An Infrared Spectral Match Between GEMS and Interstellar Grains

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Infrared spectral properties of silicate grains in interplanetary dust particles (IDPs) were compared with those of astronomical silicates. The ~10-micrometer silicon-oxygen stretch bands of IDPs containing enstatite ($MgSiO_3$), forsterite (Mg_2SiO_4), and glass with embedded metal and sulfides (GEMS) exhibit fine structure and bandwidths similar to those of solar system comets and some pre–main sequence Herbig Ae/Be stars. Some GEMS exhibit a broad, featureless silicon-oxygen stretch band similar to those observed in interstellar molecular clouds and young stellar objects. These GEMS provide a spectral match to astronomical "amorphous" silicates, one of the fundamental building blocks from which the solar system is presumed to have formed.

Interplanetary dust particles (IDPs) collected in the stratosphere are from asteroids and comets (*1*). The "chondritic porous" (CP) subset of IDPs are likely cometary because they have fragile microstructures, high carbon abundance, and high content of Mg-rich silicates, and some have high atmospheric entry speeds (*2, 3*). Comets are primitive small bodies that are believed to contain interstellar and circumstellar silicates as well as other presolar components (for example, organic compounds) (*3–6*). A population of glassy silicate grains known as GEMS are found within the matrices of CP IDPs (*7*). The physical properties of GEMS are exotic (for example, they contain superparamagnetic metal inclusions) but similar to those of equally exotic astronomical "amorphous" silicate grains that are ubiquitous throughout interstellar and circumstellar space (*7–9*). Optical evidence of these grains is found in astronomical infrared (IR) spectra where bands at ~10 and ~18 μm, corresponding to the Si-O stretch and Si-O-Si bending mode vibrations in silicates, are observed (in absorption and emission) along multiple lines of sight (*10*).

We measured the IR (~10 μm) bands of GEMS in CP IDPs and compared them with those of interstellar and circumstellar silicates and silicates in solar system comets. Measuring the IR properties of GEMS is difficult because (i) they are too small to analyze using conventional laboratory IR spectrophotometers and (ii) they are almost always found mixed with other submicrometer silicate minerals. We analyzed IDP thin sections (up to 15 μm in diameter) containing GEMS mixed with other glassy silicates and submicrometer enstatite and forsterite crystals, as well as regions (~6 μm in diameter) of thin sections where GEMS are the only silicate minerals present (*11*). Infrared spectral data were acquired using the high-intensity light line at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. NSLS is ideally suited for analyzing tiny ($\sim10^{-13}$ g) objects like GEMS because the IR beam spot provided by the beamline is brighter than that of conventional IR spectrophotometers by more than two orders of magnitude (*12*).

GEMS are usually found within the matrices of IDPs mantled with or embedded in amorphous carbonaceous material (Fig. 1A). Nanometer-sized inclusions of FeNi metal (kamacite) and Fe-sulfide grains within GEMS are embedded in a glassy silicate matrix (Fig. 1, A and B). The glass is Mg-rich (Mg/Si ratio = 0.25 to 2), Fe-depleted (Fe ≤ 5 weight %), and stoichiometrically enriched in O [probably as hydroxyl (–OH)] (*7, 13*). Some GEMS exhibit a compositional gradient of decreasing Mg/Si from the center toward the outer surface (*7*). Other GEMS also contain "relict" sulfide or Mg-rich silicate crystalline grains toward their centers (Fig. 1, C and D), some of which exhibit heavily etched microstructures (Fig. 1D). The textures, mineralogy, O enrichments, and Mg gradients are consistent with the exposure of GEMS to ionizing radiation (*7*).

The 10-μm band from a GEMS-rich IDP (L2008V42A) was compared with those of silicates in comets and circumstellar dust (Fig. 2). The IDP band exhibits peaks at ~9.5 and ~11.2 μm, due to enstatite and forsterite crystals, respectively, and broad peak structure between 9.6 and 10.2 μm, due to GEMS and other glassy silicates. This ~10-μm band structure is typical of GEMS-rich cometary

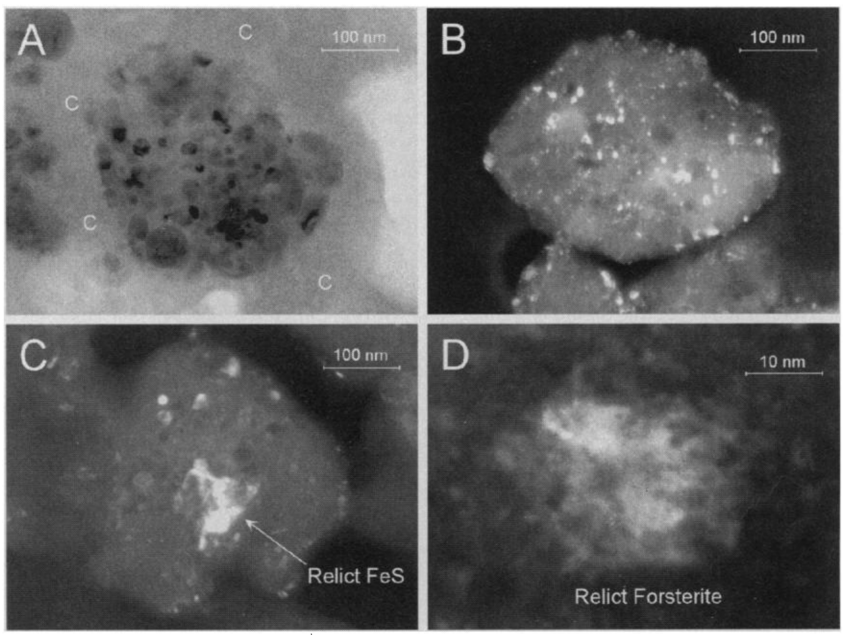

Fig. 1. Transmission electron micrographs of GEMS within thin sections of chondritic IDPs. (**A**) Bright-field image of GEMS embedded in amorphous carbonaceous material (C). Inclusions are FeNi metal (kamacite) and Fe sulfides. (**B**) Dark-field image. Bright inclusions are metal and sulfides; uniform gray matrix is Mg-rich silicate glass. (**C** and **D**) Dark-field images of GEMS with "relict" Fe sulfide and forsterite inclusions.

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IDPs (*14*). Comets Hale-Bopp (C/1995 O1) and Halley are well-studied solar system comets for which high signal-to-noise ~10-μm spectral data are available (*15, 16*). Both comets exhibit peaks at ~9.4 and 11.2 μm (attributed to enstatite and forsterite, respectively) and broad maxima at 9.8 to 10 μm (attributed to glassy silicates) (*15, 16*). HD163296 is a pre–main sequence Herbig Ae/Be star with a silicate-rich disk (*17*). The 10-μm band exhibits peaks at ~9.5, ~10, and 11.2 μm and is similar to that of solar system comets (Fig. 2, B to D).

We compared the ~10-μm band from GEMS with those of interstellar and circumstellar "amorphous" silicates (Fig. 3). The GEMS spectrum (Fig. 3A) was obtained from a region of a thin section of IDP L2011*B6 where GEMS are the only silicates present. The same clump of GEMS is present in four thin sections of L2011*B6, and a similar ~10-μm profile was collected in each case. The band is broad and featureless, and it peaks at ~9.8 μm with an IR excess or asymmetry on the long-wavelength side (Fig. 3A). Similar featureless bands obtained from GEMS-rich thin sections imply that, depending on composition and mineralogy [for example, Mg/Si ratio and relict grains (Fig. 1, C and D)], the peak position of GEMS may vary between 9.3 and 10.4 μm (Fig. 4). Elias 16 (in Taurus) and Trapezium (in Orion) are interstellar molecular cloud environments (Fig. 3, B and C) (*18, 19*). Their smooth, asymmetric spectra with maxima at ~9.8 μm and an IR excess on the long-wavelength side are similar to those of GEMS (compare Fig. 3, A, B, and C). DI Cephei (a T Tauri star) exhibits a ~10-μm band typical of the dust around many young stellar objects (YSOs) (Fig. 3D) (*20*). μ-Cephei is an evolved (post–main sequence) M-type supergiant star (Fig. 3E) (*21*). Its circumstellar ~10-μm band is similar to but narrower than those of GEMS, Elias 16, Trapezium, and DI Cephei.

The ~18-μm Si-O-Si bending band of GEMS-rich thin sections is difficult to measure because the low sample mass and aperture-induced diffraction effects (*11*) reduce signal at wavelengths greater than 15 μm. Broad, featureless bands in several spectra exhibit intensity maxima that vary between 18 and 20 μm, together with superimposed sharper bands due to submicrometer enstatite and forsterite crystals (*22*). Astronomical "amorphous" silicate ~18-μm bands are also broad with an absorption/emissivity maximum at ~18.5 μm (*23*). The ~18-μm bands of other natural and synthetic amorphous (glassy) silicates vary between 18 and 23 μm (*24*).

The spectrum of GEMS matches the spectra of interstellar molecular cloud dust (for example, Elias 16 and Trapezium), YSOs (for example, DI Cephei), and the M-type supergiant μ-Cephei (Fig. 3). Many YSOs, such as DI Cephei, also have emission or absorption profiles that can be fit with the Trapezium emissivity when optical depth effects are taken into account (*19, 20*). No other single natural or synthetic silicate has so far been found to match astronomical "amorphous" silicates. Bandwidths of most meteoritic (and terrestrial) silicates vary between 1.7 and 2.5 μm (*14, 18, 24*), whereas bandwidths of astronomical amorphous silicates vary between 2.5 and 3.5 μm (full width at half-maximum) (*10, 18*). The GEMS feature matches the molecular cloud dust in terms of bandwidth, maximum absorption/emissivity at 9.7 to 9.8 μm, and long-wavelength asymmetry.

In addition to the ~10-μm spectral match (Fig. 3), the isotopic compositions of some GEMS-rich IDPs link them to an interstellar molecular cloud environment. Although nonsolar isotopic abundances have not yet been observed in GEMS (*25*), ^{15}N excesses (–93 to +500 per mil) as well as huge D/H excesses (500 to +50,000 per mil) approaching the values observed in cold interstellar molecular clouds (10^4 to 10^6 per mil) have been observed in GEMS-rich IDPs (*26*). The excesses are believed to reflect the preservation of molecular cloud organic components that experienced extreme mass fractionation during low-temperature ion molecule reactions. Using electron energy-loss spectroscopy, Keller *et al.* (*27*) showed that the nitrogen in a ^{15}N-enriched IDP is localized within the carbonaceous phase, which coats and encapsulates GEMS (for example, Fig. 1A). Therefore, it is plausible that the mantles were deposited on the GEMS within a presolar molecular cloud (*4*). In principle, observation of nonsolar isotopic abundances within individual GEMS using a new generation of high spatial resolution ion microprobe would rig-

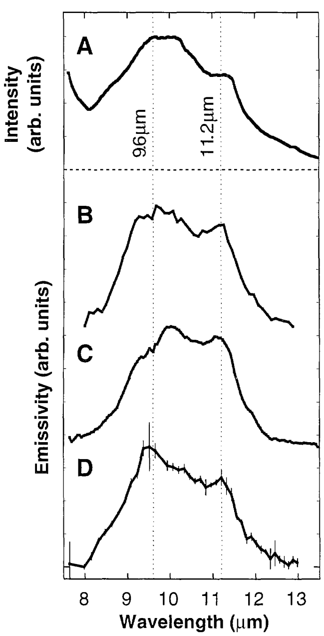

Fig. 2. Comparison of the 10-μm Si-O stretch bands of a "GEMS-rich" IDP and astronomical silicates. (**A**) Chondritic IDP L2008V42A. Profile derived from transmittance spectrum. (**B**) Comet Halley (*15*). (**C**) Comet Hale-Bopp (*16*). (**D**) Late-stage Herbig Ae/Be star HD163296 (*17*). The structure at 9.5 μm in (B), (C), and (D) is due to telluric O_3.

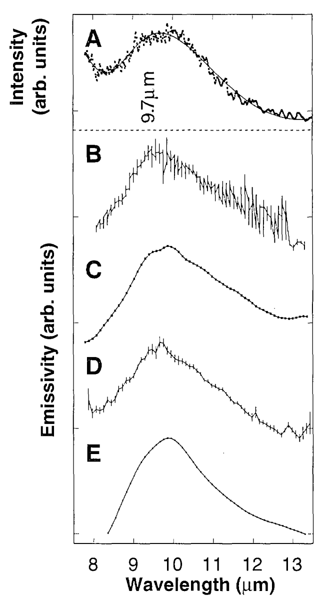

Fig. 3. Comparison of the 10-μm Si-O stretch bands of GEMS with astronomical silicates. (**A**) GEMS (in IDP L2011*B6). (**B**) Elias 16 molecular cloud (*18*). (**C**) Trapezium molecular cloud (*19*). (**D**) Pre–main sequence T Tauri YSO DI Cephei (*20*). (**E**) Post–main sequence M-type supergiant μ-Cephei (*21*).

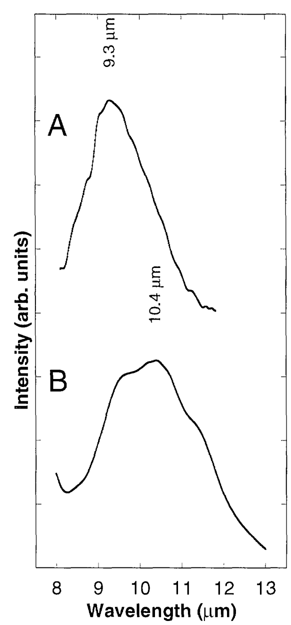

Fig. 4. The 10-μm Si-O stretch bands from two GEMS-rich IDPs. (**A**) IDP L2011*B5: GEMS with <10% enstatite (thin section). (**B**) IDP L2021C4: GEMS mixed with minor forsterite [fragments in KBr, see (*11*)].

orously establish their presolar origins (*28*). On the other hand, failure to observe an isotope anomaly would not rule out a presolar origin. Because typical interstellar grains undergo extensive processing through shocks and irradiation exposure during their lifetimes ($\sim 10^8$ years), it is likely that their isotopic compositions become homogenized (*29*). The homogenized chondritic ("cosmic") elemental compositions of GEMS are perhaps evidence of this processing (*7, 25*).

The "chondritic" element abundances in GEMS are generally consistent with those of interstellar silicate grains (*7, 30, 31*). Inferred abundances of most lithophile elements (for example, Na, Mg, Al, Ca, and K) in interstellar dust are compatible with silicate mineralogy. Sulfur does not appear to be depleted from the gas phase in the diffuse interstellar medium (*30, 31*), but there is evidence of sulfur depletion in interstellar molecular clouds (*32*). Because GEMS contain sulfur (*7*), they are more consistent with grains in interstellar molecular clouds. In warm (>100 K) or shocked interstellar clouds, Fe tends to stay in grains, whereas Si returns to the gas phase (*30, 31, 33*). In GEMS, Fe is concentrated in metal and sulfide nanocrystals (Fig. 1), but Si is within nonstoichiometric (silicate) glass, which may be more susceptible to erosion and sputtering (*7, 34*).

The enstatite and forsterite crystals in GEMS-rich IDPs resemble the Mg-rich silicate mineralogy of comets inferred from their spectra (*5, 15*) and in situ sampling of comet Halley (*16, 17, 35*). The Infrared Space Observatory (ISO) detected spectral peaks of submicrometer forsterite and enstatite crystals in the spectra of comet Hale-Bopp, in the disks of late-stage YSOs, and in the circumstellar shells of some evolved stars (*6, 36*). Submicrometer enstatite and forsterite crystals are rare or absent in chondritic meteorites and micrometeorites but are conspicuously abundant in GEMS-rich chondritic IDPs (*3*). Some of these crystals exhibit crystallographic or compositional evidence of growth from the vapor phase (*3, 37*), which is the principal mechanism of grain growth in circumstellar outflows. It is possible that some of the enstatite and forsterite crystals in cometary IDPs are also presolar circumstellar grains (*37*).

The $\sim$10-μm spectral match between some GEMS and astronomical amorphous silicates adds to the physical, chemical, isotopic, and mineralogical data linking GEMS to a presolar interstellar molecular cloud, presumably the local molecular cloud from which the solar system formed. Superparamagnetic (FeNi) metal inclusions in GEMS (Fig. 1) provide a logical explanation, first proposed by Jones and Spitzer (*38*), for the observation that (dielectric) interstellar "amorphous" silicate grains cause polarization of starlight by aligning themselves in the galactic magnetic field (*9*). If GEMS are indeed astronomical amorphous silicates, one of the long-sought building blocks of the solar system has been found because, before the collapse of the solar nebula, most of the heavy elements in the solar system were carried within these grains (*30, 31, 38*). The 10-μm Si-O stretch feature of IDPs composed of GEMS, enstatite, forsterite, and other glassy silicates resembles solar system comets and some circumstellar silicates. In contrast to meteorites, GEMS-rich "CP" IDPs collected in the stratosphere may be relatively pristine aggregates of presolar interstellar and circumstellar dust and therefore the most primitive astrophysical materials available for laboratory investigation.

References and Notes

1. S. A. Sandford and R. M. Walker, *Astrophys. J.* **291**, 838 (1985); D. E. Brownlee, *Annu. Rev. Earth Planet. Sci.* **13**, 147 (1985); S. A. Sandford, *Fund. Cosmic Phys.* **12**, 1 (1987); S. F. Dermott *et al.*, *Nature* **369**, 719 (1994).
2. J. P. Bradley and D. E. Brownlee, *Science* **231**, 1542 (1986); K. L. Thomas *et al.*, *Geochim. Cosmochim. Acta* **57**, 1551 (1993); D. E. Brownlee *et al.*, *Lunar Planet. Sci. Conf.* **XXV**, 185 (1994); S. A. Sandford and J. P. Bradley, *Icarus* **82**, 146 (1989).
3. J. P. Bradley, T. P. Snow, D. E. Brownlee, M. S. Hanner, in *Solid Interstellar Matter: The ISO Revolution*, L. d'Hendecourt, C. Joblin, A. Jones, Eds. (Les Houches 11, EDP Sciences, Les Ullis, France; Springer-Verlag, Berlin, 1999), pp. 298–315.
4. J. M. Greenberg, in *Comets*, L. L. Wilkening, Ed. (Univ. of Arizona Press, Tucson, AZ, 1982), pp. 131–163; L. B. F. M. Waters *et al.*, *Nature* **391**, 868 (1998).
5. D. H. Wooden *et al.*, *Astrophys. J.* **517**, 1034 (1999).
6. J. Crovisier *et al.*, *Science* **275**, 1904 (1997).
7. J. P. Bradley, *ibid.* **265**, 925 (1994).
8. G. J. Flynn, *Nature* **371**, 287 (1994).
9. GEMS are glassy spheroids, 0.1 to 0.5 μm in diameter, with nanometer-sized opaque (metal and sulfide) inclusions embedded in nonstoichiometric Mg-silicate glass, and chondritic bulk compositions (Fig. 1) (*7*). These properties are exotic (relative to other natural silicates) but similar to those of astronomical "amorphous" silicate grains [P. G. Martin, *Astrophys. J.* **445**, L63 (1995)]. Observations and theory suggest that the astronomical silicates are predominantly amorphous (glassy), spheroidal in shape, and "dirty" (light absorbing) because they contain opaque inclusions, some or all of which may be superparamagnetic [A. A. Goodman and D. C. B. Whittet, *ibid.* **455**, L181 (1995)]. The size range of the grains inferred from extinction is 0.1 to 0.5 μm [S. H. Kim, P. G. Martin, P. D. Hendry, *ibid.* **422**, 164 (1994)], and their bulk compositions inferred from interstellar gas phase abundances are about chondritic (*31*).
10. J. Gürtler, T. Henning, J. Dorschner, *Astron. Nachr.* **310**, 319 (1989).
11. Fragments of IDPs were pressed into potassium bromide (KBr) crystals. Thin sections of IDPs embedded in sulfur were produced using an ultramicrotome equipped with a diamond knife [see J. P. Bradley, L. P. Keller, K. L. Thomas, T. B. VanderWood, D. E. Brownlee, *Lunar Planet. Sci. Conf.* **XXIV**, 173 (1993)]. We examined the thin sections ($<$100 nm thick) using a 200-keV transmission electron microscope. Transmission IR spectra were collected over the wavelength range of 2.5 to 25 μm (4000 to 400 cm^{-1}) with an aperture (from 12 to 20 μm^2) positioned around each specimen. Background IR spectra were acquired from the carbon thin-film substrate along side the specimens. Final baseline corrected and smoothed spectra were obtained by subtracting the background from the sample spectrum. Between 256 and 1000 scans (interferograms) were averaged from each specimen with a spectral resolution of 4 cm^{-1}.
12. J. Reffner *et al.*, *Synch. Rad. News* **7**, 30 (1994); G. L. Carr, J. A. Reffner, G. P. Williams, *Rev. Sci. Instrum.* **66**, 1490 (1995).
13. D. E. Brownlee, D. J. Joswiak, J. P. Bradley, *Lunar Planet. Sci. Conf.* **XXX**, 2031 (1999).
14. J. P. Bradley, H. Humecki, M. S. Germani, *Astrophys. J.* **394**, 643 (1992); J. P. Bradley *et al.*, *Lunar Planet. Sci. Conf.* **XXIX**, 1737 (1998).
15. H. Campins and E. Ryan, *Astrophys. J.* **341**, 1059 (1989).
16. M. S. Hanner *et al.*, *Earth Moon Planets*, in press.
17. M. L. Sitko, C. A. Grady, D. K. Lynch, R. W. Russell, M. S. Hanner, *Astrophys. J.* **510**, 408 (1999).
18. J. E. Bowey, A. J. Adamson, D. Whittet, *Mon. Not. R. Astron. Soc.* **298**, 131 (1998); J. E. Bowey, thesis, University of Central Lancashire (1997).
19. M. S. Hanner, T. Y. Brooke, A. T. Tokunaga, *Astrophys. J.* **438**, 250 (1995).
20. M. S. Hanner, T. Y. Brooke, A. T. Tokunaga, *ibid.* **502**, 871 (1998).
21. D. K. Aitken *et al.*, *Mon. Not. R. Astron. Soc.* **230**, 629 (1988).
22. J. P. Bradley *et al.*, *Lunar Planet. Sci. Conf.* **XXX**, 1835 (1999).
23. J. P. Simpson, *Astrophys. J.* **368**, 570 (1991); Th. Henning and R. Stognienko, *Astron. Astrophys.* **280**, 609 (1993).
24. J. R. Stephens and R. W. Russel, *Astrophys. J.* **228**, 780 (1979); T. J. Millar and W. W. Duley, *Mon. Not. R. Astron. Soc.* **191**, 641 (1980); M. Madon and G. D. Price, *J. Geophys. Res.* **94**, 687 (1989); J. Jäger *et al.*, *Astron. Astrophys.* **339**, 904 (1998); J. Dorschner, B. Begemann, Th. Henning, C. Jaeger, H. Mutschke, *ibid.* **300**, 503 (1995).
25. J. P. Bradley and T. Ireland, in *Physics, Chemistry, and Dynamics of Interplanetary Dust*, B. Å. S. Gustafson and M. S. Hanner, Eds. (ASP Conference Series 104, Astronomical Society of the Pacific, San Francisco, 1996), pp. 275–282.
26. S. Messenger and R. M. Walker, in *Astrophysical Implications of the Laboratory Study of Presolar Materials*, T. J. Bernatowicz and E. Zinner, Eds. (AIP Conference Proceedings 402, American Institute of Physics, Woodbury, NY, 1998), pp. 545–564.
27. L. P. Keller *et al.*, *Lunar Planet. Sci. Conf.* **XXVIII**, 707 (1997).
28. F. J. Stadermann, R. M. Walker, E. Zinner, *ibid.* **XXX**, 1407 (1999).
29. J. A. Nuth, in *Meteorites and the Early Solar System*, J. Kerridge and M. S. Mathews, Eds. (Univ. of Arizona Press, Tucson, AZ, 1988), pp. 984–991.
30. U. J. Sofia, J. A. Cardelli, B. D. Savage, *Astrophys. J.* **430**, 650 (1994); B. D. Savage and K. R. Sembach, *Annu. Rev. Astron. Astrophys.* **34**, 279 (1996).
31. T. P. Snow and A. N. Witt, *Astrophys. J.* **468**, L65 (1996).
32. D. J. Jansen, E. F. van Dishoeck, J. H. Black, *Astron. Astrophys.* **282**, 605 (1993).
33. L. Spitzer and E. L. Fitzpatrick, *ibid.* **409**, 299 (1993); *ibid.* **445**, 196 (1995).
34. K. Thiel, J. P. Bradley, R Spohr, *Nucl. Tracks Rad. Meas.* **15**, 385 (1988); J. P. Bradley *et al.*, *Lunar Planet. Sci. Conf.* **XXVII**, 149 (1996).
35. J. D. Bregman *et al.*, *Astron. Astrophys.* **187**, 616 (1987); E. K. Jessberger, A. Christoforidis, J. Kissel, *Nature* **332**, 691 (1988).
36. L. B. F. M. Waters *et al.*, *Astron. Astrophys.* **315**, L361 (1996); C. Waelkens, L. B. F. M. Waters, M. S. de Graauw, *ibid.*, p. L245; K. Malfait *et al.*, *ibid.* **332**, L25 (1998).
37. J. P. Bradley, D. R. Veblen, D. E. Brownlee, *Nature* **301**, 473 (1983).
38. R. V. Jones and L. Spitzer, *Astrophys. J.* **147**, 943 (1967).

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