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site containing Permian leaves, yet unstudied, was found approximately 2 km farther south.

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The Meteorite-Asteroid Connection: Two Olivine-Rich Asteroids

Abstract. *Two asteroids have clear indications of olivine-rich surface petrology without any indication of pyroxene or plagioclase, suggesting that the olivine may be quite pure. They provide probable examples of mantles of differentiated parent asteroids exposed by fragmentation and are good candidates for the parent bodies of the unusual olivine meteorite Brachina or the olivine-iron alloy meteorites called pallasites.*

Meteorites recovered on the earth represent, at least in part, fragments from collisions among the asteroids. The variety of compositional types among the asteroids, as deduced from their telescopically observed colors and spectral reflectivities, is at least comparable to the diversity of petrological types of meteorites. Associating specific meteorite types with particular asteroids is an endeavor that has met with increasing success in telescopic surveys and laboratory spectral studies (1).

Early spectrophotometry of asteroids in the wavelength range 0.3 to 1.1 μm (1), as well as the more recent eight-color photometric survey of asteroids (2, 3), revealed a small number of objects having a relatively steep rise in reflectance toward the red end of the photovisual spectrum but with a downturn at about 0.9 μm . The olivine absorption band was suspected as the cause of the downturn but, without measurements of the infrared side of the band, olivine was difficult to confirm as a principal mineral constituent (1, 4). Broadband photometry in the near infrared (1.2 to 2.2 μm) also suggested that this spectral class of asteroids may be olivine-rich (5), but the firm identification of olivine requires spectral information of higher resolution than broadband photometry can provide in this wavelength region. Such data exist for a small but representative selection of asteroids of widely recognized types (C, S, M, D, and others), but none shows the characteristic olivine spectral signature (a combination of three overlapping bands that appear as a single broad absorption band centered at 1.06 μm) without the interfering strong bands of pyroxene (6). Asteroids with nearly pure olivine spectra with no pyroxene bands were, we believe, unknown before this study.

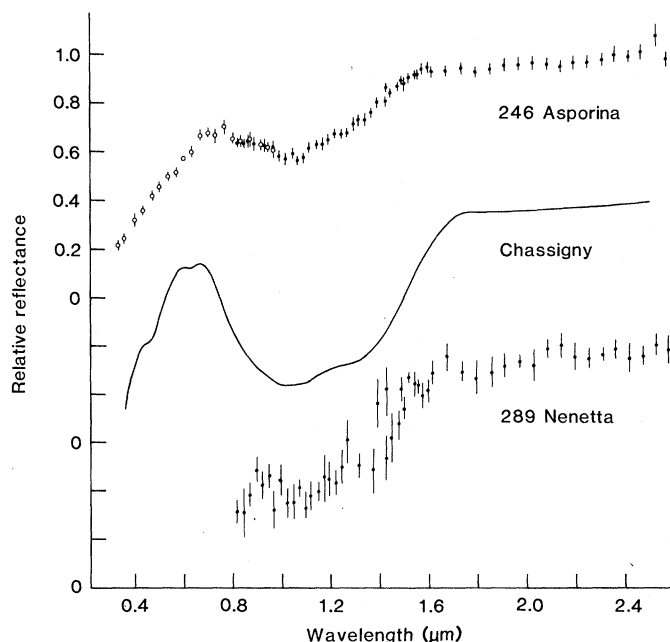
The possible existence of olivine-rich asteroids is of interest because olivine is an igneous silicate mineral that is found in pure or nearly pure assemblages only as a result of differentiation. In terrestrial volcanic settings it is the material that settles to the bottom of a magma chamber, and it is sometimes erupted onto the surface in a late stage of basaltic volcanism. In once-melted asteroids it could be a major constituent of the mantle or of certain mantle zones. Extraterrestrial sources of such material must exist because we have two meteorites that are nearly pure olivine (Chassigny and Brachina). Their origin is of special interest because their existence indicates the occurrence of secondary events on asteroids, and their visibility requires the exposure of asteroid interiors.

We made spectrophotometric observations in the near infrared (0.8 to 2.6

μm) of two of the five known A-class asteroids found from JHK photometric surveys (5) and identified them as olivine-rich. We used the NASA 3-m Infrared Telescope Facility on Mauna Kea, Hawaii, with an indium antimonide photometer equipped with two circular variable-interference filters (CVF's) for wavelength separation. The first CVF has a wavelength bandpass of 3 percent over the range 0.75 to 1.5 μm , and the second has a 5 percent bandpass between 1.4 and 2.8 μm . When used in the step-and-integrate mode in the usual way for infrared photometry, the two filters allowed us to obtain a complete spectrum from 0.8 to 2.6 μm (where the telluric water absorption cuts off the signal) in about 15 minutes. Several individual runs were averaged and ratioed to the spectrum of a solar-type star observed on the same night at the same air mass in order to remove the effects of the telluric atmospheric absorptions and the color of the sunlight illuminating the asteroids (7).

The resulting spectra of 246 Asporina and 289 Nenetta are plotted in Fig. 1. Additional spectral data are available for Asporina in the region 0.3 to 0.97 μm (8, 9); these are included in our plot as open circles, normalized to our data in the region of overlapping wavelengths. Nenetta is significantly fainter than Asporina, and the data are correspondingly lower in quality. Both asteroids show the spectral signature of olivine without the pyroxene bands at 0.9 and 1.8 μm . Pyroxene and olivine are usually found together, as in the spectrum of 349 Dembowska (6) and in all 11 of a recently studied sample of S-type asteroids (10).

Fig. 1. Relative reflectance spectra of Asporina and Nenetta, obtained by ratioing the asteroids to solar-type stars and normalizing to 1.0 in the points at the longest wavelengths. The line in the middle is a reflectance spectrum of the olivine cumulate meteorite Chassigny, showing a pronounced olivine band at 1.06 μm . None of the spectra shows the commonly encountered pyroxene bands at 0.9 and 1.8 μm .



Studies of olivine-pyroxene mixtures (4, p. 91; 11) indicate that the pyroxene should be visible if it exceeds 10 percent of the mixture. Asporina and Nenetta, therefore, have < 10 percent pyroxene. Similarly, plagioclase feldspar becomes visible through its spectral signature if the fractional quantity exceeds about 10 percent.

Also shown in Fig. 1 is the reflectance spectrum of a powdered sample of the meteorite Chassigny (11). Chassigny and a similar meteorite, Brachina, are the only two known olivine cumulate meteorites and are 92 and 79 percent olivine by weight, respectively, with additional augite and a hydrous amphibole called kaersutite. Chassigny and the rare basaltic achondrites called nakhlites and shergottites (eight known specimens), are anomalous meteorites because of their young age of about 1.3 billion years (12), compared with ~ 4 billion years for other achondrites. Once classified as a chassignite, Brachina was recently found to be a more "normal" meteorite genetically unrelated to Chassigny; its age is 4 billion years or more and its trace element chemistry is different (12). The close similarity of the spectra of the two asteroids and the olivine cumulate meteorite in Fig. 1, along with additional spectral studies of olivine and olivine cumulate rocks (13–15), shows that Asporina and Nenetta can be classified as unusual objects, spectrally dominated by olivine and lacking in pyroxene.

Various studies (13–15) show three effects that alter the depth, band center, and shape of the olivine absorption band, potentially giving additional information. These effects include particle size, presence of opaques, and olivine composition that varies in a solid solution series, $(\text{Mg}, \text{Fe})_2\text{SiO}_4$. The magnesium-rich end-member is forsterite and the iron-rich end-member is fayalite.

As particle size decreases, absorption weakens and reflectivity increases. Studies of terrestrial olivines (15) and fayalitic olivine (14) show that the best match to the 1- μm band in Asporina is a laboratory sample having coarse grains mixed with a substantial fraction of grains < 45 μm in size. Somewhat coarser material could explain the somewhat deeper band in Nenetta, with the fines having sizes closer to 70 μm (14).

Opaque minerals in the pulverized olivine also reduce the strength of the absorption band, but lower the albedo instead of raising it as pulverization does. Opaque mineral grains in the olivine on Asporina would qualitatively be consistent with the geometric albedo of 0.14. More opaques on Asporina than on

Nenetta could explain Asporina's weaker absorption. A candidate opaque material would be a metal phase, which would also help explain the strong overall reddening of the spectrum (1, 8, 9, 11). We can, in fact, reproduce the Asporina spectrum fairly well with a calculated mix of two separate spectra, one-third of the surface area being a medium octahedrite iron meteorite and two-thirds Chassigny. This fractional combination of iron and olivine is a plausible composition for the pallasites, which consist of coarse olivine crystals in a matrix of metal. This suggests that these meteorites, instead of resembling dunite-like pure olivine cumulates like Chassigny or Brachina, resemble pallasite meteorites—stony irons that are about 65 percent forsteritic olivine by volume.

The forsterite/fayalite ratio of the olivine is thus of considerable interest. Hunt and Salisbury (14) showed that as the forsterite content drops and fayalite increases, the 1.0- μm band deepens, the band minimum shifts to longer wavelengths, and the longward shoulder shifts to longer wavelengths. Pure forsterite has no 1.06- μm absorption band, but a few percent fayalite produces a detectable band. Fayalite-rich olivine produces a deep band with a minimum shifted to about 1.11 μm and a shoulder at around 2.0 μm . From Hunt and Salisbury's data on artificial olivines of various (unspecified) "size ranges," we find that the best overall match to Asporina would be a forsteritic olivine with forsterite mole percentages of about 60 to 90. The best match to Nenetta would be forsteritic olivine with forsterite mole percentages of about 40 to 80. Note the reported forsterite percentages in the following olivine-rich objects: Apollo 17 lunar dunites, 86 to 89 (16); pallasites, 79 to 89 (17); Chassigny, 67 (12); and Brachina, 67 (12). The olivine compositions of the asteroids suggested by the spectral signatures are thus in the range for known planetary samples of olivine cumulates from small planetary bodies.

The effects of particle size, opaques, and forsterite/fayalite ratio are intermingled, so it is difficult to prove, for example, that a somewhat more fayalitic composition may not be offset by a somewhat smaller particle size. Nonetheless, because most meteoritic olivine is forsteritic, we suggest that the most probable physical nature of these asteroids is a surface regolith of pulverized, forsteritic olivine-rich material with less than 10 percent pyroxene and a possible large fraction of metal.

Such asteroids are of considerable theoretical interest for two reasons. First,

they offer prime examples of asteroid mantles exposed by fragmentation. As such, they testify to both differentiation and fragmentation among asteroids. [For example, a recent model of a differentiated asteroid (10) calls for a mantle of olivine surrounding an iron core: Asporina and Nenetta could be such mantles exposed by fragmentation. Similarly, a recent model of asteroid collisional evolution (18) calls for fragmentation leaving strong pallasite cores around 70 km in diameter: Asporina could be such an exposed core.] Second, these asteroids are excellent candidates for parent bodies of certain meteorites: either the rare brachinite type of olivine cumulate meteorite or the most abundant pallasite type. Indeed, on the basis of the spectra, they offer one of the best available matches between asteroids and meteorites.

Our example of the spectral match with the olivine cumulate Chassigny requires a final comment. Because of their young solidification ages, Chassigny, the nakhlites, and the shergottites have been proposed as nonasteroidal meteorites, possibly blasted off lava flows or magma chambers on Mars (19). Our spectral match is not meant to imply that Chassigny came from an asteroid instead of Mars, but only to confirm the spectral match with an olivine cumulate meteorite; we would prefer to show also a spectrum of Brachina, but to our knowledge one has not yet been measured. Because Chassigny is so closely associated with nakhlites and shergottites (20), to argue that Chassigny came from an asteroid is to argue that all came from the same anomalously youthful asteroid. We are not prepared to advocate this. Our finding probably has little bearing on the issue of possible meteorites from Mars; instead, the two asteroids studied here may be parent bodies of Brachina or the pallasites. While magmatism and subsequent disruption of asteroids in the past 1 to 2 billion years should not be dismissed, recent activity of this kind is not compatible with current models of asteroid evolution.

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Native Cellulose: A Composite of Two Distinct Crystalline Forms

Abstract. *Multiplicities in the resonances of chemically equivalent carbons, which appear in the solid-state carbon-13 nuclear magnetic resonance spectra of native celluloses, have been examined at high resolution. The patterns of variation are consistent with the existence of two distinct crystalline forms. One form is dominant in bacterial and algal celluloses, whereas the other is dominant in celluloses from higher plants.*

The resonance multiplicities reported in the solid-state ^{13}C nuclear magnetic resonance (NMR) spectra of native celluloses (1, 2) have been examined at higher resolution for a variety of native forms and for a sample of regenerated cellulose I. The pattern of variation among spectra of the native forms suggests that they are all composites of two distinct crystalline forms of cellulose. This observation provides a basis for reassessing some of the conflicting interpretations of data concerning the structures of native celluloses.

Significant questions remain with respect to the structure of native celluloses. These include the symmetry of the unit cell and its application in the analysis of diffraction data (3) as well as the conformational differences, or lack thereof, between native cellulose and its most common alternate polymorph (4). The solid-state ^{13}C NMR spectra represent an important source of new information that can help to resolve these questions.

A number of groups have reported spectra of different celluloses (1, 2, 5).

Although spectra of pure samples of cellulose II could be rationalized in terms of nonequivalent sites within a unique unit cell, the spectra of native celluloses reveal multiplicities that cannot be so explained. The observations summarized here result from our effort to interpret these multiplicities in spectra of higher resolution.

We recorded the spectra by applying the cross polarization-magic angle spinning (CP-MAS) technique in a high-field instrument (6). This method involves cross polarization to enhance the ^{13}C signal, high-power proton dipolar decoupling to eliminate dipolar line-broadening due to protons, and spinning of the sample about an axis at a particular angle to the static field to eliminate chemical shift anisotropy. The methods and considerations involved in the acquisition and interpretation of the spectra have been discussed (2, 7). Those central to the point of this report will be reviewed briefly.

The samples included a bacterial cellulose from *Acetobacter xylinum*, an algal cellulose from *Valonia ventricosa*, and

two fibrous celluloses, cotton linters and ramie. Finally, celluloses of the pure polymorphic forms I and II were regenerated by procedures developed in one of our laboratories (8).

The spectra of the native celluloses, many of which have been reported (2), are shown together with that of the regenerated cellulose I in Fig. 1. The accepted assignments to the different carbons in the anhydroglucose units are as indicated at the top of Fig. 1. The features between 70 and 81 parts per million are assigned to C-2, C-3, and C-5 collectively, because at present there is no basis for individual assignment. The assignments of the resonances due to C-1, C-4, and C-6, however, are firmly established on the basis of comparison with oligosaccharides and model compounds. The structural implications of the resonance profiles of each of these carbons are our central concern.

The regions of the spectrum corresponding to C-4 and C-6 are similar in that in most of the spectra both include a cluster of sharper resonances and a broader upfield wing. Each of the broader wings is associated both with the surfaces of crystalline domains, on the basis of morphological considerations, and with regions of three-dimensional disorder, on the basis of comparisons of the cotton linters spectrum with spectra of a hydrocellulose and an amorphous cellulose. In the case of C-1, it appears that the sharper components overlap the resonance associated with the less ordered domains.

The sharper components of the C-4, C-6, and C-1 resonances possess multiplicities that suggest that they arise from magnetically nonequivalent sites within crystalline domains. The most important feature in Fig. 1 is the pattern of variation of the multiplets, primarily at C-4 but also at C-1 and C-6. These lines differ among the samples; the relative intensities are not constant, and they are not in the ratios of small whole numbers as would be expected if they arose from different sites within a single unit cell. The native celluloses are, therefore, composites of two or more crystalline forms. But the spectral intensities are not consistent with the possibility of three independent crystal forms, each giving rise to a single resonance in the C-1, C-4, and C-6 regions. A model based on two independent crystalline forms remains the simplest plausible proposal. And indeed a decomposition of the spectra on the basis of such a model has been accomplished.

The approximate component spectra of the two forms are illustrated in Fig. 2