Meteoritics & Planetary Science 46, Nr 8, 1082–1096 (2011) doi: 10.1111/j.1945-5100.2011.01215.x

Understanding the mechanisms of formation of nanophase compounds from Stardust: Combined experimental and observational approach

Neyda M. ABREU^{1*}, Frans J. M. RIETMEIJER², and Joseph A. NUTH III³

¹Earth Science Program, Pennsylvania State University—Du Bois Campus, Du Bois, Pennsylvania 15801, USA
²Department of Earth and Planetary Sciences, 1-University of New Mexico, Albuquerque, New Mexico 87131–0001, USA
³Astrochemistry Branch, Code 691, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA
*Corresponding author. E-mail: abreu@psu.edu

(Received 11 October 2010; revision accepted 01 May 2011)

Abstract-We have experimentally produced nanophase sulfide compounds and magnetite embedded in Si-rich amorphous materials by flash-cooling of a gas stream. Similar assemblages are ubiquitous, and often dominant components of samples of impact-processed silica aerogel tiles and submicron grains from comet 81P/Wild 2 were retrieved by NASA's Stardust mission. Although the texture and compositions of nanosulfide compounds have been reproduced experimentally, the mechanisms of formation of these minerals and their relationship with the surrounding amorphous materials have not been established. In this study, we present evidence that both of these materials may not only be produced through cooling of a superheated liquid but they may have also been formed simultaneously by flashcooling and subsequent deposition of a gas dominated by Fe-S-SiO-O₂. In a dust generator at the Goddard Space Flight Center, samples are produced by direct gas-phase condensation from gaseous precursors followed by deposition, which effectively isolates the effects of gasphase reactions from the effects of melting and condensation. High-resolution transmission electron microscopy images and energy-dispersive spectroscopy analysis show that these experiments replicate key features of materials from type B and type C Stardust tracks, including textures, distribution of inclusions, nanophase size, and compositional diversity. We argue that gas-phase reactions may have played a significant role in the capture environment for nanophase materials. Our results are consistent with a potential progenitor assemblage of micron and submicron-sized sulfides and submicron silica-bearing phases, which are commonly observed in chondritic interplanetary dust particles and in the matrices of the most pristine chondritic meteorites.

INTRODUCTION

NASA's Stardust mission collected dust from the coma of comet 81P/Wild 2, which impacted the ultralow density, silica aerogel collection tiles at 6.1 km s⁻¹ (Brownlee et al. 2006). Each comet particle penetrated these tiles creating a well-defined track. Although stardust tracks have diverse morphologies, they are frequently comprised of bulbous cavities with emanating slim, elongated features termed styli (Hörz et al. 2006). The track length depended on the mass of the largest grains, which in some cases became the terminal particle(s) at the end of each stylus (Brownlee et al. 2006; Zolensky et al. 2006). These terminal particles consist of a single mineral (i.e., plagioclase, pyroxene, olivine, pyrrhotite) or a mineral assemblage such as sulfide-Mgrich silicate-aggregate particles, CAI-like entities, or chondrule-like fragments (e.g., Brownlee et al. 2006; Zolensky et al. 2006; Matrajt et al. 2008; Nakamura et al. 2008a; Simon et al. 2008; Jacob et al. 2009; Joswiak et al. 2009). Track morphology was largely determined by the cohesiveness and mineralogy of the impacting comet particles (Burchell et al. 2008) and by the gas cloud generated by vaporization of a fraction of the impacting materials (Trigo-Rodríguez et al. 2008). Based on geometry, three different types of aerogel impact features (A, B, and C) have been distinguished (Hörz et al. 2006). Type A tracks are narrow carrot-shaped features, caused by a single massive grain that may have shed some of its adhered materials in its wake along the track length. Type B tracks have a large bulbous cavity that expands from the penetration hole and narrows down-track into a single stylus, or occasionally styli, with terminal particles at the very end. Micrometer-sized (1-5 µm) mineral fragments are found scattered along the length of these styli. These fragments include Mg-rich, Ca-free and Ca-rich pyroxenes, Mg-Fe-olivine, and Fe-Ni-sulfides (e.g., Zolensky et al. 2006; Leroux et al. 2008a; Tomeoka et al. 2008). Finally, type C tracks occur as broad cavities lined with fine particles, and no tracks emerging from them (Hörz et al. 2006). Most particles extracted from the walls of the bulbous part of type B tracks and almost all type C tracks are irregularly shaped, clumps of Si-rich glass with nanometer-scale electron-opaque subsulfur Fe-Ni-S and Fe-Ni metal inclusions. They have been proposed to be admixed residues from numerous nanometer-scale particles of the loosely bound matrix of cometary agglomerates (Zolensky et al. 2006) or spall droplets formed from Wild 2 pyrrhotite grains (Ishii et al. 2008b). The glass is typically vesicular, and it has been suggested that it originates from quenched melts that are dominated by melted aerogel. The dominant low-Mg (typically <10 atom%—Leroux et al. 2008b; Rietmeijer 2009a), vesicular glass contains small amorphous patches of Ca, Al-rich material (Leroux et al. 2008b; Rietmeijer 2009a). The inclusion population is mineralogically diverse, ranging from Fe-S-Ni and Fe-Ni compounds (a few to about 100 nm) and Fe oxides, to enstatite and forsteritic olivine $(0.5-1 \ \mu m)$, and to pyrrhotite and Fe-silicide spheres (e.g., Zolensky et al. 2006; Nakamura et al. 2008b; Rietmeijer et al. 2008; Tomeoka et al. 2008; Rietmeijer 2009b; Stoldona et al. 2009; Velbel and Harvey 2009; Bridges et al. 2010).

Rietmeijer (2009a) suggested that any indigenous amorphous materials from comet Wild 2 probably lost their identity upon capture and assimilation into melts in the walls of expanding aerogel bulbous cavities. The time-temperature regimes associated local with hypervelocity capture in the aerogel were not sufficient to cause terminal particles to fully melt, although surface melting and abrasion features are very common. Some Wild 2 grains (larger than $\sim 0.5 \,\mu\text{m}$) preserved along track styli or embedded in the low-Mg silica glass appear to have survived intact. On the other hand, the thermal regimes in the bulbous parts caused instant melting and quenching, and/or evaporation-condensation of the smallest comet dust grains and pure silica aerogel (Rietmeijer 2009b,c). The Preliminary Examination Team studies (Science, 2006, 314:1711-1739) reported inclusions in the vesicular low-Mg silica glass whose textures are reminiscent of GEMS (glass with embedded metals and sulfides; Bradley 1994) that are found in the matrix of porous aggregate interplanetary dust particles (IDPs) (cf. Rietmeijer 1998). In fact, a small fraction of unusual Mg-rich glass has been identified (Keller and Messenger 2008). Keller and Messenger (2008) argued that the Mg-rich glass formed from extensively thermally modified GEMS-like particles indigenous to Wild 2. However, Wild 2 low-Mg glasses have different compositions. In addition to GEMS, IDPs also contain amorphous Si-rich grains with variable amounts of Mg, Fe, Ca, and Al. Vesicular glass compositions in some Stardust tracks suggest that the comet dust probably contained amorphous grains that may have originally resembled these Si-rich grains in IDPs (Rietmeijer 2009a,c). Thus, it is necessary to examine vesicular glasses in detail to distinguish between amorphous materials indigenous to the comet and glasses that formed as a consequence of the aerogel capture process.

The aerogel used in the Stardust mission was in fact not 100% pure silica, but contained elemental and particulate contaminants (Tsou et al. 2003). Indeed, aerogel adjacent to the hypervelocity-impact tracks in Stardust samples contained low abundances of these contaminants (among others, Ishii et al. 2008a: Lanzirotti et al. 2008; Stephan et al. 2008). Small amounts of Mg, Al, S, Ca, Cr, Mn, Fe, and Ni in aerogel and in the massive silica-rich rims, which are often present between flight aerogel and vesicular glass (e.g., Tomeoka et al. 2008), were interpreted as a contaminant background in the vesicular glass (Rietmeijer 2009b). Using the contaminant background values to correct the data for the vesicular silica-rich glass (hereafter vesicular glass) removes most of the low Mg values from the glass (Rietmeijer 2010).

Nanometer-sized Fe-Ni-S-bearing compounds (hereafter nanosulfide compounds) and Fe-Ni metal grains are characteristic features of Stardust glass in the bulbous parts of tracks. However, their origins remain unclear. Micrometer-size pyrrhotite grains impacting at 6.1 km s⁻¹ into Stardust aerogel reproduced the size, shape, and distribution pattern of nanosulfide compounds found in this Stardust glass, including the core-mantle texture seen in the larger nanosulfide compounds (Ishii et al. 2008a). However, this study did not account for the low amounts of Mg, Al, Ca, Cr, and Mn in the hypervelocity impact produced sample as well as the physical conditions in the experiment that caused the formation of these nanosulfide compounds. The processes that yielded the nanosulfides from modified indigenous Wild 2 grains, possibly including Fe-Nisulfide grains, essentially took place in a Fe-Ni-Si system with very low Ni abundances.

In addition to nanosulfide compounds, submicron amorphous or poorly crystalline Fe oxides have been identified in close proximity to nanosulfide compounds in two Stardust tracks (Bridges et al. 2010). The origin of these oxides is not well understood. Bridges et al. (2010) suggested that the oxides are either indigenous to Wild 2 or may have formed by capture-driven heating and oxidation of pre-existing Fe-Ni metal or by terrestrial contamination.

In this article, we experimentally explore how disequilibrium condensation from a Fe-Si-S-O gas could have produced the observed nanosulfide compounds and may have also produced Fe oxides and amorphous Si-rich materials.

METHODS

Production of Smokes

The dust generator that was used to produce the synthetic samples for this study has been described previously (e.g., Rietmeijer and Nuth 1991; Nuth et al. 1994, 2002; Withey and Nuth 1999). Smokes are produced at a total pressure of about 90 Torr ($\sim 1 \text{ kPa}$) in an atmosphere dominated by H_2 (Fig. 1). The condensable species formed via combustion from gasphase Fe-pentacarbonyl $[Fe(CO)_5]$ and silane (SiH_4) . Pure oxygen (O_2) was introduced into the stream separately, just before the furnace. Although Fepentacarbonyl and silane may not appear to be good analogs for nebular gases, iron pentacarbonyl dissociates into Fe + 5CO and silane reacts to form SiO + water in the presence of O2 at temperatures well below the temperature of the flame front. Thus, SiO and Fe occur in the gas streams. These species constituted <10% of the total gas input to the system (remainder was H_2). Elemental S was vaporized in a graphite crucible placed in the furnace. Vaporization of sulfur ran to completion, with no sulfur remaining in the crucible when examined after removal from the chamber. The total flow velocity through the furnace is typically on the order of 10-20 cm s⁻¹. A typical grain formed at the hightemperature flame front (~1500 K) near the furnace entrance will therefore spend $\ll 1$ s within the furnace following nucleation and growth. The hot gas and fresh grains are rapidly quenched as they flow into a larger stainless steel condensation chamber lined with a thick aluminum collector that remains at a temperature of approximately 300-350 K.

Metered iron pentacarbonyl:silane:molecular oxygen ratios are 50:20:40 for Run 1, and 50:20:20 for Run 2. Although thermal decomposition of Fe-pentacarbonyl introduces significant amounts of additional O into the gas streams, this O is likely to remain bonded to C or to react with CO at the temperatures of interest, resulting in the presence of the following gaseous phases in the dust



Fig. 1. Schematic diagram of the dust generator from Nuth et al. (2002) located at the Goddard Space Flight Center. Dust is produced by combustion of H-gas with small amounts of silane, iron pentacarbonyl.

generator chamber: S, Fe, SiO, O₂, H₂O, CO, and CO₂. For simplicity, hereafter, we refer to the composition of the gases as Fe:SiO:O₂, although S, H₂O, CO, and CO₂ were clearly present. Our initial experimental setup does not allow direct quantification of the species' fugacity during the gas-phase reactions. Furthermore, retrieval of samples from the Al collector and subsequent preparation for transmission electron microscopy (TEM) studies might cause oxidation of condensed materials.

Characterization

Stardust allocations from C2054,0,35,44,6 (Track 35) and C2092,2,80,47,6 (Track 80) were embedded in Embed812 epoxy, and each allocation consisted of several serial sections that were placed on a 10-nm amorphous carbon film supported on a Cu TEM grid at NASA Johnson Space Center Stardust Curatorial Facility. The sections are about 70 nm thick. For details, see Zolensky et al. (2006, Supplemental data) and for details on the high-resolution TEM (HRTEM) analyses, see Rietmeijer (2009b). Analyses of the Stardust samples were conducted at the Electron Microbeam Analysis Facility at the Department of Earth and Planetary Science, University of New Mexico.

Samples retrieved from the Al collector ranged from fine-grained powders to millimeter-thick films. We prepared these smokes for TEM analysis by gently grinding them into thin powders and immediately mixing them with M-bond epoxy resin that was allowed to cure at room temperature to avoid self-annealing that may have resulted in crystal growth. This epoxy mixture was then pressed between two pieces of Si, and thinned to electron transparency at low temperatures (<100 K) in a Fischione Ion Mill Model 1010 at the Materials Characterization Lab, Pennsylvania State University. The silicon substrate in these sections is completely featureless, homogenous, and relatively resistant to ion milling, thus easily distinguishable from samples.

Four TEM sections were prepared from Run 1 smokes, and three samples were prepared from Run 2. All experimentally produced samples were examined using a JEOL 2010F FEG TEM/scanning transmission electron microscope (STEM) equipped with an ultra-thin window X-ray energy dispersive spectrometer (EDS) at the Material Characterization Laboratory at Pennsylvania State University. Acquisition and processing of digital TEM images was conducted using GATAN Digital Micrograph imaging software version 1.8.4. Quantification of EDS data was performed using the Cliff-Lorimer thin film approximation (Cliff and Lorimer 1975). EDS was collected in the STEM configuration using a 1 nm beam diameter. A counting time of 100 s was used to minimize the effects of beam damage and drift, while retaining meaningful counting statistics. Compositions of grains that did not withstand EDS beam damage for 100 s were not included in the analysis.

RESULTS

TEM Observations of Stardust Track 80 and Track 35

We studied samples from two bulbous, type B tracks, 35 (Fig. 2a) and 80 (Fig. 2b), using TEM/EDS. Track 35 has a single long stylus with a terminal particle at the end and many short styli emanating from the bulbous part. Track 80 is mostly a bulbous cavity with three short styli. Measured compositions were corrected for the background values of Fe, Ni, and S in both tracks following the procedure described by Rietmeijer (2010). Our observations of nanophase S-bearing particles are consistent with previous work (Zolensky et al. 2006; Leroux et al. 2008b; Tomeoka et al. 2008; Velbel and Harvey 2009), in which compositions range from pure-Fe and low-Ni iron nanosulfide compounds to pure sulfur (Figs. 3a and 3b). Although the compositions in Track 35 show a continuous range from Fe-metal to FeS₂, the nanosulfides in Track 80 show a gap between composition S = 30 and 40 atom% (Figs. 3a and 3b). Both tracks show nanosulfide compositions ranging from FeS₂ to the sulfur apex, and in fact contain pure-S spots in the low-Mg vesicular glass matrix. These full ranges of nanosulfide compositions are consistent with the hypothesis (Zolensky et al. 2006) that impact heating caused continuous sulfur loss from FeS (troilite and/or pyrrhotite) grains from comet Wild 2 that eventually led to pure metal grains, as complementary sulfur is present



Fig. 2. Optical images of Track 35 (C2054,0,35,44,6 keystone) and Track 80 (C2092,2,80,47,6 keystone). Both tracks are classified as type B (source: NASA Johnson Space Center Stardust Curatorial Website). a) Track 35 also has a large bulbous cavity and a single long stylus. Track 35 has a length/depth ratio of ~1.17 (cm) and multiple grains <40 μ m. b) Track 80 has a large bulbous cavity with three terminal particles of the order of 15, 8, and 7 μ m in size at the end of three styli that measure in the order of about 4800 and 4475 μ m in length.

in the vesicular glass matrix. A rough estimate suggests that about 20% of the "missing" sulfur was volatilized and had diffused into the surrounding aerogel (Ishii et al. 2008c).

There is no evidence in these two samples for mass balance. Although the data are few, some of the high-S nanosulfide compositions at about S = 80 atom% match the composition of a FeS₄ phase. In addition, we show the Fe, Ni, S, and Si contents measured in allocation C2054,0,35,44,6 (Fig. 3c). These regions show remarkable compositional variability.

TEM Observations of Experimentally Produced Smokes

Herein, we present TEM, HRTEM, and EDS observations of materials produced by instantaneously cooling sulfurous gas streams with two different chemical compositions, Fe:SiO:O₂ ratio of 50:20:40 for Run 1 and 50:20:20 for Run 2. Bright field TEM (BFTEM) images show that all the sections contain abundant nanocrystalline phases embedded in amorphous Sibearing materials (e.g., Figs. 4 and 5). No crystalline silicates were identified. Although samples from Runs 1 and 2 show some mineralogical and compositional differences, there are no major textural differences among these products. The textures resemble Stardust samples.



Fig. 3. Ternary diagrams showing analytical AEM/energy dispersive spectrometer data from Stardust's low-Mg glass with embedded nanocrystals from Track 35 and Track 80. A gray triangle shows the composition of stoichiometric troilite for reference. a) Fe-Ni-S (atom%) ternary diagram showing 124 analyses from Track 35. These data were corrected for background-level contaminants from silica aerogel impurities by Rietmeijer (2009a, 2010). The average values and standard deviations are as follows, Fe = 53.9 \pm 23.7 atom%, Ni = 0.6 \pm 1.4 atom%, and S = 25.5 \pm 24.4 atom%. Although most data points cluster within ± 10 atom% of stoichiometric troilite, compositions range from pure Fe to pure S. Pure-S spots in the silica glass that were Fe free may be either S that is physically entrapped perhaps in an aerogel pore, or has chemically bonded with Si-O. Ni is below detection limits for most analyses, particularly in all analyses that contain less than 50 atom % S. When present, Ni <7 atom % with an average of 2.1 atom%. b) Fe-Ni-S (atom%) ternary diagram showing a total of 100 analyses from Track 80. These data were normalized according to the procedure in Rietmeijer (2009a, 2010). Data from Track 80 closely resemble data from Track 35. However, many more areas (28 of the 100 analyses) are exclusively composed of S, which results in higher average S-contents than in Track 35. These S-rich regions are commonly embedded in Si-rich materials. None of the data points show Ni contents in the excess of 5.7 atom%. The average values and standard deviations are as follows, Fe = 47.0 \pm 33.4 atom%, Ni = 0.8 \pm 1.6 atom%, and S = 52.2 ± 34.2 atom%. c) Fe-Si-S (atom%) ternary diagram of low-Mg silica glass with the typical opaque nanocrystals from Track 35. There is a great deal of compositional variability, as reflected by the Si average value and standard composition of Si = 45.3 ± 24.8 atom %. d) Fe-Si-S (atom %) ternary diagram of similar regions from Track 80. Si average value and standard composition of Si = 66.6 ± 25.8 atom%.

Nanosulfide Compounds

Products from Run 1 and Run 2 present abundant nanosulfide compounds that closely resemble the finergrained nanosulfide compounds observed in samples from multiple Stardust tracks (e.g., Track 10: Zolensky et al. 2006; Track 3: Leroux et al. 2008b, 2009; Velbel and Harvey 2009; Track 80: Stoldona et al. 2009; Tracks 35 and 80 from this work) in terms of distribution,



Fig. 4. Transmission electron microscope images of typical electron-opaque nanocrystals from Run 1 and Run 2 smokes. a) Bright field TEM image showing high densities of Fe-S-nanoparticles with compositions near troilite (Sulf) embedded in amorphous (Amorp) Fe-Si-rich materials. b) High-resolution TEM (HRTEM) of a troilite crystal, with inset showing corresponding fast Fourier transform (FFT) down [010] zone axis. c) HRTEM image of a Fe-rich S-core particle with a pseudo S-rich mantle from a sample of Run 2. d) HRTEM image of a very rare magnetite crystal with FFT down [001] zone axis.

size, and composition (Figs. 4a-d and 5). Nanosulfide particles are heterogeneously distributed throughout different regions of amorphous materials. Their distribution varies widely, as explained in the following section. These particles are generally rounded. Fe-S grains with diameters generally < 30 nm (Fig. 4), as is the case for a large fraction of the nanosulfides in Stardust samples (e.g., Zolensky et al. 2006; Leroux et al. 2008b, 2009; Velbel and Harvey 2009). As a consequence of the extremely fine-grained nature of these compounds, we were rarely able to obtain single phase analyses from individual grains (Fig. 5). This is caused by beam overlap with the surrounding amorphous material. This situation arises because many grains are smaller than the thickness of the ion-milled foil (30-70 nm) and hence surrounding amorphous silicates and other grains may be present above and below individual grains in the electron beam path. These overlaps also resulted in low levels of Si measured in Fe-S grains, as shown in Fig. 5. Furthermore, some grains are composed of non-concentric nanometer and subnanometer Fe-metal-Fe-sulfide intergrowths that oftentimes cannot be resolved by the EDS beam, which has an approximate diameter of 1 nm. Some crystals were identified as troilite, based on their composition and fast Fourier transform (FFT) patterns (Fig. 4b). However, most experimentally produced nanosulfide compounds appear to be non-stoichiometric and often Fe-rich (average about 68 atom% Fe-Fig. 5), owing to metallic-Fe intergrowths as evidenced by their strained appearance. Compositionally, nanosulfide compounds in Stardust tracks are generally very Fe rich. In the different tracks that Zolensky et al. (2006) initially examined, approximately half of the grains have compositions between stoichiometric FeS and Fe-rich troilite. These compositions are consistent with those measured in later studies, including this work (e.g., Leroux et al. 2009; Velbel and Harvey 2009; Figs. 3a and 3b). We show that our experimental products obtained by vapor-phase condensation reproduce the compositional diversity observed in Stardust samples.

Although there is a close textural match between small nanosulfide compound grains from Stardust samples



Fig. 5. Ternary diagrams Fe-Si-S (atom%) showing analytical data from nanocrystals from Run 1 and Run 2 obtained using AEM (EDS analyses). A gray triangle shows the composition of stoichiometric troilite for reference. Although a small beam diameter (1 nm) and relatively low counting times (100 s) were used to minimize overlap with surrounding Si-rich amorphous materials and drift, low levels of Si are due to beam overlap. Analyses with high Si-contents (>20 atom%) were not included, as they signify excessive overlap/drift. A total of 25 analyses were collected from nanocrystals from Run 1, and 10 analyses were collected from nanocrystals from Run 2. The spread of chemical compositions observed in Stardust's nanosulfides (data from Fig. 3) is shown as a gray arrow for reference.

and samples produced by our experiments, the coremantle texture observed in large (>50 nm) Stardust Fe-Ni-S nanograins (e.g., Keller et al. 2006; Leroux et al. 2008b) was extremely rare in samples from our experiments, occurring only rarely in Run 2. Our experiments did not reproduce the most S-rich compositions in Stardust samples, as reported in Fig. 3. We note that such S-rich compositions were also not reported in the hypervelocity capture experiment of pyrrhotite into silica aerogel (Ishii et al. 2008a). In particular, numerous regions from Track 80 showed nearly pure-S compositions. However, these regions generally contained minor amounts of S (<10 atom%) and abundant Si. It is possible that these regions do not represent actual grains. Instead, they may be areas in which S and SiO vapor have simultaneously condensed. In the case of the experimentally produced nanosulfide compounds, individual features were selected for analysis, therefore precluding the analysis of Sidominated materials. Alternatively, the absence of pure S-grains in experimentally produced samples may be attributed to the relatively high volatility of sulfur, which has a boiling point of 444.6 °C. During the experiment, the total pressure of the chamber is maintained constant by continuously evacuating gases through a roughing pump. It is possible that if S did not immediately react with other gases in the stream and be deposited on the Al collector, it could be extracted through this process.

Fe Oxides

In addition to nanosulfide compounds, rare, rounded, mottled Fe oxides (40-60 nm diameter) have been identified as magnetite based on composition, characteristic 2.5-Å d-spacings, and indexing of FFT patterns (Fig. 4d). Nanophase magnetite occurs in close proximity to nanosulfide compounds in some products from Run 1. However, similar occurrences have not been identified in samples from Run 2, which was conducted under more reducing conditions (50% less O_2) in the dust generator flame in comparison with Run 1. It is not clear whether these nanocrystals were deposited as metallic Fe, such as the metallic Fe produced in the absence of SiO by Nuth et al. (1994) and by Withey and Nuth (1999), and were later rapidly oxidized during sample preparation. It is not possible to reconstruct whether Fe metal was produced by extrapolating results from SiO-free experiments or not, because the presence of SiO causes variable redox conditions (i.e., Si, SiO, Si₂O₃, SiO₂ species) within the chamber. However, in light of the presence of Fe oxides in experimental products, the protocol of sample retrieval and preparation will be modified to minimize the possibility of oxidation of nanoparticles in the future.

Detailed textural comparison between these experimentally produced oxides and Fe oxides retrieved by Bridges et al. (2010) from Stardust's tracks 41 and 121 is not possible, as no HRTEM images are currently available for those samples. It is clear that the experimentally produced magnetite grains are approximately a fourth of the size of the ones observed in Stardust's tracks by Bridges et al. (2010) and are crystalline. Differences in sizes may be attributed to truncated growth of experimentally created magnetite grains (or metallic-Fe precursors) by flash cooling in the dust generator. The reason why experimentally produced magnetite is crystalline and Stardust nanometer-scale magnetite appears to be amorphous is unclear. We speculate that the smaller grains in our experiments are crystalline because at the experimental conditions their surface free energy stabilized the crystalline form. Alternatively, Stardust's unstable magnetite crystals amorphized during the quenching stage in the abundant hot silica melt. Furthermore, unlike Stardust samples, our samples show no association to metallic Fe, which is conspicuously absent from our experimental products.

Absence of metallic Fe in experimental samples will be explored in more detail in future work.

Amorphous Materials

We refer to these amorphous materials hereafter as amorphous silicates to distinguish them from glasses and gels, both of which have liquid precursors. Furthermore, glasses and gels have higher degrees of short-range crystallographic order than the materials we have produced. In the case of amorphous materials from Stardust, we use the terminology commonly used in the literature and refer to these materials as glass because we cannot rule out the possibility that a small fraction might have had a liquid precursor.

The textures and compositions of amorphous silicates vary widely at the nm scale. Using BFTEM, we identified three different types of textures: (1) smooth, (2) spherical, and (3) vesicular. These textures showed individual chemical trends and different abundances of electron-opaque nanoparticles. The most common textures observed in samples from both Run 1 and Run 2 are regions with no other features except for the presence of electron-opaque nanoparticles (Fig. 6a). We call these regions "smooth." Smooth regions are texturally similar to samples from Stardust Track 35, such as the ones documented by Velbel and Harvey (2009) and shown in Fig. 6b. As in the Stardust samples, nanosulfide compounds and sparsely distributed magnetite (collectively referred as nanoparticles) are randomly distributed within the amorphous material. Smooth regions showed significant variation in nanoparticle density, as shown in Fig. 6c. Similar high nanosulfide compound density has also been observed in Stardust samples (Figs. 6d and 6e, modified from Zolensky et al. 2006). We also identified clusters of numerous rounded (presumably spherical) subdomains that appear to have deposited as individual amorphous grains. These regions are characterized by containing fewer nanocrystals (Fig. 6f). We refer to this texture as "spherical," to distinguish it from the more common, smooth regions. Finally, we identified very rare vesicular regions in the samples from Run 2 (Figs. 7a and 7b) that show similarities to vesicular glass in Stardust samples observed (Leroux et al. 2008b; shown in Figs. 7c and 7d). The vesicular regions in our experiments are generally devoid of nanoparticles. However, these porous materials may be contiguous to both smooth and spherical grains, presenting a very similar distribution to Stardust samples.

The compositions of amorphous materials are shown in Fig. 8 and compared with Stardust data for low-Mg glass with embedded electron-opaque nanocrystals. High sulfur contents in smooth regions resulted, at least in part, from beam overlaps between amorphous silicates and very small nanosulfide compounds, which are particularly abundant in smooth regions (Fig. 6c) compared with spherical regions (Fig. 6f), in which nanosulfide compounds tend to be rare. Moderate to extensive beam overlap may occur because many grains are smaller than the thickness of the ion-milled foil (30-70 nm), and hence surrounding matrix material (typical amorphous silicate material) may be present above and below individual grains in the electron beam path. The smooth regions have less variation in Si contents ($\sim 5 \pm 1.5$ atom% for Run 1 and $\sim 29 \pm 8$ atom% in Run 2—Fig. 8a) than spherical (~15 \pm 11 atom% for Run 1 and ~20 \pm 12 atom% in Run 2—Fig. 8b), which show substantial variations. Heterogeneities in Si content from one region to another suggest that mixing among the different gas streams in the chamber was not uniform, which may have resulted in compositionally heterogeneous submicron domains.

Unlike smooth and spherical regions, rare vesicular areas of amorphous silicates (Fig. 8c) were nearly and exclusively composed of Si-rich (51 atom%, with a 24 atom% standard deviation) and Fe (35 atom%, with a 28 atom% standard deviation), occurring in variable amounts. Only low levels of S (<5 atom%) were detected. Taken together, amorphous materials observed in samples from Run 1 and Run 2 replicate the compositional diversity observed in low-Mg glass from Stardust Track 35, as shown in the Fe-Si-S ternary diagram in Fig. 8d.

The key results from the amorphous materials are as follows. In Fig. 8a (Run 1), we have reproduced the full range of Fe-S compound compositions as were observed for the nanometer-scale Fe-free and low-Ni Fe-S compounds in Stardust glass samples (cf. Figs. 6d, 7c, and 7d). Second, we have reproduced the smooth and vesicular amorphous silicate textures observed in Stardust samples. Finally, variations in Si contents in amorphous materials are either caused by mixing variable proportions of condensed phases or by variable mixing of gas species. The first possibility requires mixing between Fe-S compounds and pure condensed amorphous ferrosilica material such as the materials produced by Rietmeijer et al. (2009). Alternatively, the diversity in smoke compositions may be a result of variable mixing among the Fe-S-Si-O vapor streams. This second possibility is consistent with smoke compositional variations being most pronounced for the spherical silicate, in which there are very low abundances of opaque Fe-S inclusions and therefore, compositional variations cannot be attributed to mixing between the two dominant solid phases.

DISCUSSION

The preliminary studies of the bulk chemical composition of comet Wild 2 reported that its elemental



Fig. 6. Bright field transmission electron microscope (BFTEM) images of typical regions from Run 1 and Run 2 experimental samples and from Stardust's low-Mg silica glass with embedded nanocrystals from the literature. a) Electron micrograph from a typical "smooth" region of amorphous (Amorp) Si-bearing materials from Run 1. Smooth regions are the most common textural occurrences in both Run 1 and Run 2. b) Electron micrograph from a region from Stardust Track 35 modified from Velbel and Harvey (2009). This image, taken at a similar magnification as (a), shows a similar texture as in the experimental samples. c) BFTEM image of a smooth region from Run 1, showing a particularly concentration of electron-opaque phases. d) TEM image of a Fe-S-rich region in Track 10, modified from Zolensky et al. (2006). e) Close-up of the image shown in (d), modified from Zolensky et al. (2006). f) Electron micrograph of a spherical region with multiple subdomains.

abundances generally fall within a factor of two of chondritic values for most elements with a few exceptions that included S, which appeared substantially depleted (Flynn et al. 2006; Zolensky et al. 2006). Zolensky et al. (2006) hypothesized that this depletion responded to losses of sulfur from cometary Fe sulfides due to



Fig. 7. Bright field transmission electron microscope (BFTEM) images of vesicular Si-rich amorphous materials in samples from Run 2 and from a Stardust track. a) Vesicular Fe and Si-rich amorphous material. Note that this region does not contain nanophase particles. Also, note that this vesicular region presents a very sharp interphase with more typical smooth amorphous materials. b) Close-up of boxed region in (a) showing details on the void. c) Pure vesicular silica glass modified from Leroux et al. (2008b). d) Close-up of boxed region in (c) that shows textural similarities with experimentally produced vesicular amorphous materials shown in (a) and (b).

hypervelocity capture heating. According to this hypothesis, sulfur could have been either lost to space or retained in the surrounding aerogel, consequently augmenting the sulfur background in the collection tiles. High-S, Fe-S "hot spots" were subsequently identified in vesicular glass in Stardust allocations: C2054,0,35,44,6 and C2054,0,35,24,1 (Track 35; Leroux et al. 2008b). Although these observations suggest that some fraction of sulfur from Wild 2 was indeed retained within the aerogel, the mechanism(s) by which this occurred merits further examination. Leroux et al. (2009) have argued that hot spots formed by mingling of cometary Fe sulfides and aerogel melts. We present an alternative, yet nonexclusive explanation below. Furthermore, the relationship between pre-existing sulfides and the observed electronopaque nanophases in low-Mg silica glass has not been established.

We present evidence that fine-grained (< 30 nm) nanophase sulfide compounds, nanophase magnetite, and closely associated Si-rich glass in Stardust samples may form directly by condensation of a gas dominated by Si, Fe, S, and O that was produced in the upper bulbous parts of some of the tracks in the aerogel by evaporation of nanograins in Wild 2 aggregate particles and the silica aerogel of the capture tiles. We argue that the smallest Wild 2 grains in the Stardust samples show evidence of melting and of gas-phase chemical reactions that make the survival of indigenous nanophase cometary dust very unlikely. Finally, we speculate that the progenitor of these pockets of amorphous silicate with embedded Fe-sulfide nanograins contained a combination of submicron- and nano-sized sulfides and submicron silica-bearing phases similar to those found in porous chondritic aggregate IDPs and in the fine-grained matrices of some very pristine carbonaceous chondrites.



Fig. 8. Ternary diagrams Fe-Si-S (atom%) showing analytical data for smooth, spherical, and vesicular amorphous regions from Run 1 and Run 2 obtained using AEM (EDS analyses) and compared with Stardust data from Track 35. a) Ternary diagram of data from smooth regions. A total of 64 analyses were collected from smooth regions in samples of Run 1 and 14 analyses from samples of Run 2. Note that although Fe and S vary significantly, Si contents remain relatively constant. b) Fe-Si-S (atom%) ternary diagram of data spherical regions (25 analyses from Run 1 and 20 analyses from Run 2). c) Ternary diagram of data from rare vesicular amorphous materials (14 analyses), which have only been identified in samples from Run 2. These regions are S poor compared with smooth and spherical amorphous materials. d) Ternary diagram showing the compositional range span by each type of amorphous occurrence shaded in gray. Data from low-Mg silica glass in the allocation from Track 35 are also shown. Note that amorphous experimental materials reproduce the compositional variability observed in Stardust glasses.

Vapor-Phase Condensed Smokes and Stardust Samples

Bright-field TEM images of Stardust vesicular, low-Mg, silica glass show abundant, circular, electronopaque inclusions, ranging from a few nanometers up to approximately 200 nm (Leroux et al. 2008b, 2009; Nakamura et al. 2008b; Rietmeijer et al. 2008; Tomeoka et al. 2008; Zolensky et al. 2008; Rietmeijer 2009b; Velbel and Harvey 2009; Bridges et al. 2010). Although these nanophase particles have a wide range of sizes, Sanders and Velbel (2010) determined that the diameter distribution peaks for 10 nm particles and rapidly tails off for higher diameters. Therefore, our experiments replicate the characteristics of the great majority of Stardust nanosulfide compounds, whose diameters are < 30 nm. We have accomplished this by vapor-phase condensation of Fe, S, SiO gas streams. These finer-grained Fe-sulfide inclusions in the Stardust samples appear homogeneous (Leroux et al. 2008b), as are most of the experimentally produced Fe-S nanoparticles. Furthermore, our experiments have also produced nanophase magnetite crystals that may resemble those in Stardust samples. These observations show unequivocally that direct condensation of a parcel of gas can reproduce

the textures, grain size distributions, and the compositions of small electron-opaque inclusions observed in Stardust low-Mg silica glass. Although experimentally produced Fe oxides are significantly smaller and clearly crystalline, unlike those observed by Bridges et al. (2010) in Stardust samples, their presence suggests that Stardust Fe oxides (or precursor metal) may form by the same process as nanosulfides compounds.

Despite general similarities between Stardust low-Mg silica glass and synthetic samples, these materials do not share certain characteristics. For example, large (30–80 nm) Fe-S-bearing nanoparticles as observed in Stardust samples were extremely rare in the samples from our experiments. In our experiments, the largest grains are approximately 30 nm in size (Fig. 4c), and they do not show clear evidence of the core-mantle texture with a Fe-metal core and a FeS rim that was seen in the Stardust samples (Leroux et al. 2008b, 2009; Velbel and Harvey 2009) and produced in the hypervelocity impact experiment simulating the opaque nanograin sizes and textures (Ishii et al. 2008b). Implications of the absence of larger grains and their characteristic core-mantle texture are discussed in the following section.

The presence of sulfur in experimentally created, inclusion-free, amorphous materials shows that Fe, S, and SiO are miscible in the gas phase at the conditions generated in our experiments. Based on these observations, we suggest that quenched S-bearing silicate glasses observed in Stardust samples (e.g., Figs. 3c and 3d) may indeed form by disequilibrium gas-solid condensation.

Finally, regions containing Ca-Mg-bearing glass in Stardust tracks are inclusion-free (Leroux et al. 2008b; Rietmeijer 2009b). These regions are probably remnants from cometary silicates and/or amorphous grains (Leroux et al. 2008b; Rietmeijer 2009b,c). Although we have not attempted to synthesize materials with these compositions, formation of sulfides from Ca- and Mgbearing gases will be explored experimentally in future studies.

Condensation in the Disequilibrium Regime

Three main hypotheses have been proposed for the origin of electron-opaque inclusions. Leroux et al. (2008b, 2009) suggested that some of the metallic-Fe inclusions were formed from iron that was originally present in comet Wild 2's smallest Mg,Fe-silicates. Based on the shapes and concave interfaces of nanosulfides in silica glass, Velbel and Harvey (2009) submitted that the features in track 35 support conditions of nanosulfide melts and vapor. Finally, Rietmeijer et al. (2008) proposed that decomposition of nano Fe-sulfide-metal grains in Wild 2 agglomerates and the formation of

Fe-silicides occurred in a vapor-phase regime. These hypotheses are not mutually exclusive.

Ishii et al. (2008b) have experimentally demonstrated that nanophase mono-sulfide crystals embedded in amorphous silica may form during the hypervelocity capture of micrometer-sized Fe-sulfide particles in the underdense silica Stardust aerogel. These experiments showed that sulfidization of pre-existing metal, as suggested by Leroux et al. (2008b, 2009), may not be the dominant mode of sulfide formation in Stardust samples. However, a disadvantage of hypervelocity-impact aerogel experiments is that the effects of melting argued by Velbel and Harvey (2009) and vaporization suggested by Rietmeijer et al. (2008) cannot be individually assessed. Thus, the last two hypotheses cannot be tested by this method. In contrast, our experiments isolate gas-phase reactions and subsequent deposition and self-annealing from the effects of melting and solidification.

Our observations of nanosulfides embedded in amorphous silicates are most consistent with the scenario envisioned by Rietmeijer et al. (2008). According to Rietmeijer (2009a), pre-existing cometary Fe-Ni sulfides vaporized in the expanding cavities in the aerogel. These gases gave rise to nanosulfides in low-Mg silica glass. Such a formation mechanism leads to deep metastable eutectic compositions that account for departures from stoichiometric sulfide compositions reported for Stardust nanosulfides. Following this line of reasoning, SAED data for the nanosulfides with compositions ranging from almost pure metal and FeS suggest they are "frozen" non-equilibrium compounds that can be (1) random nanometer-scale mixtures of Fe-Ni sulfide and Fe metal, or perhaps Fe oxide or (2) eutectic intergrowths of Fe-Ni sulfide and Fe metal. This model also explains the formation of coexisting Stardust Fe-silicides (Rietmeijer et al. 2008). The hypothesis of a nonequilibrium vaporphase regime may appear somewhat problematic for sulfides that contain even small amounts of Ni. such as Stardust nanosulfides. However, after correcting to measured low-Ni nanosulfide compositions with the background values for Fe, Ni, and S, the overwhelming of nanosulfides become pure-Fe-sulfide majority compounds, but with a small fraction still containing a trace amount of Ni (Figs. 3a and 3b).

Nanosulfides produced in our vapor-phase deposition experiments (Fig. 5) show a comparable compositional range as observed in the two Stardust track samples, but no pure sulfur grains, as explained above. Although the data set for the vapor-phase condensed nanosulfides is limited, there are concentrations at FeS, FeS₂, and FeS₄ (Rietmeijer 2010). The deposition experiment produces many low-S nanosulfides and Fe-metal with compositions similar to those in the samples from tracks 35 and 80 that showed low Ni contents for nanosulfides

in this particular compositional range. Although the condensing gas phase in the experiment was Ni free, Fe-S nanocrystalline compounds in Stardust low-Mg silica glass 2 included very low Ni contents. Low Ni content in the Fe-S nanoparticles (e.g., Figs. 3a and 3b) suggests that Ni partitioning into nanosulfide compounds was not favored during hypervelocity collection and modification. Although the larger and more refractory comet Wild 2 particles, including indigenous Fe-sulfides, may not have been assimilated during hypervelocity capture, more common nanometer-scale phases probably had a different fate. Dominguez (2009) calculated that before the radius of the track reached a few times, the radius of the impacting comet particle, aerogel, would reach temperatures high enough to vaporize. Furthermore, Trigo-Rodríguez et al. (2008) demonstrated that to create the tracks' bulbous cavities, the impacting particles must generate significant amounts of vapor. If volatile-rich, nanophase chondritic or IDP-like phases underwent similar processing, vaporization and subsequent gas-phase reactions probably dominated the chemistry in type B and type C tracks. Our experiments demonstrate that flash condensation of such a gas results in the same texture and compositional trend observed in type B and type C track samples.

Finally, the absence of nanoparticles in the larger (30–80 nm) range as well as only a few occurrences of their typical core-mantle texture from our experimental samples suggests that gas deposition may not be their dominant mechanism of formation. Instead, thermal processing of micron-sized Fe-sulfide precursors, such as the micrometer pyrrhotite utilized in the Ishii et al. (2008b) experiments may be necessary to explain these features. It is possible that only the larger nanoparticles were partially to completely melted and reduced during capture, giving rise to the core-mantle texture. Therefore, we suggest that Stardust low-Mg glass samples record the combined effect of capture-driven evaporation and melting of indigenous cometary samples.

CONCLUSIONS

We have succeeded in simultaneously producing nanophase Fe-sulfide compounds and Fe oxides (i.e., magnetite) embedded in amorphous silicates by instantaneous cooling of a Fe-Si-S-O-bearing gas. Although our experimental protocol included a limited number of reactants compared with the comet-aerogel system, the samples produced replicate of some of the key characteristics of the low-Mg silica glass observed in type B and type C Stardust tracks. On the basis of these similarities, we argue that Stardust nanosulfides and the surrounding amorphous silica-rich materials may have formed by direct disequilibrium condensation of a gas dominated by SiO, Fe, S, and O_2 .

These observations are consistent with the scenario proposed by Rietmeijer et al. (2008), in which Stardust's vesicular, low-Mg, silica glass with embedded electronopaque nanosulfide compounds do not represent indigenous cometary materials. Instead, they may have formed through evaporation/deposition, melting/ condensation, and mixing of cometary materials and aerogel upon collection. Finally, our observations suggest that the precursor materials of these pockets of amorphous silicate with embedded Fe-sulfide nanograins probably consisted of a combination of micron- and nano-sized sulfides and submicron silica-bearing phases consistent with materials found in matrix of porous chondritic IDPs and in the matrices of some type 3.0 carbonaceous chondrites.

Acknowledgments-We are indebted to Dr. Elizabeth Dickey, Dr. Joseph Kulik, Dr. Trevor Clark, and Mr. Joshua Maier for their invaluable and continuous assistance at the TEM facilities. We also thank Dr. H. Leroux, Dr. L. P. Keller, and Dr. M. A. Velbel for the thorough and constructive reviews, which improved the quality of this manuscript, as well as Dr. N. Chabot for her helpful editorial management. NMA was supported by Small Research AAS/NASA, MRSEC, and DuBois Educational Foundation grants and the Materials Summer Research Fellowship/Penn State Materials Characterization Lab. Electron microscopy was carried out at the Material Characterization Lab, Material Research Institute, Penn State University. FJMR was supported by grants NNX07AM65G through the NASA Stardust Analyses Program and NNX07AI39G, and NNX10AK28G from the NASA Cosmochemistry Program. JAN acknowledges support from the Cosmochemistry Program.

Editorial Handling-Dr. Nancy Chabot

REFERENCES

- Bradley J. P. 1994. Chemically anomalous, pre-accretionally irradiated grains in interplanetary dust from comets. *Science* 265:925–929.
- Bridges J. C., Burchell M. J., Changela H. C., Foster N. J., Creighton J. A., Carpenter J. D., Gurman S. J., Franchi I. A., and Busemann H. 2010. Iron oxides in comet 81P/Wild 2. *Meteoritics & Planetary Science* 45:55–72.
- Brownlee D., Tsou P., Aléon J., Alexander C. M. O'D., Araki T., Bajt S., Baratta G. A., Bastien R., Bland P., Bleuet P., Borg J., Bradley J. P., Brearley A., Brenker F., Brennan S., Bridges J. C., Browning N. D., Brucato J. R., Bullock E., Burchell M. J., Busemann H., Butterworth A., Chaussidon M., Cheuvront A., Chi M., Cintala M. J., Clark B. C., Clemett S. J., Cody G., Colangeli L., Cooper G., Cordier P., Daghlian C., Dai Z., D'Hendecourt L., Djouadi Z.,

Dominguez G., Duxbury T., Dworkin J. P., Ebel D. S., Economou T. E., Fakra S., Fairey S. A. J., Fallon S., Ferrini G., Ferroir T., Fleckenstein H., Floss C., Flynn G., Franchi I. A., Fries M., Gainsforth Z., Gallien J.-P., Genge M., Gilles M. K., Gillet P., Gilmour J., Glavin D. P., Gounelle M., Grady M. M., Graham G. A., Grant P. G., Green S. F., Grossemy F., Grossman L., Grossman J. N., Guan Y., Hagiya H., Harvey R., Heck P., Herzog G. F., Hoppe P., Hörz F., Huth J., Hutcheon I. D., Ignatyev K., Ishii H., Ito M., Jacob D., Jacobsen C., Jacobsen S., Jones S., Joswiak D., Jurewicz A., Kearsley A. T., Keller L. P., Khodja H., Kilcoyne A. L. D., Kissel J., Krot A., Langenhorst F., Lanzirotti A., Le L., Leshin L. A., Leitner J., Lemelle L., Leroux H., Liu M.-C., Luening K., Lyon I., MacPherson G., Marcus M. A., Marhas K., Marty B., Matrajt G., McKeegan K., Meibom A., Mennella V., Messenger K., Messenger S., Mikouchi T., Mostefaoui S., Nakamura T., Nakano T., Newville M., Nittler L. R., Ohnishi I., Ohsumi K., Okudaira K., Papanastassiou D. A., Palma R., Palumbo M. E., Pepin R. O., Perkins D., Perronnet M., Pianetta P., Rao W., Rietmeijer F. J. M., Robert F., Rost D., Rotundi A., Ryan R., Sandford S. A., Schwandt G. S., See T. H., Schlutter D., Sheffield-Parker J., Simionovici A., Simon S., Sitnitsky I., Snead C. J., Spencer M. K., Stadermann F., Steele A., Stephan T., Stroud R., Susini J., Sutton S. R., Suzuki Y., Taheri M., Taylor S., Teslich N., Tomeoka K., Tomioka N., Toppani A., Trigo-Rodríguez J. M., Troadec D., Tsuchiyama A., Tuzzolino A. J., Tyliszczak T., Uesugi K., Velbel M., Vellenga J., Vicenzi E., Vincze L., Warren J., Weber I., Weisberg M., Westphal A. J., Wirick S., Wooden D., Wopenka B., Wozniakiewicz P., Wright I., Yabuta H., Yano H., Young E. D., Zare R. N., Zega T., Ziegler K., Zimmerman L., Zinner E., and Zolensky M. 2006. Comet 81P/Wild 2 under a microscope. Science 314:1711-1716.

- Burchell M. J., Fairey S. A. J., Wozniakiewicz P., Brownlee D. E., Hörz F., Kearsley A. T., See T. H., Tsou P., Westphal A., Green S. F., Trigo-Rodríguez J. M., and Domingúez G. 2008. Characteristics of cometary dust tracks in Stardust aerogel and laboratory calibrations. *Meteoritics & Planetary Science* 43:23–40.
- Cliff G. and Lorimer G. W. 1975. The quantitative analysis of thin specimens. *Journal of Microscopy* 103:203–207.
- Dominguez G. 2009. Time evolution and temperatures of hypervelocity impact-generated tracks in aerogel. *Meteoritics & Planetary Science* 44:1431–1443.
- Flynn G. J., Bleuet P., Borg J., Bradley J. P., Brenker F. E., Brennan S., Bridges J., Brownlee D. E., Bullock E. S., Burghammer M., Clark B. C., Dai Z. R., Daghlian C. P., Djouadi Z., Fakra S., Ferroir T., Floss C., Franchi I. A., Gainsforth Z., Gallien J., Gillet P., Grant P. G., Graham G. A., Green S. F., Grossemy F., Heck P. R., Herzog G. F., Hoppe P., Hörz F., Huth J., Ignatyev K., Ishii H. A., Janssens K., Joswiak D., Kearsley A. T., Khodja H., Lanzirotti A., Leitner J., Lemelle L., Leroux H., Luening K., MacPherson G. J., Marhas K. K., Marcus M. A., Matrajt G., Nakamura T., Nakamura-Messenger K., Nakano T., Newville M., Papanastassiou D. A., Pianetta P., Rao W., Riekel C., Rietmeijer F. J. M., Rost D., Schwandt C. S., See T. H., Sheffield-Parker J., Simionovici A., Sitnitsky I., Snead C. J., Stadermann F. J., Stephan T., Stroud R. M., Susini J., Suzuki Y., Sutton S. R., Taylor S., Teslich N., Troadec D., Tsou P., Tsuchiyama A., Uesugi K., Vekemans B., Vicenzi E. P., Vincze L., Westphal A. J.,

Wozniakiewicz P., Zinner E., and Zolensky M. E. 2006. Elemental compositions of comet 81P/Wild 2 samples collected by Stardust. *Science* 314:1731–1735.

- Hörz H., Bastien R., Borg J., Bradley J. P., Bridges J. C., Brownlee D. E., Burchell M. J., Chi M., Cintala M. J., Dai Z. R., Djouadi Z., Dominguez G., Economou T. E., Fairey S. A. J., Floss C., Franchi I. A., Graham G. A., Green S. F., Heck P., Hoppe P., Huth J., Ishii H., Kearsley A. T., Kissel J., Leitner J., Leroux H., Marhas K., Messenger K., Schwandt C. S., See T. H., Snead C., Stadermann F. J., Stephan T., Stroud R., Teslich N., Trigo-Rodríguez J. M., Tuzzolino A. J., Troadec D., Tsou P., Warren J., Westphal A., Wozniakiewicz P., Wright I., and Zinner E. 2006. Impact features on Stardust: Implications for comet 81P/Wild 2. Science 314:1716–1719.
- Ishii H. A., Brennan S., Bradley J. P., Luening K., Ignatyev K., and Pianetta P. 2008a. Recovering the elemental composition of comet Wild 2 dust in five Stardust impact tracks and terminal particles in aerogel. *Meteoritics & Planetary Science* 43:215–231.
- Ishii H. A., Bradley J. P., Dai Z. R., Chi M., Kearsley A. T., Burchell M. J., Browning N. D., and Molster F. 2008b. Comparison of comet 81P/Wild 2 dust with interplanetary dust from comets. *Science* 319:447–450.
- Ishii H. A., Brennan S., Bradley J. P., Pianetta P., Kearsley A. T., and Burchell M. J. 2008c. Sulfur mobilization in Stardust impact tracks (abstract #1561). 39th Lunar and Planetary Science Conference. CD-ROM.
- Jacob D., Stodolna J., Leroux H., Langenhorst F., and Houdellier F. 2009. Pyroxene microstructure in comet 81P/Wild 2 terminal Stardust particles. *Meteoritics & Planetary Science* 44:1475–1488.
- Joswiak D. H., Brownlee D. E., Matrajt G., Westphal A. J., and Snead C. J. 2009. KosmochloricCa-rich pyroxenes and FeO-rich olivines (Kool grains) and associated phases in Stardust tracks and chondritic porous interplanetary dust particles: Possible precursors to FeO-rich type II chondrules in ordinary chondrites. *Meteoritics & Planetary Science* 43:1561–1588.
- Keller L. P. and Messenger S.. 2008. Relict amorphous silicates in Stardust samples (abstract #5227). *Meteoritics & Planetary Science* 43.
- Keller L. P., Bajt S., Baratta G. A., Borg J., Bradley J. P., Brownlee D. E., Busemann H., Brucato J. R., Burchell M., Colangeli L., D'Hendecourt L., Djouadi Z., Ferrini G., Flynn G., Franchi I. A., Fries M., Grady M. M., Graham G. A., Grossemy F., Kearsley A., Matrajt G., Nakamura-Messenger K., Mennella V., Nittler L., Palumbo M. E., Stadermann F. J., Tsou P., Rotundi A., Sandford S. A., Snead C., Steele A., Wooden D., and Zolensky M. E. 2006. Infrared spectroscopy of comet 81P/Wild 2 samples returned by Stardust. *Science* 314:1728–1731.
- Lanzirotti A., Sutton S. R., Flynn G. J., Newville M., and Rao W. 2008. Chemical composition and heterogeneity of Wild 2 cometary particles determined by synchrotron X-ray fluorescence. *Meteoritics & Planetary Science* 43:197–213.
- Leroux H., Jacob D., Stodolna J., Nakamura-Messenger K., and Zolensky M. E. 2008a. Igneous Ca-rich pyroxene in comet 81P/Wild 2. American Mineralogist 93:1933–1936.
- Leroux H., Rietmeijer F. J. M., Velbel M. A., Brearley A. J., Jacob D., Langenhorst F., Bridges J. C., Zega T. J., Stroud R. M., Cordier P., Harvey R. P., Lee M., Gounelle M., and Zolensky M. E. 2008b. A TEM study of thermally modified comet 81P/Wild 2 dust particles by interactions with the

aerogel matrix during the Stardust capture process. *Meteoritics & Planetary Science* 43:97–120.

- Leroux H., Roskosz M., and Jacob D. 2009. Oxidation state of iron and extensive redistribution of sulfur in thermally modified Stardust particles. *Geochimica et Cosmochimica Acta* 73:767–777.
- Matrajt G., Ito M., Wirick S., Messenger S., Brownlee D. E., Joswiak D., Flynn G., Sandford S., Snead C., and Westphal A. 2008. Carbon investigation of two Stardust particles: A TEM, NaniSIMS, and XANES study. *Meteoritics & Planetary Science* 43:315–334.
- Nakamura T., Noguchi T., Tsuchiyama A., Ushikubo T., Kita N. T., Valley J. W., Zolensky M. E., Kakazu Y., Sakamoto K., Mashio E., Uesugi K., and Nakano T. 2008a. Chondrule-like objects in short-period comet 81P/Wild 2. *Science* 321:1664–1667.
- Nakamura T., Tsuchiyama A., Akaki T., Uesugi K., Nakano T., Takeuchi A., Suzuki Y., and Noguchi T. 2008b. Bulk mineralogy and three-dimensional structures of individual Stardust particles deduced from synchrotron X-ray diffraction and microtomography analysis. *Meteoritics & Planetary Science* 43:247–259.
- Nuth J. A., III, Berg O., Faris J., and Wasilewski P. 1994. Magnetically enhanced coagulation of very small iron grains. *Icarus* 107:155–163.
- Nuth J. A., III, Rietmeijer F. J. M., and Hill H. G. M. 2002. Condensation processes in astrophysical environments: The composition and structure of cometary grains. *Meteoritics & Planetary Science* 37:1579–1590.
- Rietmeijer F. J. M. 1998. Interplanetary dust particles. In *Planetary materials*, edited by Papike J. J. Washington, D.C.: Mineralogical Society of America. pp. 2-1–2-95.
- Rietmeijer F. J. M. 2009a. Chemical identification of comet 81P/Wild 2 dust after interacting with molten silica aerogel. *Meteoritics & Planetary Science* 44:1121–1132.
- Rietmeijer F. J. M. 2009b. Stardust glass: Indigenous and modified comet Wild 2 particles. *Meteoritics & Planetary Science* 44:1707–1715.
- Rietmeijer F. J. M. 2009c. A cometary aggregate interplanetary dust particle as an analog for comet Wild 2 grain chemistry preserved in silica-rich Stardust glass. *Meteoritics & Planetary Science* 44:1589–1608.
- Rietmeijer F. J. M. 2010. Fe-Ni-S Compositions after background correction: An ongoing study of the properties of Wild 2 smallest sulfide grains in quenched superheated aerogel (abstract #1239). 41st Lunar and Planetary Science Conference. CD-ROM.
- Rietmeijer F. J. M. and Nuth J. A., III. 1991. Tridymite and maghemite formation in a Fe-SiO smoke. Proceedings, 21st Lunar and Planetary Science Conference. pp. 591–599.
- Rietmeijer F. J. M., Nakamura T., Tsuchiyama A., Uesugi K., Nakano T., and Leroux H. 2008. Origin and formation of iron-silicide phases in the aerogel of the Stardust mission. *Meteoritics & Planetary Science* 43:121–134.
- Rietmeijer F. J. M., Pun A., and Nuth J. A., III. 2009. Dust formation and evolution in a Ca-Fe-SiO-H₂-O₂vapour phase condensation experiment and astronomical implications. *Monthly Notices of the Royal Astronomical Society* 396:402–408.
- Sanders N. E. and Velbel M. A. 2010. The size distribution of Stardust metal sulfide droplets (abstract #1533). 41st Lunar and Planetary Science Conference. CD-ROM.

- Simon S. B., Joswiak D. J., Ishii H. A., Bradley J. P., Chi M., Grossman L., Aléon J., Brownlee D. E., Fallon S., Hutcheon I. D., Matrajt G., and McKeegan K. D. 2008. A refractory inclusion returned by Stardust from comet 81P/Wild 2. *Meteoritics & Planetary Science* 43:1861–1877.
- Stephan T., Rost D., Vicenzi E. P., Bullock E. S., MacPherson G. J., Westphal A. J., Snead C. J., Flynn G. J., Sandford S. A., and Zolensky M. E. 2008. TOF-SIMS analysis of cometary matter in Stardust aerogel tracks. *Meteoritics & Planetary Science* 43:233–246.
- Stoldona J., Jacob D., and Leroux H. 2009. A TEM study of four particles extracted from the Stardust track 80. *Meteoritics & Planetary Science* 44:1511–1518.
- Tomeoka K., Tomioka N., and Ohnishi I. 2008. Silicate minerals and Si-O glass in comet Wild 2 samples: Transmission electron microscopy. *Meteoritics & Planetary Science* 43:273–284.
- Trigo-Rodríguez J. M., Domínguez G., Burchell M. J., Hörz F., and Llorca J. 2008. Bulbous tracks arising from hypervelocity capture in aerogel. *Meteoritics & Planetary Science* 43:75–86.
- Tsou P., Brownlee D. E., Hörz F., Sandford S. A., and Zolensky M. E. 2003. Wild 2 and interstellar sample collection and Earth return. *Journal of Geophysical Research* 108:E8113–E8134.
- Velbel M. A. and Harvey R. P. 2009. Along-track compositional and textural variation in extensively melted grains returned from comet 81P/Wild 2 by the Stardust mission: Implications for capture-melting process. *Meteoritics & Planetary Science* 44:1519–1540.
- Withey P. A. and Nuth J. A., III. 1999. Formation of singlemagnetic-domain iron particles via vapor-phase nucleation: Implications for the solar nebula. *Icarus* 139:367–373.
- Zolensky M. E., Zega T. J., Yano H., Wirick S., Westphal A. J., Weisberg M. K., Weber I., Warren J. L., Velbel M. A., Tsuchiyama A., Tsou P., Toppani A., Tomioka N., Tomeoka K., Teslich N., Taheri M., Susini J., Stroud R., Stephan T., Stadermann F. J., Snead C. J., Simon S. B., Simionovici A., See T. J., Robert F., Rietmeijer F. J. M., Rao W., Perronnet M. C., Papanastassiou D. A., Okudaira K., Ohsumi K., Ohnishi I., Nakamura-Messenger K., Nakamura T., Mostefaoui S., Takashi Mikouchi T., Meibom A., Matrajt G., Marcus M. A., Leroux H., Lemelle L., Le L., Lanzirotti A., Langenhorst F., Krot A. N., Keller L. P., Kearsley A. T., Joswiak D., Jacob D., Ishii H., Harvey R., Hagiya K., Grossman L., Grossman J. N., Graham G. A., Gounelle M., Gillet P., Genge M. J., Flynn G., Ferroir T., Fallon S., Ebel D. S., Dai Z., Cordier P., Clark B., Chi M., Butterworth A. L., Brownlee D. E., Bridges J. C., Brennan S., Brearley A., Bradley J. P., Bleuet P., Bland P. A., and Bastien R. 2006. Mineralogy and petrology of comet Wild 2 nucleus samples. Science 314:1735–1739.
- Zolensky M., Nakamura-Messenger K., Sverdrup J., Rietmeijer F., Leroux H., Mikouchi T., Ohsumi K., Simon S., Grossman L., Stephan T., Weisberg M., Velbel M., Zega T., Stroud R., Tomeoka K., Ohnishi I., Tomioka N., Nakamura T., Matrajt G., Joswiak J., Brownlee D., Langenhorst F., Krot A., Kearsley A., Ishii H., Graham G., Dai Z. R., Chi M., Bradley J., Hagiya K., Gounelle M., and Bridges J. 2008. Comparing Wild 2 particles to chondrites and IDPs. *Meteoritics & Planetary Science* 43:261–272.