DISCOVERY OF Mg-RICH PYROXENES IN COMET C/1995 O1 (HALE–BOPP): PRISTINE GRAINS REVEALED AT PERIHELION

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Abstract. The NASA Ames HIFOGS spectrometer observed comet C/1995 O1 (Hale-Bopp) at epochs including 96 Oct 7-14 UT (2.8 AU), 97 Feb 14-15 UT (1.2 AU), 97 Apr 11 UT (0.93 AU), and 97 Jun 22, 25 UT (1.7 AU). The HIFOGS 7.5–13.5 μ m spectrophotometry (R = 360 - 180) of the silicate feature at 2.8 AU is identical in shape to the ISO SWS spectra of comet Hale-Bopp (Crovisier et al., 1997); the strong 11.2 μ m peak in the structured silicate feature is identified as olivine. Upon close passage to the sun, the HIFOGS spectra at 1.2 AU and 0.93 AU reveals strong peaks at 9.3 μ m and 10.0 μ m. The post-perihelion 10 μ m silicate feature at 1.7 AU is weaker but has nearly the same shape as the pre-perihelion spectra at 1.2 AU, reverting to its pre-perihelion shape: there is no change in the dust chemistry by close passage to the sun. The appearance of the strong peaks at 9.3 $\mu {
m m}$ and 10.0 $\mu {
m m}$ at $r_h \lesssim$ 1.7 AU is attributed to the rise in the contribution of pryoxenes (clino-pyroxene and orthopyroxene crystals) to the shape of the feature, and leads to the hypothesis that the pyroxenes are significantly cooler than the olivines. The pyroxenes are radiating on the Wien side of the blackbody at 2.8 AU and transition to the Rayleigh-Jeans tail of the blackbody upon closer approach to the Sun. Composite fits to the observed 10 μ m silicate features using IDPs and laboratory minerals shows that a good empirical fit to the spectra is obtained when the pryoxenes are about 150 K cooler than the olivines. The pyroxenes, because they are cooler and contribute significantly at perihelion, are more abundant than the olivines. The perihelion temperature of the pyroxenes implies that the pyroxenes are more Mg-rich than the other minerals including the olivines, amorphous olivines, and amorphous pyroxenes. The PUMA-1 flyby measurements of comet P/Halley also indicated an overabundance of Mg-rich pryoxenes compared to olivines. Comet Hale-Bopp's pyroxenes are similar to pyroxere IDPs from the 'Spray' class, known for their D-richness and their unaltered morphologies: Hale-Bopp's Mg-rich pyroxenes may be pristine relic ISM grains.

Keywords: Comet, infrared, dust, silicates, olivine, pyroxene



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1. Introduction

Comets are the frozen reservoirs of pristine early solar nebula material. In contrast, even the most primitive meteorites contain reprocessed silicates; for example, some carbonaceous meteorites contain Mg-rich olivine crystals with Fe-rich olivine rims, conclusive of secondary heating events. Thus, comets are the best reservoir for the study of the first solar nebula silicate condensates and the presolar silicates accreted from the interstellar medium.

Comet grains are studied by rendevous spacecraft, by remote sensing (groundbased and spaceborne IR spectroscopy) and by laboratory study of interplanetary dust particles (IDPs) of cometary origin (having stratospheric entrance velocities of ≥ 15 km s⁻¹ with no substantial loss of volatiles, Flynn et al., 1995). By identification with terrestrial minerals, IDPs are grouped into three classes according to their IR spectra: olivines (11.2 and 10.0 μ m peaks), pyroxenes (9.3 and 10.5 μ m peaks), and layer-lattice silicates (~9.8 μ m broad peak). Pyroxene IDPs are the most Mg-rich, the most fluffy, having a granular carbonaceous matrix (Bradley, 1988), and often contain pryoxene crystals with radiation tracks indicative of lowdosage long-term exposure such as expected for the interstellar medium (Bradley et al., 1997). Olivine IDPs are less porous compared to the pyroxene IDPs, and have a glassy matrix (Bradley, 1988). Layer-lattice silicates (smectites) are much denser, containing aqueously altered material, "tar balls", and probably are asteroidal in origin (Bradley, 1988). Cluster (highly porous and fragile) IDPs have substantial deuterium enrichments (Messenger et al., 1996); some IDPs are interstellar relic grains.

Theoretical thermal equilibrium condensation sequences computed for the solar nebula predict the first silicate mineral to condense was forsterite, i.e., pure-Mg olivine $[Mg_yFe_{(1-y)}]_2SiO_4$ with y = 1.0, and the next silicate to condense was enstatite, i.e., pure-Mg pyroxene $Mg_xFe_{(1-x)}SiO_3$ with x = 1.0 (Larimer, 1967). Small amounts of manganese and iron were probably incorporated from the gas phase into the extremely Mg-rich olivines and pyroxenes (Wai and Wasson, 1977), as evidenced by the study of MnO/FeO ratios in unequilibrated chondrites and in IDPs (Klöck et al., 1989). For comet Halley, PUMA-1 mass spectrometry deduced Mg-rich pyroxenes were the dominant silicate mineral species (Schulze et al., 1997), in apparent contrast with ground-based spectroscopy which identified olivines as a major mineral component (Bregman et al., 1997; Bradley et al., 1988; Campins and Ryan, 1989). The Mg-content of cometary olivines and pryoxenes investigates the gas phase chemistry, radial mixing, and the survival of interstellar relic grains in the early solar nebula.

2. 10 μ m Silicate Spectra and Mineral Fits

The NASA Ames HIFOGS (Witteborn et al., 1991) was used to observe the mid-IR spectrum (7.5–13.5 μ m) of the inner coma of comet Hale–Bopp with an aperture 3" and a resolving power of R = 360-180 at the 2.3-m Wyoming Infrared Observatory (WIRO) and the 3.0-m NASA Infrared Telescope Facility (IRTF). High quality spectra were obtained on 96 Oct. 07–14 UT, 97 Feb. 14–15 UT, 97 Apr. 11 UT, and 97 Jun. 22, 25 UT; for details of the observation and analysis see Wooden et al. (1999a). Both IDP fits and laboratory mineral fits to the 4 epochs of HIFOGS silicate spectra were made, and a brief synopsis of the mineral fits is shown in Figures 1 and 2. Figure 1 shows the shape and strength (flux density divided by a blackbody continuum fit to $\lambda \le 7.8 \ \mu$ m and $\lambda \ge 2.5 \ \mu$ m) of the silicate feature as observed by HIFOGS in 96 Oct 07–14 UT at 2.8 AU (8 nights scaled and smoothed in the upper plot) and in 97 Apr 11 UT at 0.93 AU (just 10 days prior to perihelion in lower plot), compared to a five component mineral fit.

The strength and shape of Hale-Bopp's silicate feature changed as the comet approached and receded from perihelion. The silicate feature increased in contrast relative to the continuum from 2.5 to 3.0 when r_h decreased from 2.8 AU to 0.93 AU, significantly larger than comet Halley's silicate strength of ~ 1.8 (Hanner et al., 1994). The silicate feature also increased in complexity: the 9.3 μ m shoulder in Hale–Bopp's silicate feature increased to become a distinct 9.3 μ m peak, the 10.0 μ m peak increased, a narrow 10.5 μ m peak appeared, and the 11.2 μ m peak increased and narrowed. In Figure 1, the changes in the silicate feature structure are modeled by the sum of a constant multiple (constant fractional abundance) of optical extinctions Q_{ext} of (crystalline) olivine (Koike et al., 1993), amorphous olivine, and amorphous pyroxene (Dorschner et al., 1995) assigned the temperature of the observed 10 μ m continuum plus a constant multiple of Q_{ext} of clino-pyroxene and ortho-pyroxene (C. Koike pers. comm.) fitted to a temperature of about 150 K cooler than the other species. The (crystalline) pyroxenes were too cool, radiating on the Wien side of the Planck curve, to contribute significantly to the 10 μ m silicate feature at 2.8 AU, but warmed enough to be seen at 10 μ m as the comet approached perihelion (Wooden et al., 1999a).

The ISO SWS spectra on 96 Oct 06 UT (Crovisier, 1997; Crovisier et al., 1997), observed just one day prior to the HIFOGS spectra on 96 Oct 07–14 UT, strongly constrains the contribution of cooler (crystalline) pyroxenes: even though the pyroxenes are too cool to radiate at 10 μ m, they are warm enough to radiate at 18–35 μ m. Figure 2 is the mineral fit shown in the upper panel of Figure 1 at 2.8 AU but multiplied by a ~200 K blackbody and scaled for comparison with the ISO SWS spectrum; the HIFOGS spectra is plotted by the heavy solid line to show its remarkable similarity to the larger beam satellite data. The mineral model for Hale–Bopp (heavy dotted line) provides a good match to the relative strengths of the 24-, 29- and 33- μ m peaks, with a reasonable match for the 19 μ m peak. A total mineral fit with forsterite, i.e., pure-Mg olivine (Koike et al., 1993), substituted for



Figure 1. Mineral model fit to HIFOGS 10 μ m silicate features at 2.8 AU (96 Oct. 07–14 UT) and 0.93 AU (97 Apr. 11 UT), using a combination of olivine, amorphous olivine, amorphous pyroxene at the temperature of the observed 10 μ m continuum and clino-pyroxene and ortho-pyroxene at a cooler temperature equal to a constant fraction of (~0.6×) the 10 μ m continuum.



Figure 2. Mineral model fit to HIFOGS 96 Oct 07-14 UT and ISO SWS 96 Oct 06 UT spectra.

olivine (all parameters fixed) is also shown in Figure 2 by the light long-dashed line, to demonstrate that olivine fits better than forsterite, primarily by the fact that the 33- μ m peak is too strong and secondly by the 18- and 23- μ m peaks are too narrow for forsterite as compared to olivine.

3. Cool Mg-Rich (Crystalline) Pyroxenes: Implications

The changes in the shape of Hale–Bopp's 10 μ m silicate feature with heliocentric distance are empirically modeled by the incorporation of pyroxene crystals which are about 150 K cooler than the other mineral species, which include (crystalline) olivine, amorphous olivine, and amorphous pyroxene. The pyroxenes are therefore more poorly coupled to the sunlight than the other minerals. If the other minerals are the temperature ~400 K at perihelion ($\simeq 10 \ \mu$ m continuum temperature) while the pyroxenes are ~250 K, then when in radiative equilibrium the pyroxene's wavelength-averaged visible absorptivity is, by the forth-power of the temperature ratio, one-sixth that of the other species.

Increasing the Mg content of pyroxenes and olivines has the effect of decreasing the optical density (OD = ln[I/I₀]) and wavelength of their optical resonances (Burns, 1993). The same effect is seen in the IR resonances, although the correlation is not as tight. For example, the 11.3 μ m forsterite peak shifts to 11.0 μ m for x = 0.95, and then shifts to longer wavelengths (Koike et al., 1993). By comparison of complex indices of refraction (k) for amorphous olivines and amorphous pyroxenes (Dorschner et al., 1995), the olivines are a few times more optically active for the same Mg-content, but not enough to account for the deduced large temperature difference in the mineral species in Hale–Bopp. By Mie scattering computations of $\langle Q_{\text{ext}} \rangle$ for 0.25 and 0.5 μ m grains using Dorschner et al.'s optical constants, if the olivines were fifty percent Mg-rich, i.e., $[Mg_yFe_{(1-y)}]_2SiO_4$ with y = 0.5, then the pyroxenes would have to be much more Mg-rich to be 150 K cooler, i.e., $Mg_xFe_{(1-x)}SiO_3$ with $x \ge 0.8$. The resonance peak in extremely Mg-rich pyroxene IDPs is also at 9.3 μ m (Bradley et al., 1992). The ortho- and clino-pyroxenes used in the mineral fit have $x \simeq 0.9$ (Koike et al., 1993; C. Koike, pers. comm.). Thus, in comet Hale–Bopp the pyroxene crystals are probably more Mg-rich than other species.

Because the pyroxenes are cooler, they are Mg-rich, and by the fact they are seen at perihelion, they are a few times more abundant than the olivines and amorphous species. Thus, the apparent paradox (Section 1) of the PUMA-1 flyby results that discovered an abundance of Mg-rich pryoxenes over olivines (Schulze et al., 1997) is resolved by this discovery of a less optically active mineral component in Hale–Bopp's coma.

The Mg-rich pyroxene crystals in Hale–Bopp may be the interstellar relic pyroxene crystals in IDPs found by Bradley and collaborators (Section 1). In the IDP fits to Hale–Bopp's silicate feature presented in Wooden et al. (1999b), the pyroxene IDPs which best fit are 'Mac' and 'Spray4a' (Sandford and Walker, 1984) and are both members of the 'cluster IDPs' class (Sandford, pers. comm.) which have significant D-enrichments (Messenger et al., 1996) and show no significant alteration before incorporation into parent bodies (Bradley, 1994). Thus, the Mg-rich pyroxenes in Hale–Bopp may be pristine interstellar relic grains.

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References

- Bradley, J. P.: 1988, Geochim. Cosmochim. Acta 52, 889.
- Bradley, J.: 1994, Geochim. Cosmochim. Acta 58, 2123.
- Bradley, J. P., Humecki, H. J., and Germani, M. S.: 1992, ApJ 294, 643.
- Bradley, J. P., Sandford, S. A., and Walker, R. M.: 1988, in J. F. Kerridge and M. S. Matthews (eds.), *Meteorites and the Early Solar System*, University of Arizona Press, Tucson, p. 861.
- Bradley, J. P., Brownlee, D. E., and Snow, T. P.: 1997, 'From Stardust to Planetesimals', in Y. J. Pendleton and A. G. G.M. Tielens (eds.), *ASP Conf. Ser. 122*, p. 217.

- Bregman, J. D., Campins, H., Witteborn, F. C., Wooden, D. H., Rank, D. M., Allamandola, L. J., Cohen, M., and Tielens, A. G. G. M.: 1987, *A&A* 187, 616.
- Burns, R. G.: 1993, *Mineralogical Applications of Crystal Field Theory*, Cambridge University Press, New York, Ch. 5.
- Campins, H. and Ryan, E.: 1989, ApJ 341, 1059.
- Crovisier, J.: 1997, Earth, Moon, and Planets 79, in press.
- Crovisier, J., Leech, K., Bockelée-Morvan, Brooke, T. Y., Hanner, M. S., Altieri, B., Keller, H. U., and Lellouch, E.: 1997, *Science* 275, 1904.
- Dorschner, J., Begemann, B., Henning, Th., Jäger, C., and Mutschke, H.: 1995, A&A, 300, 503.
- Flynn, G. J. et al.: 1995, LPS 26, 407.
- Gehrz, R. D. and Ney, E. P.: 1992, Icarus 100, 162.
- Hanner, M. S., Lynch, D. K., and Russell: 1994, ApJ 425, 274.
- Klöck, W., Thomas, K. L., McKay, D. S., and Palme, H.: 1989, Nature 339, 6220.
- Koike, C., Shihai, H., and Tsuchiyama, A.: 1993, MNRAS 264, 654.
- Larimer, J. W.: 1967, Geochim. Cosmochim. Acta 31, 1215.
- Messenger, S., Walker, R. M., Clemett, S. J., and Zare, R. N.: 1996, LPS 27, 867.
- Sandford, S. A. and Walker, R. M.: 1985, ApJ 291, 838.
- Schulze, H., Kissel, J., and Jessberger, E. K.: 1997, 'From Stardust to Planetesimals', in Y. J. Pendleton and A. G. G. M. Tielens (eds.), ASP Conf. Ser. 122, p. 397.
- Wai, C. M. and Wassen, J. T.: Earth Planet. Sci. Lett. 36, 1.
- Witteborn, F. C., Bregman, J. P., Rank, D. M., and Cohen, M.: 1991, in R. E. Stencel (ed.), Proc. of the 1991 North American Workshop on Infrared Spectroscopy, University of Colorado, Boulder, p. 29.
- Wooden, D. H., Harker, D. E., Woodward, C. E., Butner, H. M., Koike, C., Witteborn, F. C., and McMurtry, C. W.: 1999a, *ApJ* 517, 1034.
- Wooden, D. H., Butner, H. M., Harker, D. E., and Woodward, C. E.: 1999b, Icarus, accepted.