

# Reports

## Acid Dissolution Experiments: Carbonates and the 6.8-Micrometer Bands in Interplanetary Dust Particles

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A chemical dissolution experiment on an interplanetary dust particle (IDP) showed that carbonates, not acid-insoluble organic compounds, were responsible for virtually all the absorption at 6.8 micrometers seen in the infrared spectra of this particle. The IDP examined had an infrared spectrum characteristic of layer-lattice silicates and belongs to a class of IDP's whose spectra resemble those of protostellar objects like W33 A, which also exhibit a band at 6.8 micrometers.

**M**OST INTERPLANETARY DUST PARTICLES (IDP's) collected in the stratosphere fall into one of three infrared classes. These classes are referred to as olivines, pyroxenes, and layer-lattice silicates, after the terrestrial minerals that provide the best match to the silicate bands observed at 10  $\mu\text{m}$  in the IDP spectra (1).

The layer-lattice silicate infrared class of IDP's is of particular interest since its spectra match those taken from W33 A (1, 2), an astronomical infrared object that may be a solar system in the process of formation (2). Since the collected IDP's may contain material that has remained relatively unaltered since the formation of the solar system, they may represent the products of processes similar to those now occurring in W33 A.

The infrared spectra of objects like W33 A contain several absorption bands, most of which have at least tentative identifications. In addition to the identified bands, many of these objects exhibit a well-defined absorption band at 6.8  $\mu\text{m}$  (3). The source of this band is not known, but possibilities include hydrocarbons (4) and carbonates (1, 5).

A 6.8- $\mu\text{m}$  band is seen in most of the spectra from IDP's in the layer-lattice silicate class. In the case of the IDP's, the 6.8- $\mu\text{m}$  band was attributed to the asymmetric stretching vibrations of carbonates (1). This tentative identification was confirmed by the observation of the corresponding, but weaker, 11.4- $\mu\text{m}$  carbonate band in the spectrum of Calrissian, a particle with an extremely strong 6.8- $\mu\text{m}$  feature (Fig. 1). The weaker, narrower 11.4- $\mu\text{m}$  band is due to the  $\text{CO}_3$  scissors-mode vibration.

Confirmation of the presence of carbonates in this class of the IDP's has been provided by transmission electron microscopy (TEM) electron diffraction studies (6).

Carbonates may not be responsible, however, for the entire absorption at 6.8  $\mu\text{m}$  seen in the IDP spectra. Other possibilities include (i) the layer-lattice silicates themselves, (ii) hydration effects in the layer-lattice sili-

cates, and (iii) hydrocarbons, all of which have been suggested as the source of this band in astrophysical sites (3, 4).

The first two alternatives cannot be responsible for the 6.8- $\mu\text{m}$  band seen in the laboratory spectra. The 6.8- $\mu\text{m}$  band strengths seen in the IDP spectra do not correlate with the strengths of the 10- $\mu\text{m}$  layer-lattice silicate feature or with the strengths of the 3.0- and 6.0- $\mu\text{m}$  hydration features. In addition, a hydration experiment on an IDP dominated by layer-lattice silicates showed that the 6.8- $\mu\text{m}$  feature did not increase even after direct and prolonged exposure to water. Finally, hydrated layer-lattice silicates do not normally exhibit bands near 6.8  $\mu\text{m}$  (7).

Hydrocarbons, however, are still a possibility. Carbon is a major component of IDP's and occurs in a variety of forms (8). Secondary ion mass spectrometry measurements of deuterium ( $^2\text{H}$ ) show correlations between  $^2\text{H}$  excesses and carbon concentration, suggesting the presence of hydrocarbons (9). The presence of the C-H stretch bands at 3.4  $\mu\text{m}$  in many of the IDP infrared spectra offers supporting evidence. Unfortunately, contamination of the IDP's by silicone oil (10) complicates the spectral interpretation.

If hydrocarbons are, in fact, present in the IDP's, they are likely to be similar to those found in meteorites. Most of the hydrocarbons in meteorites are insoluble in acids (11), while even relatively mild acid treatments will remove most carbonates. Thus, if a substantial fraction of the 6.8- $\mu\text{m}$  band remains after an IDP has been treated with

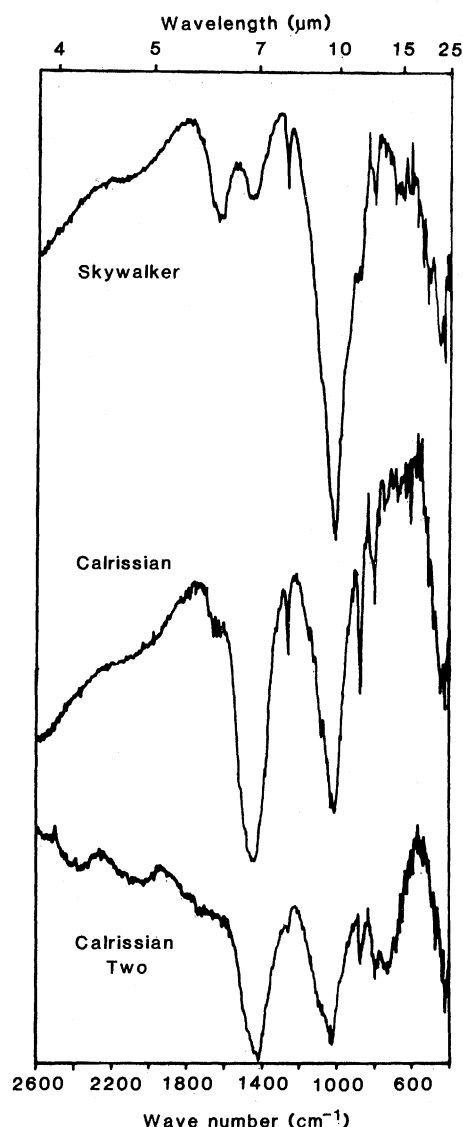
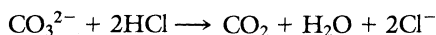


Fig. 1. Middle-infrared spectra of three IDP's in the layer-lattice silicate infrared class. The top spectrum is from the particle Skywalker and represents the spectra typical of this infrared class. The prominent bands at 9.9 and 22.4  $\mu\text{m}$  are due to the Si-O-Si stretching and bending vibrations, respectively, of phyllosilicates. The 6.0- $\mu\text{m}$  feature is caused by the  $\text{H}_2\text{O}$  bending vibrations of water trapped in the layer-lattice silicate structure. The 6.8- $\mu\text{m}$  feature, and perhaps the shoulder on the silicate band at 11.4  $\mu\text{m}$ , are interpreted as being due to carbonates. The bands at 7.9 and 12.5  $\mu\text{m}$  are due to silicone oil contamination. The bottom two spectra are from two IDP's found in close association on an impact collector. The spectrum of Calrissian shows all the infrared features seen in the previous spectrum but differs in having a 6.8- $\mu\text{m}$  band that is stronger than its associated silicate bands. The interpretation that this band is due to asymmetric stretching vibrations in  $\text{CO}_3$  is supported by the presence of the associated 11.4- $\mu\text{m}$  out-of-plane bending mode feature of carbonates. The bottom spectrum is from the particle Calrissian Two, which has a spectrum similar to Calrissian's. Calrissian Two was the particle used in the acid dissolution experiments. All the spectra were obtained with the spectrometer equipped with a 6X beam condenser.

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acids, we could conclude that hydrocarbons are probably a source of some of this absorption feature. In an attempt to determine whether an appreciable fraction of the 6.8- $\mu\text{m}$  band in the IDP spectra was caused by hydrocarbons, an acid dissolution experiment was done to remove the carbonates from Calrissian Two, a particle that exhibited a strong band at this wavelength (Fig. 1).

Carbonate minerals are destroyed by the reaction



Calcite ( $\text{CaCO}_3$ ) is rapidly removed at room temperature in a 10 percent HCl solution. Dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] is also removed at room temperature but at a lower rate. Rapid removal of siderite ( $\text{FeCO}_3$ ) requires a temperature greater than 50°C. Since many of the carbonates in the IDP's are rich in iron and magnesium (6), the acid dissolution experiment was done at 60°C.

Calrissian Two, the IDP examined, was collected and curated using techniques described earlier (1). The particle had an elemental pattern similar to that seen in carbonaceous meteorites, was approximately 20  $\mu\text{m}$  in diameter, and had a mass of about 10 ng. Calrissian Two was found in the same spray of material on a collector plate that contained Calrissian, and the two particles are believed to be closely related. The particle was crushed between two quartz plates, and material adhering to one of the plates was used to make an infrared mount. The material on the other quartz plate was subjected to an approximately 10-second exposure to 10 percent HCl at 60°C. The particle was observed through a stereomicroscope during the acid exposure. The sample may have effervesced during the chemical treatment (due to escaping  $\text{CO}_2$ ), but optical distortion caused by the acid droplet makes this uncertain. After the etched material had dried, it was also made into an infrared mount. The carbonate grains in Calrissian were small (100 to 3000 Å in diameter), numerous, and distributed throughout the particle (6), so both halves of Calrissian Two are expected to have contained many carbonate grains.

Because of the small size of the samples, it was necessary to place the mounts at the focus of a beam condenser in the spectrometer. The unetched sample was first examined with a Nicolet 7199 Fourier transform infrared spectrometer equipped with a 6X beam condenser. Approximately 200,000 interferograms were integrated over a 2-day period to get the desired signal-to-noise ratio (1), and the resulting spectrum is shown in Fig. 1. The etched sample proved to be too small for this technique, however, and both the unetched and etched samples

were reexamined with a similar spectrometer equipped with a more powerful beam condenser (12). Both of these spectra are shown in Fig. 2.

The 6.8- $\mu\text{m}$  band is present in the spectra of the unetched sample taken with both spectrometers. The removal of the prominent 6.8- $\mu\text{m}$  band from the lower spectrum in Fig. 2 indicates that the source of this feature has been removed by the acid treatment. Both spectra in Fig. 2 show prominent 3.0- $\mu\text{m}$  hydration bands and 10- $\mu\text{m}$  silicate bands. The acid treatment apparently also altered the silicates in the particle slightly. Bands near 6.0  $\mu\text{m}$  in both spectra may be due to water. The band at 7.9  $\mu\text{m}$  and some or all of the band at 3.4  $\mu\text{m}$  in the top spectrum are due to silicone oil contamination. The interferences at 4.3  $\mu\text{m}$  in both spectra are due to residual atmospheric  $\text{CO}_2$  in the spectrometer.

While most of the 6.8- $\mu\text{m}$  band is removed by the acid treatment, several small features may still be present at 5.8, 6.3, and 7.1  $\mu\text{m}$ . These band positions are not inconsistent with the expected absorptions from func-

tional groups like  $-\text{COOH}$  and  $-\text{CH}=\text{CH}_2$ . Because of the weakness of the bands and the possibility of silicone oil interference, it is not certain that the features are from hydrocarbons associated with the IDP.

The disappearance of the 6.8- $\mu\text{m}$  band in the spectrum obtained from the acid-etched sample shows that most of the 6.8- $\mu\text{m}$  band is caused by carbonates or other easily soluble phases. If hydrocarbons were responsible, they would have to be removed by short exposures to HCl but be insoluble in the xylene used to clean the silicone oil collecting medium off the particles during the curation procedure. Since the strength of the 6.8- $\mu\text{m}$  band relative to the 10- $\mu\text{m}$  silicate feature seems to correlate roughly with the abundance of carbonates as seen in the TEM (6), it is most likely that carbonates are responsible for essentially all of the 6.8- $\mu\text{m}$  band. The problematic possible minor bands at 5.8, 6.3, and 7.1  $\mu\text{m}$  remaining after acid treatment suggest the presence of a minor hydrocarbon component that can survive acid treatments.

The demonstration that chemical dissolution experiments are possible on extremely small particles opens up several possibilities for future investigation. It may now be possible to carry out dissolution experiments on IDP's similar to those done on meteorites in which the silicates are removed by alternating HF and HCl dissolutions. In meteorites this process concentrates phases containing isotopic anomalies (13).

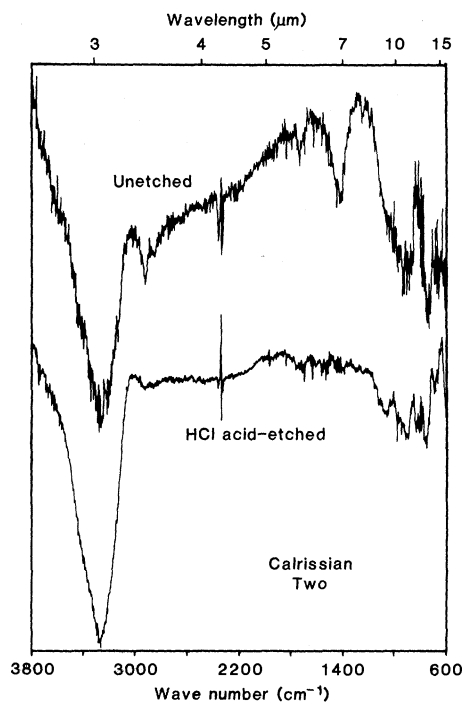


Fig. 2. Infrared spectra from different portions of Calrissian Two. The top spectrum was taken from the same unetched sample that produced the bottom spectrum in Fig. 1. The bottom spectrum was taken from the portion of Calrissian Two that was etched by acid. The acid exposure removes the 6.8- $\mu\text{m}$  carbonate feature seen in the top spectrum. The bands at 3.0 and 6.0  $\mu\text{m}$  in both spectra are due to O-H stretching and H-O-H bending vibrations of water trapped within the layer-lattice silicates. Silicone oil is probably responsible for the narrow bands at 3.4 and 7.9  $\mu\text{m}$ . The narrow features at 4.3  $\mu\text{m}$  are caused by residual atmospheric  $\text{CO}_2$  in the spectrometer.

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