CARBONATE IN COMETS: A COMPARISON OF COMETS 1P/HALLEY, 9P/TEMPLE 1, AND 81P/WILD 2. G. J. Flynn[1], H. Leroux[2], K. Tomeoka[3], N. Tomioka[3], I. Ohnishi[3], T. Mikouchi[4], S. Wirick[5], L. P. Keller[6], C. Jacobsen[5] and S. A. Sandford[6], [1]Dept. of Physics, SUNY-Plattsburgh, 101 Broad St., Plattsburgh, NY 12901 (george.flynn@plattsburgh.edu), [2]Laboratoire de Structure et Propriétés de l'Etat Solide, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, France, [3]Dept. Earth & Planetary Science, Kobe University, Nada, Kobe 657-8501 Japan, [4]Dept. Earth & Planetary Science, University Tokyo, Tokyo, Japan, [5] Dept. of Physics, SUNY-Stony Brook, Stony Brook, NY 11794, [6]NASA Ames Research Center, Moffett Field, CA 94035.

Introduction: Comets are generally believed to have formed in a cold region, trapping in the cometary ices the original low-temperature condensate grains of our Solar System. These grains would have been preserved in cold-storage, at a temperature below the freezing point of CO_2, for the last 4.5+ billion years.

Carbonates are common in hydrous meteorites and hydrous interplanetary dust particles (IDPs), where they are believed to have formed by parent-body aqueous processing. Since simple models of cometary evolution involve no aqueous processing, carbonates were generally presumed not to occur in comets. However, Toppani et al. [1] have performed experiments that indicate carbonate can be formed by non-equilibrium condensation in circumstellar environments where water is present as a vapor, not as a liquid. This suggests carbonate might have condensed in cold regions of the Solar Nebula, and might be present in comets.

Carbonate in Comets: The two VEGA spacecraft and the Giotto spacecraft that flew through the coma of Comet 1P/Halley in 1986 determined the elemental composition of Halley dust particles using impact ionization mass spectrometers. The dust particles were separated into groups based on their element abundance patterns. One group consisted of particles with high Mg but relatively low Si. Many of these grains also had high C/S ratios, indicating they were not Mg-sulfides, causing Fomenkova et al. [2] to identify this group as Mg-carbonate grains. A weak infrared emission feature at 6.8 µm, attributed to carbonate, was also observed in Comet Halley [3]

A projectile from the Deep Impact spacecraft struck Comet 9P/Temple 1, producing a dust plume that was examined using the infrared spectrograph on the Spitzer Space Telescope. Lisse et al. [4] associated a strong emission between 6.5 and 7.2 µm with carbonate. After subtraction of strong silicate features, they identified weaker features suggesting that both Mg- and Fe-carbonate were present [4].

The Stardust spacecraft collected dust from Comet 81P/Wild 2 and delivered that material to Earth in January 2006. Because carbonate has a strong absorption feature at ~290 eV (see Figure 1), the Scanning Transmission X-Ray Microscope (STXM) is an efficient tool to search for carbonate grains in ultramicrotome sections. Rare carbonate grains were identified in fragments extracted from five Wild 2 tracks using X-Ray Absorption Near-Edge Structure (XANES) spectroscopy and Transmission Electron Microscopy (TEM) [5]. Thus far, three large calcite grains, 700, 500, and 400 nm in size, two 500 nm dolomite grains, seven 200 nm sized calcite grains, two 100 nm sized calcite grains, and <20 nm sized ferroan magnesite grains have been identified in Wild 2 samples. Many more smaller (<20 nm in size) carbonates have been tentatively identified in two of the tracks. The identification is tentative because these small crystals fall apart in the electron beam and because of their size they are below the spatial resolution of the STXM. But, Cluster Analysis of STXM stack data identifies a large area that likely contains <20 nm in size carbonate grains and this area is similar to the area where TEM data tentatively identifies small calcite crystals (Fig. 1).

Size Distribution of Carbonate in Comets: Of the 2368 spectra considered by Fomenkova et al. [2], 15% of those smaller than 10^{-15} grams were identified as Mg-carbonate while only 8% of those $>10^{-15}$ grams were identified as Mg-carbonate. Among the mineral grains identified in the Wild 2 samples, carbonates were generally very small, ranging from 20 nm in size ($\sim 2 \times 10^{-17}$ grams) to ~700 nm (`5×10^{-13} grams) [5], while much larger silicate grains, up to ~10 µm ($\sim 3 \times 10^{-9}$ grams), were identified [6].

Abundance of Carbonate in Comets: The abundance of grains in the group identified as Mg-carbonate varied significantly from the VEGA-1 to the VEGA-2 analyses, with Mg-carbonate constituting about 7% of the total mass of particles measured by VEGA 1 but only 1% of the total mass measured by VEGA 2. The VEGA instruments only measured particles over the range from 5×10^{-17} grams to 5×10^{-12} grams – about 20 nm to 1 µm. The abundance of carbonate at larger sizes was not determined, but the data indicated a decrease in carbonate abundance with increasing mass [2].

Carbonate was rare among the grains extracted from the Wild 2 tracks. However, many of the non-carbonate grains extracted from Wild 2 tracks were significantly larger than the carbonate grains analyzed at Halley.

Estimating the total amount of carbonate in the Wild 2 samples is difficult, partly because of their small size but also because many carbonates may have decomposed during the high-temperature regime of the

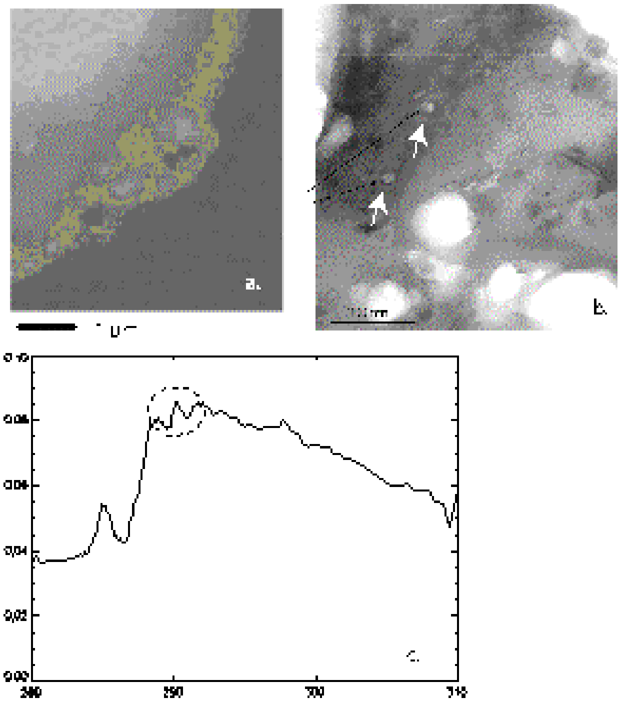

Figure 1: STXM image (a) of a fragment from Stardust Track 16 and the spectrum from the area of this image highlighted in green. The absorption peak near 290 eV (circled) is consistent with carbonate. TEM image of a fragment from Stardust Track 1 (b) also shows small carbonate (at arrows).

hypervelocity capture into aerogel, since carbonates undergo thermal decomposition at T > 800°C.

To assess the possibility of carbonate contamination in the Stardust aerogel, a combined STXM and TEM search of flight aerogel containing no tracks is being undertaken.

The signal intensity in infrared emission spectroscopy is proportional to the surface areas of the emitting minerals. Thus, the size-frequency distribution of the grains is critical. Lisse et al. [4] appear to have used the same particle size distribution for the carbonate an silicate components of the Temple 1 dust. However, both the VEGA observations at Comet Halley [2] and the laboratory analysis of Wild 2 grains [5] indicate that cometary carbonates are very small, while the Wild 2 results indicate that many silicate minerals sometimes occur as much larger grains [6]. All of the carbonates found, thus far, in Wild 2 samples are less then 1 micron in size and most of the grains were significantly smaller then 200 nm in size). Thus, although the Temple 1 results show a weighted surface area ratio for Mg-carbonate to olivine (forsterite + fayalite) of 0.075, the resulting mass ratio would be much smaller if the Mg-carbonate has a smaller size distribution than the olivine.

Origin of Carbonate in Comets: There are two obvious possibilities for the origin of carbonate in comets. The first, aqueous processing, might occur in pockets of fluid produced by the heat and shock of large collisions. Farinella and Davis [7] modeled the collision rate in the Kuiper Belt, and concluded that most 1 to 10 km Kuiper Belt objects are collision fragments from larger bodies. Thus an aqueous origin for cometary carbonate is possible. If so, other aqueous minerals are likely to be found in association with these carbonate.

A second possibility is that the carbonate in comets is a direct nebular condensate. Rietmeijer [8] reported a Mg-carbonate grain in an anhydrous chondritic porous IDP, and Flynn et al. [9] have found carbonate, including Mg-carbonate, in a few anhydrous IDPs. All of the carbonates reported in anhydrous IDPs are submicron in size. Carbonates have also been detected in the dust shell around evolved stars and in protostars, where liquid water is not expected [10].

Conclusions: There is evidence suggesting that carbonate is present in the three comets studied in sufficient detail to determine minor mineral components -- Halley, Temple 1, and Wild 2. For Halley and Wild 2, the measurements indicate this carbonate is very small (typically <20 nm to several hundred nm). A direct comparison of the carbonate abundances in Temple 1 and Wild 2 requires a detailed knowledge of the carbonate size-frequency distribution. An effort to determine the size frequency distribution in Wild 2, using the STXM to identify and the TEM to characterize the carbonate, is underway. Mineral associations, particularly the search for hydrous silicates associated with carbonate, may aid in determining the origin of carbonate in these comets. However, the presence of carbonates in anhydrous IDPs may indicate that carbonate also forms by processes other than aqueous alteration in the Solar System.

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