STXM Search for Carbonate in Samples of Comet 81P/Wild 2

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Abstract. We employed a Scanning Transmission X-ray Microscope (STXM) to search for carbonate in samples of dust from Comet 81P/Wild 2 collected by NASA’s Stardust spacecraft. Although carbonate was not expected in Wild 2 because it generally forms by aqueous processing, which is not thought to occur on comets, we identified two sub-micron carbonate grains in Wild 2 samples. The results demonstrate the effectiveness of the STXM as a search and identification tool for rare minerals that exhibit distinctive X-ray Absorption Near-Edge Structure (XANES) spectra.

1. Introduction
Comets are generally believed to have formed in a very cold region of our Solar System, at a temperature below the freezing point of CO₂. When they formed they trapped the original dust grains of our Solar System in the ice, where these grains have been preserved in cold-storage for the last 4.5+ billion years.

On Earth, carbonates are generally deposited from liquid water. Carbonates are common in hydrous meteorites and in 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.

2. Carbonate in comets
Toppani’s experiments suggest carbonate might have condensed in cold regions of the Solar Nebula, and might be present in comets.

2.1 Prior Results on 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. The low Si and S content caused 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/Tempel 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].

2.2. Carbonate Outside Our Solar System
Astronomical infrared observation provides the opportunity to detect minerals that condensed in the gaseous nebula around other star systems. Infrared spectra of the grains in the planetary nebula NGC 6302 and NGC 6537 from the Infrared Space Observatory have been interpreted by Kemper et al. [5] as showing diopside (CaMgSi_2O_6), dolomite (CaMg(CO_3)_2 -- a carbonate), and water ice. The spectrum indicates NGC 6302 is so hot that its emission peaks in the ultraviolet, so this planetary nebula does not contain water in the liquid phase. In addition, Ceccarelli et al. [6] reported the detection of carbonate in the protostar IRAS4. Both astronomical results remain controversial, in part because a relatively broad absorption feature is fit with a mixture of the absorptions from several reference materials, so no distinctive feature from carbonate alone was detected. Hofmeister et al. [7] provides a more complete discussion of this controversy.

2.3 Stardust Samples of Comet 81P/Wild 2
NASA’s Stardust spacecraft flew through the dust coma of Comet 81P/Wild 2 in January 2004, collecting dust by impact into ultra-low density silica aerogel [8]. These samples were delivered to Earth in January 2006, providing the first opportunity for laboratory examination of dust identified as being from a comet. The Wild 2 particles provide the first unambiguous samples of the early dust of our Solar System, preserved at low temperature in the comet since its formation.

3. Wild 2 Dust Characterization
Fragments from Wild 2 dust particles were extracted from the aerogel. Some fragments were embedded in epoxy or elemental S, prepared as ultramicrotome slices, and made available for our carbonate search.

3.1 The Scanning Transmission X-ray Microscope (STXM) as a Carbonate Identification Instrument.
We used a STXM to perform X-ray Absorption Near-Edge Structure (XANES) spectroscopy on Wild 2 samples. Pre-edge absorptions in C-, N-, and O-XANES spectra result from x-ray induced electron transitions from the core to higher electron energy levels. The energy of each pre-edge absorption is diagnostic of the functional group, and thus provides an indication of the interatomic bonding or mineralogy of the sample. For example, C-bearing minerals – graphite, diamond, C_60, and carbonate – each have a unique, easily identifiable C-XANES spectrum (as shown in Figure 1). In particular, carbonate has only a single, strong absorption, from the C-O_3 bond, near 290 eV, that distinguishes carbonate from most other carbon-bearing minerals.

Carbonate grains as small as ~50 nm can be located using the STXM to an ultramicrotome slice of the sample at two energies, one on the carbonate absorption and a second at an energy slightly above the absorption feature. Pixels showing significantly greater absorption on the C-O_3 peak can be investigated further by obtaining a full C-XANES spectrum. However, we elected to acquire a full image stack [9] over the energy range from 280 to 310 eV, Carbonate grains are immediately visible as a bright spot in the images near the C-O_3 absorption energy, and the C-XANES spectrum can be extracted from the image sequence. STXM imaging provides a rapid and reliable technique to locate and identify carbonate.

3.2 Carbonate Identification in Wild 2 Fragments
We have examined 14 ultramicrotome slices from Wild 2 fragments, 7 embedded in epoxy and 9 embedded in S. Figure 2 shows an ~200 nm carbonate found in Wild 2 particle FC4,0,3,1,2 using the STXM on beamline X1A of the National Synchrotron Light Source (Brookhaven National Laboratory). It is difficult to assess the total area of Wild 2 material we examined in the 14 sections because Wild 2 material is intermixed with compressed and/or melted aerogel in most sections. However, it is clear that the two sub-micron carbonates we identified constitute only a very small fraction of the total Wild 2 material we examined.
4. Conclusions
We have identified two carbonate grains, each smaller than 300 nm in the Wild 2 sections examined to date. The area of carbonate is very small compared to the total area of Wild 2 material we examined. Thus carbonate appears to be a rare component of Wild 2 grains. However, particle capture into aerogel at 6 km/sec is size selective. It appears that “components larger than micron-size were often well preserved, whereas smaller or finer-grained components were strongly modified” by capture [7]. If all the carbonate in Wild 2 is sub-micron in size, while silicate minerals and sulfides several microns in size were observed, the mass-fraction of carbonate in the impacting particles may never be determined because most were modified on capture. Our observations set only a lower limit on the carbonate abundance.

Our results demonstrate the effectiveness of employing a STXM to search for carbonate. Because other rare phases, including diamonds, fullerenes, nitrides, and metal-oxides, also have distinct C-, N-, or O-XANES spectra, STXMs can also be employed to search efficiently for these minerals.

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