appearance after microtomy. In Andromeda, the FGM remains embedded within a sheet of epoxy, meaning that the glass objects were separated and shaped before microtomy. Some regions, especially around the periphery, have vesicular



Figure 1: (A) TEM brightfield image of Daisy showing a rounded morphology and embedded crystals. The scale bar is 100 nm. (B) EDS map with C (red), S (green), O (blue) showing that the object contains sulfides and is surrounded by sulfides and epoxy. (C) EDS map with Si (red), Mg (green), O (blue) showing the object is Mg rich relative to surrounding silicate. (D) EDS map with Fe (red), Ni (green), S (blue) showing Ni-rich metal, Ni-poor metal and sulfide.



Figure 2: Plot of the elemental composition of a suite of GEMS in anhydrous IDPs normalized to Si in At% from Bradley and Ireland[11] compared to Daisy. Chondritic composition is also plotted.

amorphous silicate typical of outgassing during hypervelocity capture[2] and appear to be modified. Volatile elements are retained in the FGM. Assuming excess SiO_2 and FeS, the elements Na, Mg, Al, P, Ca, Cr, and Ni are all chondritic within a factor of three except for K which is 5x chondritic.

Figure 1A shows a TEM brightfield of a rounded object ("Daisy") that contains nanocrystals similar to GEMS in anhydrous IDPs. Figure 1B is an EDS map of the object showing that the particle is surrounded by epoxy (C, red), not aerogel. Sulfides are present in and around the object. Figure 1C shows that the object is rich in Mg, unlike nearby silicate material. Figure 1D shows that the object contains both Ni-rich and Ni-poor Fe metal grains.

The same TEM section also contains an object which appears to be an ultra-fine grained polyphase unit (UFG-PU) containing Mg, Cr+Al, and Fe-Ni-S hotspots. Diffraction shows peaks consistent with spinel plus olivine and/or pyroxene. HR imaging shows lattice fringes throughout the object so it is mostly crystalline. It is surrounded by epoxy with other silicate material nearby that is chemically distinct. The Si-normalized bulk composition of the UFG-PU is chondritic within a factor of three for Na, Mg, Al, Si, P, K, Ca, Ti, Cr, and Mn. Fe and Ni are 0.2-0.3 chondritic and S is 0.05x chondritic. The compositions are consistent with compositions for UFG-PUs reported by Reitmeijer[7]. For comparison against Rietmeijer[8], we computed the pixel by pixel dispersion in Mg/(Mg+Fe), or Mg#, and (Mg+Fe)/Si from the EDS map and found that the variation in Si content is 6x the variation in Mg#.

Other phases include kosmochloric clinopyroxene, and numerous objects which could be polyphase units in various states of preservation. Nearly all phases show excess K/Si.

Preservation of material: The permeability of the Andromeda FGM to epoxy shows that it is highly porous. The isolated nanophases encased in epoxy show that it is highly friable. We conclude that the FGM is not sintered except in the altered regions. By contrast, nanophases in Febo's FGM are embedded in an interconnected silicate web. Previous researchers have remarked that the Febo FGM is primitive, but shows some evidence of alteration or sintering[9]. For this reason, it is likely that the unaltered regions within the Andromeda FGM is more primitive than the FGM in Febo.

Evidence for a GEMS: Ishii *et al.*[10] noted that sulfides mix with aerogel during hypervelocity capture and create GEMS-like objects. Since the mixing is between sulfide and SiO_2 (aerogel), the objects produced are devoid of Mg and Fe, and have excess Si. Daisy contains chondritic Mg, no excess Si, and Fe in the same range as in IDP GEMS. It is not possible to produce Daisy through mixing of sulfide and aerogel alone, but would have had to incorporate an Mg-, Al-, Na-, Ca-rich phase as well.

Figure 2 shows the measured elemental abundances of GEMS from anhydrous IDPs by Bradley and Ireland[11]. Daisy shows an excess in O and depleted Al and S as compared with chondritic just like GEMS in IDPs. Daisy also has Na, P, K and Ti within a factor of ≈ 2 of chondritic normalized to Si.

Na and K are both highly volatile elements. Capture pro-

cessing heats glass and releases volatile elements that recondense on surrounding material. The redeposition volume is often larger than the source volume so the volatile concentration is often reduced. Daisy is 3x enriched in Na relative to the surrounding material, and slightly depleted in K relative to the surrounding material. If we assume that Daisy is an unheated GEMS, then the chondritic Na is reasonable for primitive unaltered material. The K is 1.5x chondritic, which is perhaps also reasonable, but significant K is seen throughout the FGM and the material within a hundred nm of Daisy is 2x chondritic in K. It is possible that a nearby K-rich phase was volatilized and excess K diffused over the entire region including Daisy. If Daisy had been formed by capture heating then there is no obvious way to enrich the Na and surround it with euhedral sulfides. We conclude Daisy is unlikely to be a capture product but likely native to the comet. Further, Daisy is consistent in composition and morphology with GEMS found in CP-IDPs.

Ultra-fine grained Polyphase Unit: The UFG-PU shows characteristics typical of UFG-PUs in IDPs including morphology, composition, and crystal phases[7, 1]. Rietmeijer[8] found that UFG-PU's show a larger dispersion in the silica content than in Mg# and interpreted this as evidence of closed system formation. This UFG-PU follows the same systematics with the silica varying much more than the Mg#. It is thus far indistinguishable from UFG-PUs seen in CP-IDPs.

Preserved FGM in general: There are now three Stardust particles that have shielded FGM in varying states of preservation. Febo shielded FGM which is mildly altered but may have preserved remnants, especially of the more refractory components[3]. Iris shielded silicate material containing containing sulfides and an enstatite whisker[12]. Andromeda appears to have shielded a GEMS and UFG-PU. While it is possible that IDP components differ from Comet Wild 2, it seems very likely that many of the components seen in IDPs are also present in Wild 2. For quantitative comparison, there is still the extreme difficulty of understanding the selective destruction of delicate phases such as GEMS and presolar grains by the aerogel capture process.

Acknowledgments: NCEM is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC02-05CH11231.

References: [1] Rietmeijer, F. J. M. (1998). *Planetary Materials*, Ch 2. [2] Leroux, H., *et al.* (2009). *GCA*, 73(3), 767-777. [3] Brownlee, D., *et al.* (2006). *Science*, 314(5), 1711. [4] Joswiak, D., *et al.* (2012) *MAPS*, 47, 471. [5] Westphal, A. J., *et al.* (2004). *MAPS*, 39(8), 1375-1386. [6] Gainsforth, Z., *et al.* (2014). *Microsc. Microanal.* 20(S3), 1682-1683. [7] Rietmeijer, F. J. M. (2009). *MAPS*, 44(10), 1589-1609. [8] Rietmeijer, F. J. M. (1996). LPSC, 1073. [9] Ishii, H. A., Bradley, J. P. (2015). *MetSoc.* [10] Ishii, H. A., *et al.* (2008). *Science*, 319, 447. [11] Bradley, J., Ireland, T. (1996). *Phys. Chem. Dyn. Interplanetary Dust*, 104, 275-282. [12] Stodolna, J. (2014). *EPSL*, 388, 367-373.

Fun Note: The name Daisy was chosen after Daisy kept satisfying all the criteria of GEMS that we could find. It was commented, "If it walks like a duck, and it quacks like a duck, then ..."