High-albedo asteroid 434 Hungaria: Spectrum, composition and genetic connections

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Abstract—New data in the wavelength region of approximately 0.4–2.5 μm have been obtained for asteroid 434 Hungaria. This is the most complete visible to near-infrared spectrum to date for this object. The near-infrared portion of the spectrum (about 0.8–2.5 μm) is smooth, featureless, and agrees well in the overlap region with new visible region data. However, visible region (about 0.45–0.9 μm) data appear to exhibit weak, broad spectral absorption features near 0.5, 0.6–0.7, and 1 μm. If real, the presence of such features would strongly constrain the compositional determination of Hungaria since it has a relatively high albedo of 46%. Most minerals that exhibit similar absorption features, and are commonly found in meteorites, have a much lower albedo. Asteroid 434 Hungaria has been observed more than six times in these overlapping spectral regions, and it is now possible to assess its mineral composition with some confidence. The dominant phase on this asteroid is an iron-free mineral, probably enstatite. Hungaria may contain secondary phases causing subtle, visible-region absorption features. Alternatively, the surface layer(s) of the asteroid may be contaminated by an absorbing species from an external source.

INTRODUCTION

Professor Max Wolf discovered 434 Hungaria in 1898 at the University of Heidelberg, and it was named in remembrance of an astronomical meeting held in Budapest that same year (Schmadel, 1992). When asteroid taxonomic systems were first being developed (e.g., Chapman et al., 1975), they consisted of very few individual classes. These early, broad, taxonomic classes were designated C type for "carbonaceous" and S type for "silicaceous". A third class of asteroids, which fell outside the parameters for C or S types, was called U type for "unclassified". 434 Hungaria originally was categorized as a U type. Later, when wider spectral wavelength coverage and more polarimetric and albedo information was gathered, it became possible to further subdivide the asteroid taxonomy (e.g., Zellner and Gradie, 1976; Morrison, 1977; Bowell et al., 1978). Hungaria was then classified as an E type along with 44 Nysa and 64 Angelina. These objects had significantly higher albedos than most asteroids. The only meteorites that appeared to be analogous to these bright asteroids, the enstatite achondrites (aubrites or E achondrites), contained an essentially iron-free pyroxene, enstatite, as their major silicate component. Hence, the "E" designation was chosen for these high-albedo asteroids.

Chapman and Gaffey (1979) reclassified Hungaria when their new 24-filter spectrum did not match previous data on the asteroid. They stated that the new spectrum of Hungaria bore some similarity to that of 4 Vesta (the original V-type asteroid), but instead labeled Hungaria once again as a U type. As taxonomic classifications evolved (e.g., Tholen, 1984) and more observations were made of Hungaria (e.g., Zellner et al., 1985), it became obvious that it was only the 24-filter spectrum that was at odds with all other spectral data. Spectral observations of Hungaria published subsequently (Sawyer, 1991; Bus, 1999; Kelley and Gaffey, 1999; Carvano et al., 2001) agree with the E-type classification. Therefore, the E-class designation for Hungaria has been firmly reestablished.

Based on a dynamical study of eight asteroids in the Hungaria region, Lemaître (1994) described a "potential new family" with 434 Hungaria as the lowest numbered member of this group. It should be noted that Williams (1989, 1992) defined previously a dynamical Hungaria family. The entire Lemaître (1994) dynamical group is a subset within the Williams list of probable and possible members. More recent dynamical family classification schemes (e.g., Zappalà et al., 1995) do not define a family in this region.
TELESCOPIC SPECTRAL OBSERVATIONS AND DATA REDUCTION

Near-infrared observations of 434 Hungaria were made with a facility instrument mounted on the NASA infrared telescope (IRTF) at Mauna Kea Observatory (MKO) on 1993 October 12 U.T. and again on 1995 May 1 U.T. (Table 1). Reflectance spectra of Hungaria were obtained using two continuously variable filters (CVF) installed in a liquid-helium-cooled dewar (Primo 2) with an indium-antimonide (InSb) detector. Data were measured in 52 channels over the spectral interval of 0.83–2.57 μm with a spectral resolution (Δλ/λ) of ~3% (Short CVF: 2–3% and Long CVF: 2–4%). In this instrumental configuration, spectra were obtained in two wavelength segments (Short CVF: 0.83–1.6 μm, 32 channels, and Long CVF: 1.49–2.57 μm, 20 channels).

Visible-region observations of Hungaria were made with a facility instrument mounted on the University of Hawaii 2.24 m telescope at MKO on 1997 January 14 and 16 U.T. (Table 1). Reflectance spectra of the asteroid were obtained using the wide field grism spectrograph with the Z135 camera and 2.75 x 303 arcsec slit (oriented north–south) in front of a Tektronix 2048 x 2048 charge-coupled device (CCD) mounted in a liquid-nitrogen-cooled dewar. Useable data were measured in ~1400 channels over the spectral interval of 0.4–0.95 μm with a spectral resolution (Δλ/λ) of ~0.1%.

Weather conditions at the summit of Mauna Kea on the night of 1993 October 12 U.T. were clear and calm with only distant, thin cirrus clouds at sunset and sunrise. The circumstances permitted a little more than 10 h of observing under subarcsec seeing conditions. Hardware and software problems as well as occasional light cirrus clouds plagued the night of 1995 May 1 U.T. Despite these difficulties, ~4 h of observing were carried out under ~1 arcsec seeing, and 434 Hungaria was observed in a clear sky. 1997 January 14 and 16 U.T. were very clear, but somewhat windy. Both nights had sustained winds in excess of 20 mph for much of the 10–10.5 h spent observing. During periods of stronger gusts (40–50 mph) it was necessary to observe only in the downwind part of the sky to avoid telescope vibrations. Intermittent, poor weather conditions notwithstanding, very good data were obtained for Hungaria at both telescopes.

Corrections for the instrumental response function and for the difference in atmospheric transmission as a function of wavelength and path lengths were made from comparison observations of calibrated standard stars. Observations of approximately solar-type "local" standard stars were interspersed with observations of the asteroid to determine the atmospheric extinction coefficients directly. A primary local standard, located in the same portion of the sky as 434 Hungaria (Table 2), generally provided the best atmospheric correction and was consequently used in the final data reduction process.

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**Table 1.** Circumstances and aspect data for observations of asteroid 434 Hungaria.

<table>
<thead>
<tr>
<th>Date (2000 coord.)</th>
<th>Universal time</th>
<th>R.A.</th>
<th>Dec.</th>
<th>λ</th>
<th>δ</th>
<th>r (AU)</th>
<th>Δ (AU)</th>
<th>β (°)</th>
<th>Data sets*</th>
</tr>
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<tr>
<td>1993 October 12</td>
<td>10:08–11:19</td>
<td>01h 41m</td>
<td>-10° 32'</td>
<td>160.4</td>
<td>-69.7</td>
<td>1.913</td>
<td>0.943</td>
<td>10.1</td>
<td>10S 4L</td>
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<tr>
<td>1995 May 1</td>
<td>11:09–12:02</td>
<td>13h 30m</td>
<td>+16° 48'</td>
<td>346.5</td>
<td>+76.2</td>
<td>1.932</td>
<td>1.020</td>
<td>17.6</td>
<td>3S 2L</td>
</tr>
<tr>
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<td>08:09–08:52</td>
<td>04h 48m</td>
<td>-13° 47'</td>
<td>211.9</td>
<td>-33.3</td>
<td>2.066</td>
<td>1.344</td>
<td>23.2</td>
<td>6 spectra</td>
</tr>
<tr>
<td>1997 January 16</td>
<td>08:11–09:00</td>
<td>04h 47m</td>
<td>-13° 21'</td>
<td>211.4</td>
<td>-33.3</td>
<td>2.067</td>
<td>1.359</td>
<td>23.5</td>
<td>5 spectra</td>
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</tbody>
</table>

*Number of observations obtained in the short (S) and long (L) wavelength CVF segments (IRTF), or number of CCD spectra (U.H. 2.24 m).

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**Table 2.** Local standard stars observed with 434 Hungaria.

<table>
<thead>
<tr>
<th>Date (U.T.)</th>
<th>Star</th>
<th>Spectral type</th>
<th>Angular separation from asteroid (°)</th>
<th>Type of standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>1993 October 12</td>
<td>SAO128553</td>
<td>G5</td>
<td>3.1</td>
<td>Primary local</td>
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<tr>
<td>1993 October 12</td>
<td>SAO164082</td>
<td>G5</td>
<td>19.4</td>
<td>Secondary local</td>
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<tr>
<td>1995 May 1</td>
<td>SAO99433</td>
<td>F5</td>
<td>4.9</td>
<td>Primary local</td>
</tr>
<tr>
<td>1995 May 1</td>
<td>SAO120107</td>
<td>G5</td>
<td>10.8</td>
<td>Secondary local</td>
</tr>
<tr>
<td>1997 January 14</td>
<td>BS 1431</td>
<td>G5</td>
<td>0.36</td>
<td>Primary local</td>
</tr>
<tr>
<td>1997 January 14</td>
<td>SAO99433</td>
<td>F5</td>
<td>27.1</td>
<td>Secondary local</td>
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<td>1997 January 16</td>
<td>SAO60171</td>
<td>G5</td>
<td>46.7</td>
<td>Secondary local</td>
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<td>1997 January 16</td>
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<td>G5</td>
<td>0.37</td>
<td>Primary local</td>
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<tr>
<td>1997 January 16</td>
<td>SAO120107</td>
<td>G5</td>
<td>21.3</td>
<td>Secondary local</td>
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<tr>
<td>1997 January 16</td>
<td>SAO99433</td>
<td>F5</td>
<td>26.6</td>
<td>Secondary local</td>
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At least one secondary local standard star, which was farther away from the asteroid, was used as a check on the data reduction with the primary local standard. Two Hardorp (1978) type I solar-analog (calibration standard) stars, 16 Cyg B (SAO 31899, HD 186427, HR 7506) and 64 Hyades (SAO 93936, HD 28099), were also observed (Table 3).

For each standard star, extinction coefficients (slopes) and intercepts for each night were computed from the linear least-squares fit to the log of the measured standard star flux vs. airmass for each CVF step or CCD channel. In the SPECR program (spectrum processing routines—a PC-based version of the code of Clark, 1980) used in this data reduction, the set of extinction slopes and intercepts that model the standard star flux vs. airmass is termed a "starpack". Starpacks were calculated for different permutations of the observations of each local and solar-analog standard star on each night (e.g., all observations through the night, the premeridian and postmeridian observations separately, the sets of observations immediately before and after a series of asteroid measurements, including and excluding flux measurements which appeared to be of poor quality, etc.).

Individual asteroid observations were reduced to a series of alternate asteroid/local standard star flux ratios using all of the alternate extinction coefficient determinations (starpacks) derived from the various permutations of the sets of standard star observations. Each asteroid observation was reduced via 10 to 23 starpacks. The various reductions of each asteroid observation were examined to identify the reduction that most completely canceled the telluric water vapor absorption features. (This criterion will not inadvertently cancel out real "water" features in the spectra of asteroids, since the telluric water vapor features are shifted in wavelength relative to the absorption features of ice or hydrated mineral species (S. Gaffey et al., 1993).) This "best" reduction was used in the subsequent analysis. For cases where several equally good reductions were obtained, the reduction that used the largest number of standard star observations was selected. Each local standard star was reduced vs. 16 Cyg B and/or 64 Hyades to obtain solar calibrations. The new, combined visible and near-infrared spectrum of 434 Hungaria is presented in Fig. 1.

![Fig. 1. The combined visible (small, solid symbols) and near-infrared (open symbols) spectra of 434 Hungaria obtained for the present study.](image)

### Table 3. Solar-analog standard stars observed with 434 Hungaria.

<table>
<thead>
<tr>
<th>Date (U.T.)</th>
<th>Star</th>
<th>Spectral type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1993 October 12</td>
<td>16 Cyg B (SAO31899)</td>
<td>G5V</td>
</tr>
<tr>
<td>1995 May 1</td>
<td>16 Cyg B (SAO31899)</td>
<td>G5V</td>
</tr>
<tr>
<td>1993 October 12</td>
<td>64 Hyades (SAO93936)</td>
<td>G8V</td>
</tr>
<tr>
<td>1997 January 14</td>
<td>64 Hyades (SAO93936)</td>
<td>G8V</td>
</tr>
<tr>
<td>1997 January 16</td>
<td>64 Hyades (SAO93936)</td>
<td>G8V</td>
</tr>
</tbody>
</table>

HIGH ALBEDO MINERALS: A PROCESS OF ELIMINATION

There are high-albedo minerals, such as enstatite, forsterite and plagioclase, which are commonly seen in meteorites, and their likelihood as mineral components of 434 Hungaria is discussed below. However, for completeness we have evaluated austerite, borax, colemanite, datolite, gypsum, heulandite, kaolinite, laumontite, melanterite, natrolite, oligoclase, pyrophyllite, quartz, scapolite, talc, ulexite, willemite, zeolites, and more than 50 other high-albedo, rock-forming minerals (Deer et al., 1966; Klein and Hurlbut, 1985; Chesterman and Lowe, 1993) as possible candidates for the composition of 434 Hungaria (Table 4). Even though many of these minerals are extremely unlikely based on petrologic principles, some have been suggested as the primary constituents of E-type asteroids (e.g., Rivkin et al., 1995). Since a range of plausible and implausible high-albedo minerals have been suggested for E-class asteroids, it is important to consider as complete a list of high-albedo minerals as is feasible. In order to assist the petrologists of the asteroid community, it is useful to specify the particular geological, meteoritical and/or mineralogical constraints which are used to eliminate particular high-albedo minerals from consideration as E-class asteroid assemblages.

First, high-pressure phases were eliminated. Since 1 Ceres is commonly thought to represent the large end of the Main Belt asteroid size distribution, a constraint can be placed on the maximum lithostatic pressure reached inside of asteroid parent bodies. Using a typical chondritic density of 3.5 g/cm³, a simple formula can be employed (Hartmann, 1983) to show that the maximum lithostatic pressure even at the center of a Ceres-sized body is only 3 kbar. So any minerals that require formation pressures above 3 kbar were eliminated. This elimination includes some phases normally considered to be the result of high-pressure formation, but are still occasionally seen in meteorites. For example, diamonds are sometimes found in meteorites, and may be in the appropriate albedo range, but their petrogenesis does not permit large (meter to kilometer
<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Mineral group</th>
<th>Possible analog?</th>
<th>Reason for exclusion*</th>
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<td>Austinite</td>
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<td>2, 4</td>
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<td>borate</td>
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<td>2, 4</td>
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<td>Howlite</td>
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<td>2, 4</td>
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<td>borate</td>
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<td>Cerussite</td>
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<td>No</td>
<td>4</td>
</tr>
<tr>
<td>Laumontite</td>
<td>zeolite</td>
<td>No</td>
<td>4</td>
</tr>
<tr>
<td>Mesolite</td>
<td>zeolite</td>
<td>No</td>
<td>4</td>
</tr>
<tr>
<td>Natrolite</td>
<td>zeolite</td>
<td>No</td>
<td>4</td>
</tr>
<tr>
<td>Stilbite</td>
<td>zeolite</td>
<td>No</td>
<td>4</td>
</tr>
</tbody>
</table>

*Exclusion explanations: (1) high-pressure phase; (2) not found in meteorites; (3) only a minor phase in meteorites; (4) spectrum contains hydration features; (5) spectrum contains carbonate features.

scale) accumulations. Some diamonds in meteorites are carbon vapor condensates from presolar, stellar envelopes, while others formed as the result of shock events (Anders and Zinner, 1993; Haggerty, 1999). More fundamentally, it is geologically unlikely that an object with the diameter of Hungary, ~10 km (Tedesco et al., 1989; Tholen, 1999), would consist primarily of diamond. If such concentrations of this mineral exist in meteorite collections, then it is certainly a well-guarded secret! Likewise, any other high-albedo minerals seen only as rare or trace phases (Brearley and Jones, 1998; Mittlefehldt et al., 1998; Rubin, 1997a, b), or not found in meteorites (e.g., goshenite, opal, topaz), were eliminated.

Laboratory spectrometers have been used extensively to study a wide variety of high-albedo minerals (e.g., Clark et al., 1993; Cloutis et al., 2002). It is well documented that even small amounts of water incorporated into the structures of clay minerals causes strong, near-infrared absorption features. Clays in the montmorillonite and kaolinite groups that contain 13–20 wt% water (Kerr et al., 1950) exhibit spectral absorptions (Fig. 2a) of 15–44% near 1.4 and 1.9 µm (cf., S. Gaffey et al., 1993; King and Clark, 1989). The carbonate minerals calcite, magnesite, breunnerite (a ferroan magnesite), and dolomite are observed in CM and CI chondrites. It has been shown that carbonates exhibit CO₂ vibrational absorptions 25–35% deep at 2.3 µm (Fig. 2b) with a series of weaker features between 1.7 and 2.2 µm. Hydrous carbonates may produce 1.4 and 1.9 µm absorption features of 10 and 20%, respectively, with as little as 2–3 wt% water in their structures (Gaffey, 1995). In addition, a weathered sample of the Bishopsville enstatite achondrite (Fig. 2c) contains only a few tenths of a percent of water, yet shows a well-defined, water-of-hydration absorption feature at ~1.9 µm (Gaffey, 1976). With an asteroid as bright as Hungary, absorption features at approximately 1.4 and 1.9 µm due to bound OH or H₂O, if present, would be very obvious, as would a 2.3 µm carbonate feature. As discussed below, these features are not seen in the spectrum of Hungary. So hydrous mineral phases (e.g., clays, zeolites, hydroxides) and carbonates (e.g., cerussite, dolomite, wetherite) were eliminated from the list.

Feldspars are a major component of early partial melts and as such may be found in large quantities in a basaltic crust of an asteroid (e.g., 4 Vesta). Samples of such crustal units, the howardite–eucrite–diogenite group (HED) meteorites for example, are also found in meteorite collections. The igneous evolution and differentiation of an asteroid parent body with an E-chondrite starting composition might reasonably be expected to produce early partial melts resulting in a basaltic crust primarily composed of plagioclase and iron-poor or iron-free pyroxene (Keil, 1989; McCoy et al., 1999). This material would provide a better fit than most other options to the compositional and spectral criteria matching 434 Hungary. In fact, a geologic material of this nature should have been produced as a result of the aubrite parent body thermal evolution. Unfortunately, the basaltic component of the aubrite parent body has not yet been identified in the meteorite or asteroid populations. The basaltic material may have been lost due to collisional erosion, or may have been ejected due to energetic eruptions (Muenow et al., 1992; Wilson and Keil, 1991, 1996).
chondrites is forsterite, but it comprises only a portion (typically ~25% as isolated mineral grains) of the total CM2 assemblage, the remainder being primarily dark, iron-rich phyllosilicate (clay mineral) matrix.

Another mineral that is in the proper albedo range, and is found in large concentrations as the primary silicate phase in meteorites, is the iron-free pyroxene enstatite. In addition, the proportions of enstatite to other phases in E chondrites and the aubrites indicate that differentiation of such parent bodies would likely produce an enstatite-dominated mantle. Recent melting experiments with enstatite chondrites, the likely analogs of aubrite precursor materials, demonstrate that high degrees of partial melting would produce a concentrated enstatite mantle on a thermally evolved parent body (e.g., McCoy et al., 1999). This has been suggested in the past to explain the compositional nature of E-type asteroids (Zellner, 1975; Zellner et al., 1977).

**REFLECTANCE SPECTRUM OF 434 HUNGARIA**

The 52-channel, near-infrared spectrum of 434 Hungaria (Fig. 1) obtained in 1993 and 1995 for the present study is featureless within the channel-to-channel scatter. These scaled near-infrared data agree very well where they overlap with the visible region (CCD) data gathered for this project in 1997 (Fig. 1). Visible-region data collected during previous survey projects (e.g., Zellner et al., 1985; Sawyer, 1991) also compare favorably in the interval of overlap with the new infrared spectrum (Fig. 3).

Figure 4 compares the new visible-region spectrum of 434 Hungaria with data from previous surveys in the region of overlap. The eight-color asteroid survey (ECAS) data (Zellner et al., 1985) are useful to illustrate spectral slope in this case, but lack the spectral resolution to identify subtle absorption features. Burbine et al. (1998) presented an evaluation of a visible-region spectrum for Hungaria that was collected as part of the small Main Belt asteroid spectroscopic survey (SMASS) program (Bus, 1999). They described the spectrum as having an absorption feature from 0.44 to 0.51 μm, an increase in slope from 0.51 to 0.55 μm, a reddish slope from 0.55 to 0.70 μm, and a shallow absorption feature that extended past 0.92 μm. The SMASS spectrum and the 24-filter data (Chapman and Gaffey, 1979) agree very well between 0.4 and 0.8 μm. The two spectra diverge beyond 0.8 μm with the 24-filter data dropping off to a greater degree than the SMASS spectrum at longer wavelengths. The 0.5 μm feature identified by Burbine et al. (1998) appears to be present in the 24-filter data as well.

The visible-region spectrum obtained for the present study and the SMASS data (Bus, 1999) have some similarity (Fig. 4). Both spectra exhibit an apparent absorption feature near 0.5 μm and another extending beyond 0.9 μm, although the latter feature is less prominent in the newer data. The broad, shallow absorption longward of 0.9 μm is not seen in the near-infrared data, and may be due to an imperfect atmospheric correction in
the CCD data. In addition, the sensitivity of detectors used to obtain visible region data tends to drop off in this same region.

The nature of the ultraviolet spectrum of Hungaria, shortward of 0.4 μm, is unknown. It can be shown empirically that some enstatite samples, including certain crystals in aubrites (McCoy, pers. comm.), produce emissions (fluoresce) under an ultraviolet light source. The apparent feature near 0.5 μm may be a component of a fluorescence (emission) feature at shorter wavelengths. However, this has yet to be rigorously tested and quantified.

The present visible region spectrum exhibits one other broad, shallow feature centered near 0.6–0.7 μm. This subtle feature may be seen in the spectrum of Sawyer (1991) as well (Fig. 4). Although the depth of this feature (~1%) is only slightly more than the noise in the same part of the new unsmoothed, unedited spectrum (standard error of the mean on individual points is ~0.5%), and is less than the channel-to-channel scatter (~2% in the 0.6 μm region), its character remains statistically consistent (well over 200 channels exhibit the same behavior) throughout the various reduction permutations designed to remove instrument system noise and atmospheric interference. The same is not true for the apparent features near 0.5 μm and beyond 0.9 μm. These apparent features change dramatically, and even invert depending on the quality of atmospheric correction and standard star calibration. It is highly unlikely that real features in the reflectance spectrum of an asteroid would exhibit such variations with changes in the data reduction procedure. It appears more likely—but not certain—that based on these criteria, the apparent features near 0.5 μm and beyond 0.9 μm are artifacts of the reduction process, artifacts potentially present in other similar datasets. Rather than omitting these wavelength intervals from the new spectrum, we call attention to their still uncertain and possibly spurious nature. So although some investigators have interpreted these features (see below), at present it is not certain that these are real features. Whether the 0.6–0.7 μm feature is a single or composite feature is not clear at this time. In either case, a good explanation for the source of this feature has not been found.

In general, the spectral reflectance of the previous visible-region datasets increases more toward longer wavelengths (often referred to as spectral "reddening") than that of the new visible-region spectrum over the same region (Fig. 4). The only potential exception is the possibly questionable 24-filter data (Chapman and Gaffey, 1979) where the slope is more difficult to define due to relatively large errors. There are a few possible explanations for the slope differences between the various datasets. Differential refraction may alter the slope of a spectrum, but this effect generally reduces the amount of signal at shorter wavelengths and results in a positive increase in slope.

Fig. 3. (a) The eight-color asteroid survey (ECAS) spectrum (Zellner et al., 1985) of 434 Hungaria (solid symbols) plotted with the near-infrared (52-channel) spectrum obtained for the present study (open symbols). (b) The visible region spectrum of 434 Hungaria (small, solid symbols) from Sawyer (1991) combined with the near-infrared spectrum (open symbols) obtained for the present study.

Fig. 4. The visible-region spectrum of 434 Hungaria obtained for the present study (a) is compared with spectral data from previous surveys (b) in the region of overlap (1 = ECAS, Zellner et al., 1985; 2 = Sawyer, 1991; 3 = SMASS, Bus, 1999; 4 = 24-filter, Chapman and Gaffey, 1979).
The use of a wide slit in the telescope instrument configuration can avoid this problem. Also, since the new spectrum of Hungaria is flatter in this region than previous datasets, differential refraction is unlikely an issue in the present case. The slope differences may simply be due to the variety of different standard stars used to calibrate the various data. Alternatively, the slope differences could be the result of real changes across the surface of the asteroid. As discussed below, Hungaria may very well have low-albedo mineral phases or contaminants on its surface. If that is the case, it could result in rotational spectral variations.

**SURFACE COMPOSITION OF 434 HUNGARIA**

So after the process of elimination and analysis of the spectra above, what option(s) remain for the composition of 434 Hungaria? The traditional compositional interpretation (e.g., Zellner, 1975; Zellner et al., 1977) of E-type asteroids in general is that they are analogous to the enstatite chondrites (Fig. 5) and consist primarily of the iron-free pyroxene enstatite. Based on the albedo and present visible to near-infrared spectrum of Hungaria, which is not atypical of E-type asteroid spectra in this region, enstatite seems to be the likely candidate for the dominant silicate phase. However, iron-free enstatite does not exhibit the weak spectral features seen in the spectrum of 434 Hungaria.

Using SMASS data (Bus, 1999), Burbine et al. (1998) interpreted the features near 0.5 and 0.92 μm in their spectrum of Hungaria (and other E-type asteroids) to be due to the presence of troilite on the asteroid's surface. Since troilite is found in both enstatite chondrites and aubrites, this is not an unreasonable interpretation. Cloutis and Gaffey (1994) showed that the spectrum of synthetic troilite exhibits spectral absorptions at similar locations and with similar intensity. However, both Cloutis and Gaffey (1994) and Cloutis and Burbine (1999) demonstrated that natural troilite, found in meteorites derived from asteroids, does not exhibit the same absorption features as synthetic troilite. Spectra of troilite samples from the iron meteorite Mundrabilla also fail to show any absorption features near 0.5 or 0.92 μm (Britt and Pieters, 1990). Based on published work to date, it is not possible to determine currently whether this spectral difference is due to the sensitivity of FeS spectra to small changes in composition or crystal structure, or to some alteration of the meteoritic troilite in the terrestrial environment.

Burbine et al. (2001) recently performed a spectroscopic and petrologic study of enstatite chondrites along with sulfide and metal constituents from these meteorites. They found that olivine (a calcium sulfide mineral) from the Norton County aubrite exhibits visible-region spectral absorption features similar to those seen in E-class asteroids. Unfortunately, their experimental results also showed that to produce features of the same intensity seen in the asteroid spectra required a quantity of olivine more than 40× greater than that found in aubrites.

![Figure 5. Visible to near-infrared spectra for three enstatite achondrites (aubrites), the meteorite class that provides the best analogy to the spectral characteristics and composition of asteroid 434 Hungaria.](image_url)

Additional work needs to be done in this direction before oldhamite can be ruled out or confirmed as the cause of the subtle features in the spectra.

Due to the high albedo of Hungaria, strict constraints can be placed on any proposed surficial components that might cause spectral absorptions. Virtually all high-albedo minerals with strong absorption features have been eliminated above. No evidence of hydrous clays, carbonates or salts was found, as has been suggested for the composition of other E-class asteroids (e.g., Rivkin et al., 1995, 1999). This limits the possibilities to lower albedo constituents. However, in order for Hungaria to have a high albedo, there cannot be a large quantity of darker material on its surface. Clark and Lucey (1984) demonstrated that mixing just 0.03% of a fine-grained, dark material (charcoal) into a high-albedo material (ice) causes a 50% decrease in albedo. The 46% albedo of Hungaria (Tedesco et al., 1989) is somewhat lower than that of some other E-type asteroids (e.g., 44 Nysa = 55%, 214 Aschera = 52%; Tedesco et al., 1992). Therefore, a small amount of a darker, absorbing species on the surface of Hungaria does not seem unreasonable.

The intensity of the 1.9 μm features in the spectra of high-albedo (albedo > 0.4) mineral species as a function of the H₂O and OH contents were determined by S. Gaffey (1988; Fig. 9). Although those samples were carbonate minerals, the general relationship should hold for any high albedo mineral that does not have strong interfering absorptions in this spectral interval. The presence of 1 wt% "water" in the high-albedo surface material of Hungaria should produce a 1.9 μm absorption feature ~50% deep. That is, the reflectance in the center of the feature would be half of the continuum reflectance shortward and longward of 1.9 μm. The band depth would vary depending upon the form(s) of the "water" (e.g., adsorbed H₂O molecules,
fluid H₂O inclusions, structural H₂O, structural OH, etc.) present in the surface material. The error bars in the near-infrared spectrum of Hungary could allow the presence of a weak 1.9 μm feature, but certainly no deeper than 10%, and probably considerably less. Using the relationship from S. Gaffey (1988), an upper limit of 10% for the 1.9 μm feature would place an approximate upper limit of 0.1 wt% on the abundance of "water" in the high-albedo surface material of Hungary.

A more water-rich, low-albedo component (e.g., CM2 or CI1 chondritic contaminants) could be present and potentially contribute to a 3 μm absorption band. However, such a component would have to be relatively abundant to produce a significant 3 μm feature, since its low albedo means that it will contribute a relatively small fraction of the total reflected light. For example, if the surface of Hungary consisted of large areas of enstatite and CI1 chondrite material (albedo = 0.04, 3 μm band depth ~75% (e.g., Calvin and King, 1997)), one can estimate the 3 μm band depth as a function of relative areal coverage and the albedo of enstatite (AEn). Taking the albedo of Hungary as 0.46, then an AEn = 0.60 would limit the CI1 area to ~26% of the surface and produce a 3 μm band depth of ~2%. An AEn = 0.80 would limit the CI1 area to ~45% of the surface and produce a 3 μm band depth of ~3%. Less water-rich, low-albedo meteoritic assemblages (e.g., CM2 chondritic material) would produce a correspondingly weaker 3 μm band. The CI1 and CM2 chondrites do not exhibit 1.4 and 1.9 μm absorption bands (e.g., Gaffey, 1976), so their presence would not introduce such features in the spectrum of a high-albedo asteroid.

As noted above, the intimate mixture of even a small amount of dark material into a high albedo assemblage will substantially reduce the overall albedo. Correspondingly, the presence of a small amount of a dispersed, low-albedo, water-bearing phase will introduce only very weak 3 μm bands and would not be expected to produce 1.4 and 1.9 μm bands in the spectrum of such an asteroid surface.

One possible meteorite analog for the darker material on 434 Hungary is included in the Cumberland Falls aubrite. This meteorite contains coherent, black, chondritic inclusions on the centimeter scale embedded in a high-albedo, enstatite matrix. With the exception of Shallowater, all of the aubrites originate from the same parent body as Cumberland Falls (Keil, 1989), but do not include the same dark, chondritic inclusions. Clearly, at least part of the parent body of these meteorites contained dark-inclusion-bearing material, and part of it did not. If Hungary was reaccreted after the break-up of its parent body, it could very well retain material from more than one lithology. Chondritic material also may have been deposited on or near the surface as a result of impacts that caused local concentrations of darker material. So it is also not unreasonable to suppose that 434 Hungary may have areas with and without dark inclusions similar to those of Cumberland Falls. In fact, the visible-region spectrum of the Cumberland Falls chondritic inclusions, despite a much lower albedo due to the presence of trace amounts of dark inclusion material disseminated in the powder for which the spectrum was measured, is comparable in spectral shape and lack of strong features to that of Hungary (Fig. 6). The spectrum of the dark inclusions exhibits a shallow absorption feature near 0.6-0.7 μm similar to the feature in the same spectral region for Hungary. It is reasonable to conclude that the surface of 434 Hungary is primarily iron-free enstatite, possibly with a small amount of a phase similar to the Cumberland Falls chondritic inclusions.

**THE AUBRITES, 434 HUNGARIA, AND 3103 EGER**

Previously, Gaffey et al. (1992) assembled strong compositional and dynamical evidence which allowed them to conclude that 3103 Eger (designated at the time as 1982 BB) is the likely, near-Earth source of the enstatite aubrites. They suggested that Eger was in turn derived from the Hungary region of the Main Belt, and that it might have been derived from the same parent body as the Hungary family because of the similarity of certain orbital parameters. The orbital inclination of 3103 (20.9°) is in the same range as that of the Hungary family members (Table 5), and its aphelion distance (1.904 AU) is in the middle of the range of semi-major axes for those members (Williams, 1989, 1992, pers. comm.; Lemaitre, 1994). Unfortunately, in 1992 no near-infrared spectrum of 434 Hungary had been published. Likewise, at that time there was no published visible-region spectrum of 3103 Eger. Now both of these asteroids have visible to near-infrared spectra, albeit from different observing programs, which can be compared.

Kelley and Gaffey (1999) showed that within the uncertainties of the individual channel measurements the near-
TABLE 5. Hungaria dynamical asteroid family (Lemaitre, 1994; Williams, 1989, 1992, pers. comm.).

<table>
<thead>
<tr>
<th>Asteroid</th>
<th>Semi-major axis (AU)</th>
<th>Inclination (°)</th>
<th>Eccentricity</th>
<th>Taxonomic type</th>
</tr>
</thead>
<tbody>
<tr>
<td>434 Hungaria</td>
<td>1.945</td>
<td>22.5</td>
<td>0.0738</td>
<td>E</td>
</tr>
<tr>
<td>1103 Sequoia</td>
<td>1.933</td>
<td>17.9</td>
<td>0.0946</td>
<td>E</td>
</tr>
<tr>
<td>1919 Clemence</td>
<td>1.936</td>
<td>19.3</td>
<td>0.0946</td>
<td>X</td>
</tr>
<tr>
<td>1920 Sarmiento</td>
<td>1.930</td>
<td>22.8</td>
<td>0.1057</td>
<td>X</td>
</tr>
<tr>
<td>2048 Dwornik</td>
<td>1.953</td>
<td>23.8</td>
<td>0.0428</td>
<td>E</td>
</tr>
<tr>
<td>2083 Smither</td>
<td>1.872</td>
<td>18.5</td>
<td>0.0510</td>
<td>X</td>
</tr>
<tr>
<td>2491 Tvashtri</td>
<td>1.878</td>
<td>22.9</td>
<td>0.5420</td>
<td>X</td>
</tr>
<tr>
<td>2495 Noviomagnum</td>
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<td>21.1</td>
<td>0.1025</td>
<td>—</td>
</tr>
<tr>
<td>2577 Litva</td>
<td>1.904</td>
<td>22.9</td>
<td>0.1378</td>
<td>EU</td>
</tr>
<tr>
<td>3086 Kalbaugh</td>
<td>1.936</td>
<td>19.0</td>
<td>0.0265</td>
<td>—</td>
</tr>
<tr>
<td>3447 Burckhalter</td>
<td>1.991</td>
<td>20.7</td>
<td>0.0283</td>
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<tr>
<td>3880 Kaiserman</td>
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<td>17.6</td>
<td>0.0825</td>
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<tr>
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<td>0.0570</td>
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</tr>
<tr>
<td>4031 Mueller</td>
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<td>18.9</td>
<td>0.1007</td>
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<tr>
<td>4232 Aparicio</td>
<td>1.936</td>
<td>21.7</td>
<td>0.0834</td>
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</tr>
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</table>

infrared spectra of 434 Hungaria and 3103 Eger match quite well (Fig. 7). In addition, the visible-region spectrum of Eger from Barucci et al. (1998) appears to have absorption features of similar strength at the same locations as those of Hungaria in the present study. However, the Barucci et al. visible spectrum of Eger has a steeper continuum ("redder" slope) than that of Hungaria (Fig. 8). Burbine et al. (1998) also concluded that their visible-region spectra of Hungaria and Eger were very similar.

If the composition of 434 Hungaria is primarily iron-free enstatite, as it appears to be, then it is possible to begin placing constraints on the nature of the Hungaria parent body. The only petrogenetically reasonable way to produce a 10.5 km asteroid made almost entirely of pure Mg-enstatite is through igneous processing inside a larger parent body. A parent body

FIG. 7. The near-infrared (52-channel) spectrum of E-class asteroid 434 Hungaria (present study) compared with that of 3103 Eger (Gaffey et al., 1992). The data are offset in spectral albedo, but when normalized in spectral reflectance they overlap one another across most of the spectral interval.

Fig. 8. Visible region spectrum of 434 Hungaria obtained for the present study compared with 3103 Eger in the same spectral region. The data for Eger were not generally available at the time of this writing (Barucci, pers. comm.). Therefore, the Eger "spectrum" presented here was adapted from that of Barucci et al. (1998) by digitizing points from a hardcopy of the original spectrum at intervals of 0.025 μm. The Hungaria spectrum has been normalized to the digitized Eger spectrum at 0.56 μm to allow a direct comparison of spectral slope and any major absorption features.

with an enstatite chondrite starting composition that underwent a high degree of melting and differentiation would produce a mantle resembling the aerobites (enstatite achondrites) in composition (Keil, 1989; McCoy et al., 1999). The basaltic materials would be removed from the mantle as early partial melts, and could be expelled from the surface by pyroclastic eruptions (Muenow et al., 1992; Wilson and Keil, 1991) or eroded away by subsequent collisional evolution. Provided sufficient melting occurred within the parent planetesimal, denser phases such as FeNi metal and sulfides would migrate away from the mantle to form a core (Taylor, 1992; McCoy et
The enstatite in the aubrites crystallized from a melt at 1580 °C or more, and based on the cooling rates, did so at a depth of 50–100 km (Keil, 1989; Casanova et al., 1993b). Clearly sometime in solar system history many asteroids did reach temperatures high enough to produce melts with liquid/crystal ratios sufficiently large to allow core formation. The iron meteorites alone represent the exposed interiors of between 50 and 100 individual parent bodies that have been disrupted and dispersed (Keil, 2000). Since 434 Hungaria is the largest classified asteroid in its dynamical family (Lemaître, 1994; Williams, 1989, 1992, pers. comm.), its diameter places a conservative minimum on the mantle thickness of its parent body. Using the silicate/(metal + sulfide) ratios of the enstatite chondrites (Watters and Prinz, 1979; Dodd, 1987), and the method of M. Gaffey et al. (1993), it is possible to calculate the minimum size for the parent body core. A metal + sulfide core resulting from the complete differentiation of an enstatite chondrite parent body would be ~60% of the diameter of that body, or in this case 30 km provided 434 Hungaria represents the entire mantle thickness. This is a conservative estimate, and if the mantle were actually thicker than the diameter of Hungary, the core would be proportionately larger. The inner portion of the main asteroid belt, essentially the Hungary region, does not contain any known asteroids of this size or larger. So either the core fragment has been removed from this region, or it has been reduced in size by subsequent collisions. Alternatively, the Hungary parent body may have merely produced a diminutive core. Petrographic and geochemical studies of aubritic meteorites show that despite reaching a very high temperature and undergoing extensive igneous processing, metal and sulfides in the aubrite parent body may not have efficiently segregated into a core (Casanova et al., 1993a,b; McCoy et al., 1999). Certainly some degree of segregation did occur since not all enstatite aubrites are metal-rich. However, the parent body may have produced a core that was smaller than one would expect based on enstatite chondrite phase abundances. A dwarf core and/or core fragments may yet be hidden among the X-type or unclassified aubrites in the Hungary region.

CONCLUSIONS

No geologically sensible, spectrally neutral mineral phase that will maintain a high albedo for an asteroid surface while simultaneously masking strong absorption features has yet been identified. After an extensive process of elimination based on spectral, petrogenesis and meteoritic considerations, it is reasonable to conclude that the high-albedo, E-type asteroid 434 Hungaria is primarily composed of essentially iron-free enstatite. A weak, but consistent, absorption feature near 0.6–0.7 μm in the spectrum of Hungaria may indicate the presence of a small amount of a darker constituent similar to the Cumberland Falls aubrite dark, chondritic inclinations.

So we are left with at least a few possibilities to explain the spectrum of 434 Hungaria. First, the albedo for Hungaria might be in error. In which case the diameter estimate for Hungary may also be wrong. More importantly, this would provide different possibilities for the composition of Hungary. Next, there may be a secondary, lower albedo mineral phase present in the composition of Hungaria that is producing weak spectral absorption features. A very small quantity of a dark mineral could be forcing the albedo of the asteroid beyond that of some of the other, higher albedo E-type asteroids. Finally, the surface of 434 Hungaria may be contaminated by material from outside the asteroid itself, such as the chondritic inclusions seen in the Cumberland Falls meteorite. This too would accommodate the spectral and albedo requirements.

At the present time, the last alternative is preferred as the most likely based on petrogenesis considerations and meteoritic evidence. The case for a genetic connection between 434 Hungaria, 3103 Eger and the aubrites, as suggested by Gaffey et al. (1992), is strengthened by the present study.

FUTURE WORK

Appropriate observational data must be accumulated on other proposed members of this dynamical cluster to permit their compositions to be determined. While it is a useful first cut to classify additional family members (e.g., Carvano et al., 2001), only compositional analyses will permit determination of the genetic reality of this group. Additional observations are being conducted as part of the ongoing Family Asteroid Compositional Evaluation Survey (FACES) project (Kelley, 2001).

The nature of the ultraviolet-visible spectrum of enstatite aubrites and E-class asteroids must be ascertained reliably to test the reality of apparent features near 0.5 and 0.6–0.7 μm. The discrepancy between visible and near-infrared spectra in the 0.9–1.0 μm region must be resolved as well. A detailed rotational, ultraviolet-visible-near-infrared, spectrophotometric study of 434 Hungaria and other E-class asteroids would provide some of the necessary information, and the logistics of such an observational project are being investigated.

The enstatite aubrites have undergone intense geochemical scrutiny and new studies of them appear on a regular basis. By comparison, little spectroscopic work has been done on these meteorites. To either confirm or rule out the Hungary–Eger–aubrite connection, more than just additional spectra are needed. A comprehensive, parallel set of geochemical and spectroscopic analyses of a large suite of aubrite samples are required. Ideally this study would be performed on unweathered, uncontaminated grains. Fortunately, such a program is now underway (McCoy, pers. comm.) and is beginning to produce results (e.g., Burbine et al., 2001). Between the ongoing and planned projects mentioned above, the veracity of the genetic connections between the aubrites and E-type asteroids in near-Earth space and the Hungary region will be rigorously tested in the not-too-distant future.
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REFERENCES


Clay mineral–organic matter relationships in the early solar system

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Abstract—As the solar system formed, it inherited and perpetuated a rich organic chemistry, the molecular products of which are preserved in ancient extraterrestrial objects such as carbonaceous chondrites. These organic-rich meteorites provide a valuable and tangible record of the chemical steps taken towards the origin of life in the early solar system. Chondritic organic matter is present in the inorganic meteorite matrix which, in the CM and CI chondrites, contains evidence of alteration by liquid water on the parent asteroid. An unanswered and fundamental question is to what extent did the organic matter and inorganic products of aqueous alteration interact or display interdependence? We have used an organic labelling technique to reveal that the meteoritic organic matter is strongly associated with clay minerals. This association suggests that clay minerals may have had an important trapping and possibly catalytic role in chemical evolution in the early solar system prior to the origin of life on the early Earth.

INTRODUCTION

The birth of the solar system was preceded and accompanied by a prolific organic chemistry that is evidenced by the presence of organic matter in primitive extraterrestrial objects such as asteroids and comets. The carbonaceous chondrite meteorites are naturally delivered fragments of primitive organic-rich asteroids and that contain a wide variety of extraterrestrial molecules (e.g., Sephton, 2002). These meteorites allow us to study the products of early solar system prebiotic molecular evolution in the laboratory. Organic matter is most abundant in those carbonaceous chondrites that display the greatest amount of inorganic aqueous alteration products. Superficially, this correlation suggests a genetic link between organic material and aqueous alteration and/or its products. The association between organic matter and aqueous alteration is key to the interstellar-parent body hypothesis, where it is suggested that meteoritic organic compounds were initially interstellar organic molecules that underwent hydration by melting cometary ices accreted during parent body formation (Cronin and Chang, 1993).

Minerals have also been linked with the development of complex organic networks (Ponomarev et al., 1982), considered to be the forerunners of biomacromolecules. Understanding the relationships and interdependence of organic and inorganic components is essential for comprehending the processes and mechanisms involved in the evolution of organic material in the early solar system. Despite this, very little work has been carried out to investigate whether a true organic–inorganic relationship exists and, if it does, which inorganic phases play a role.

We have studied four carbonaceous chondrites—Murchison, Orgueil, Ivuna and Tagish Lake—all of which are known to have undergone aqueous alteration on their asteroidal parent bodies. The aqueous event generated a number of oxidized and hydrated mineral phases from more reduced and anhydrous precursors. The hydrated minerals are found within the chondrite matrix together with significant amounts of organic matter. Murchison is a CM2 chondrite that has experienced partial alteration and matrix material surrounds incompletely altered anhydrous precursors. Orgueil and Ivuna are CI1 chondrites that have undergone more extensive aqueous processing and consist entirely of hydrated matrix. The classification of Tagish Lake is still in dispute, but mineralogical evidence indicates that it has been subjected to aqueous alteration at a degree intermediate to type 1 and 2 chondrites (Brown et al., 2000).

In order to verify the existence of a relationship between organic and inorganic chondritic components, we have implemented a novel approach, which utilizes a labelling technique that highlights the location of organic material within whole-rock samples.

SAMPLES AND ANALYTICAL PROCEDURES

To determine the location of organic matter within the meteorites we impregnated samples with osmium tetroxide
(OsO₄) vapor. Dry whole-rock samples of Murchison, Ivuna, Orgueil and Tagish Lake were held within OsO₄ vapor inside a sealed canister for 1 week. Reactions between the organic matter and OsO₄ vapor resulted in the localized incorporation of fine-grained osmium (Os) that is readily detected using analytical scanning electron microscopy (SEM).

Elemental mapping was carried out using a JEOL JSM-840 SEM fitted with an Oxford Instrument's e-XL energy dispersive (EDS) x-ray microanalyser.

To demonstrate that organic-free meteoritic minerals do not give spurious Os incorporation, terrestrial analogue minerals were exposed to OsO₄ vapor for 1 week. Olivine, two feldspars, two pyroxenes, four carbonates, gypsum, magnetite, hematite, montmorillonite, saponite and two serpentines showed no Os-staining, except for traces on organic inclusions within gypsum.

The utility of OsO₄ impregnation to locate organic matter has been illustrated in a wide range of recent and ancient terrestrial sedimentary rocks (Aplin et al., 1992; Bishop et al., 1992; Patience et al., 1990).

**OBSERVATIONS**

Using SEM, Os incorporation within the samples was mapped using the Os-M and Os-L x-ray lines (Fig. 1). Figure 1a displays a backscattered electron (BSE) image of a Murchison chondrule surrounded by a fine-grained accretion rim and matrix. In Murchison, enrichment in Os was observed in the chondrule accretion rims (Fig. 1b,c). These accretion rims have been heavily altered on the meteorite parent body and contain signatures characteristic of clay minerals such as serpentines (Mg, Fe, Si and Ni). There is an apparent decrease in the abundance of organic matter from the hydrated outer edges of the chondrule rims towards the unaltered cores. No evidence of Os incorporation was observed in the interior of the chondrules. Figure 1d displays a BSE image of the matrix-dominated Ivuna meteorite. X-ray mapping and microanalysis of the Os-impregnated surfaces of Ivuna reveal that Os-labelled organic matter is concentrated in the clay-rich matrix (Fig. 1e,f). Furthermore, there are distinct associations between Os and those elements characteristic of clay minerals (Mg, Fe, Si and Ni). Both CI1 chondrites (Ivuna and Orgueil) and Tagish Lake provided identical results.

Other aqueously generated mineral phases in the samples, such as magnetite (Fe, O; Fig. 1e,f), sulphides (Fe, Ni and S; Fig. 1f) and carbonates (Ca and Mg) (Fig. 1c) were also subjected to x-ray mapping but contained no Os-labelled organic matter. Our Os-labelling results were corroborated with spectra taken from these aqueously produced mineral phases, which also show no evidence for the presence of Os. These observations are inconsistent with previous reports of fluorescent organic coatings around magnetite grains in Orgueil (Alpern and Benkheir, 1973). Recent transmission electron microscopy (TEM)-based analyses of Tagish Lake have identified the sites of certain carbon-bearing materials in this meteorite. Matrix sulfides in Tagish Lake appear to be coated by layers of graphitic carbon (Zolensky et al., 2002) and sub-2000 nm carbonaceous globules are present in the phyllosilicate matrix (Nakamura et al., 2001). However, these reports could not be substantiated by our method because the recalcitrant nature of graphite precludes it from being visualized by Os labelling and the carbonaceous globules are too small to be detected by our SEM-based approach.

Therefore, the Os-labelling data indicate that although organic material is linked to aqueous alteration processes that produce several hydrous mineral phases, the only organic–inorganic association of significance is that between the organic matter and the clay minerals.

**DISCUSSION**

**Implications for the Interstellar–Parent Body Hypothesis**

Current theories propose that significant amounts of meteoritic organic matter, or its precursor materials, were synthesized in an interstellar environment. The interstellar heritage of meteoritic organic matter is supported by noticeable enrichments in the heavy stable isotopes of C, N, and H (Cronin and Chang, 1993; Sephton and Gilmour, 2001). Subsequently, organic precursors synthesized in interstellar space were hydrolytically transformed to water-soluble organic compounds by aqueous reactions on the meteorite parent body. The influence that the interstellar and asteroidal environments appears to exert on the final constitution of meteoritic organic matter has led to this model being called the interstellar-parent body hypothesis (Cronin et al., 1993). Our observation that there are no associations between organic matter and aqueously generated inorganic mineral phases, other than with clay minerals, suggests that aqueous processing alone, is not the key mechanism for controlling the organic evolution on the meteorite parent body. Rather, it is the ability of aqueous alteration to generate clay minerals in close proximity to organic-rich fluids that is important.

**Parent Body Processes**

Perhaps the simplest explanation for the clay mineral–organic matter association is that the clay mineral-containing matrix has a higher porosity than the more impermeable anhydrous mineral phases. Channelling of organic-rich solutions through the matrix may have allowed the preferential accumulation of organic matter in conduits within clay–mineral dominated areas.

However, recent advances in theories of how complex organic networks form in terrestrial rocks may provide a more sophisticated explanation. In terrestrial systems, clay minerals have a propensity to adsorb organic molecules (Hedges, 1977) and this property has led to a newly proposed mechanism for the formation of high molecular weight sedimentary organic
matter. The so-called sorptive protection mechanism involves the adsorption of labile organic matter onto mineral surfaces (Collins et al., 1995) and between clay layers (Salmon et al., 2000) followed by their condensation into larger organic networks. It is possible that, during aqueous processing on the carbonaceous chondrite parent bodies, the sorptive protection mechanism was operating, leading to the trapping and modification of organic matter in coeval clay minerals.
In this context, it is interesting to note that while free or solvent-extractable organic matter may make up as much as 30% of the total carbon and nitrogen in carbonaceous chondrites, only a portion is readily extracted by solvents from whole-rock samples. The remainder is released following the removal of their inorganic surroundings by acid demineralization procedures (Becker and Epstein, 1982), a characteristic that is consistent with organic matter being bound within clay layers.

Implications for Nebula Catalytic Synthesis

The lack of an association between organic matter and inorganic phases such as magnetite and sulphides allows the relevance of other proposed theories for the origin of extraterrestrial organic matter to be constrained. Fischer–Tropsch type (FTT) catalysis has often been suggested as a method for the generation of simple organic materials in the solar nebula (Studier et al., 1968). FTT involves the production of organic compounds from CO and H₂ on the surfaces of mineral catalysts. Once produced, these compounds may be thermally processed to achieve an organic distribution similar to that seen in meteorites. Traditionally, Fe- and Ni-rich metals and sulphides have been suggested as possible nebular catalysts for this reaction. If FTT synthesis involving Fe/Ni catalysts were a dominant organic compound-forming mechanism in the early solar system, then the purported mineral catalysts found in carbonaceous chondrites would be coated with organic matter. However, in this study metals and sulphides appear to have no relationship with organic matter. Clay minerals are themselves possible FTT catalyst but appear to have formed on the meteorite parent body and not in the nebula (Bunch and Chang, 1980) although their precursor silicates may have been important nebula catalysts.

Significance for Prebiotic Molecular Evolution

The discovery that meteoritic organic compounds may be trapped and protected within a clay mineral matrix has implications for our understanding of prebiotic molecular evolution in the early solar system (Bernal, 1951). The carbonaceous chondrites contain a wide variety of water-soluble organic compounds (Cronin and Chang, 1993; Sephton, 2002). During aqueous alteration on the meteorite parent body, clay minerals may have trapped and concentrated organic compounds thereby promoting polymerization reactions (Ponomarova et al., 1982). Extrapolating forward from the snapshot of prebiotic molecular evolution recorded in carbonaceous chondrites, the accumulation, protection and consequent polymerization of organic species within a clay–mineral matrix may have facilitated the development and preservation of primitive biopolymers that laid the foundations for early life.

The recognition of clay mineral–organic matter relationships in ancient extraterrestrial samples has a bearing on the possible ubiquity of life in the early solar system. Chondritic material would have been a common component of the inner solar system shortly after its formation. Thus, the biologically useful products of clay mineral–organic matter interactions would have also been widespread, and delivered to planetary surfaces through the accretion of carbonaceous asteroids (Chyba et al., 1990). Life, therefore, may have originated on planets other than the early Earth, if suitable conditions were temporarily available. The most obvious example of which may have been the warm and wet environments of early Mars.

CONCLUSIONS

We have applied a novel Os labelling technique to locate organic material within aqueously altered carbonaceous chondrites, in order to investigate the role of aqueous processing in organic evolution. X-ray mapping of Os-stained surfaces of Murchison (CM2), Ivuna (CI1), Orgueil (C11) and Tagish Lake (CI2?) indicate a strong affiliation between Os-labelled organic matter and hydrous clay minerals. No such relationships were observed between Os-labelled organic matter and any other aqueous mineral phases. Although aqueous alteration has been considered a key process in the accumulation of organic material on the meteorite parent body, we suggest it is the ability of aqueous processes to generate clay minerals that influences the abundance of organic material in carbonaceous chondrites. Clays may act as absorbents and catalysts for the polymerisation of organic interstellar precursor molecules into the complex organic networks found in carbonaceous chondrites. This organic–inorganic link may have provided a means to trap, protect and polymerise biologically useful molecules within the early solar system prior to their delivery to planetary surfaces and possible role in the origin of life.

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REFERENCES


Heterogeneous agglutinitic glass and the fusion of the finest fraction (F³) model

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Abstract—Evidence in favor of the model fusion of the finest fraction (F³) for the origin of lunar agglutinitic glass has been accruing. They include (1) theoretical expectations that shock pulses should engulf and melt smaller grains more efficiently than larger grains, (2) experimental results of impact shock, albeit at lower than presumed hypervelocity impacts of micrometeorites on the lunar regolith, and (3) new analyses confirming previous results that average compositions of agglutinitic glass are biased towards that of the finest fraction of lunar soils from which they had formed. We add another reason in support of the F³ model. Finer grains of lunar soils are also much more abundant. Hence, electrostatic forces associated with the rotating terminator region bring the finest grains that are obviously much lighter than courser grains to the surface of the Moon. This further contributes to the preferential melting of the finest fraction upon micrometeoritic impacts. New backscattered electron imaging shows that agglutinitic glass is inhomogeneous at submicron scale. Composition ranges of agglutinitic glass are extreme and deviate from that of the finest fraction, even by more than an order of magnitude for some components. Additionally, we show how an ilmenite grain upon impact would produce TiO₂-rich agglutinitic glass in complete disregard to the requirements of fusion of the finest fraction. We propose an addition to the F³ model to accommodate these observations (i.e., that micrometeorite impacts indiscriminately melt the immediate target regardless of grain size or grain composition). We, therefore, suggest that (1) agglutinitic glass is the sum of (a) the melt produced by the fusion of the finest fraction of lunar soils and (b) the microvolume of the indiscriminate target, which melts at high-shock pressures from micrometeoritic impacts, and that (2) because of the small volume of the melt and incorporating cold soil grains, the melt quenched so rapidly that it did not mix and homogenize to represent any preferential composition, for example, that of the finest fraction.

INTRODUCTION

Micrometeoritic bombardment is the principal process of space weathering of the lunar regolith. The process produces melt and vapor. The melt bonds soil grains, forms agglutinates, and for convenience is called "agglutinitic melt", which is preserved as agglutinitic glass. The vapor, although extremely important in the context of space weathering, is not the concern of this paper, which is, instead, the melting process vis-à-vis the data gathered in recent years.

Our new nanoscale backscattered electron (BSE) imaging of agglutinitic glass, results obtained by Taylor et al. (2001), and results from modeling impacts on porous targets (Cintala, 1992), amend and enhance our understanding of lunar agglutinates and the agglutination process termed the F³ (fusion of the finest fraction) model (Papke, 1981). Taylor's is a set of micron-scale measurements showing that the proportion of agglutinitic glass (identified chemically) in lunar soils increases with decreasing grain size. Cintala quantifies melt and vapor products from porous targets. Based on these results, our previous work (Basu et al., 1975; McKay and Basu, 1983; Basu and McKay, 1985), and our current work we argue that (1) agglutinitic melts are inherently inhomogeneous; (2) the melts are the sum of an "indiscriminate melt" of a part of the target and preferential melting of the finest fraction in the target; (3) many, if not all, of the homogeneous domains in agglutinitic glass are extremely small volumes (<<10 μm³) of the total melt, which did not mix before quenching; and (4) multiple recycling events remobilize and amalgamate the micromelts into larger multiple domains of inhomogeneous glass.

We use "indiscriminate melting" to imply a melting process that is not controlled by any eutectic, peritectic, or coticetic properties of the target composition; rather, the production of a superheated melt of the volume of the target through which
high-intensity shockwaves travel before attenuation. We do not envisage this melt to have a necessarily single composition. Rather, we expect that compositional domains within the target will initially produce melts of different compositions that do not necessarily mix and homogenize before quenching. For example, feldspar-rich and pyroxene-rich domains within the melting volume will produce melts of feldspar-like and pyroxene-like compositions that may flow alongside collecting, incorporating, and entraining smaller dust grains. "Modal melting" in which the composition of the resultant melt is the same as that of the melted volume of the target, is different from our concept. The F³ model implies modal melting of the finest fraction of lunar soils. Inhomogeneous indiscriminate melting in addition to F³ is the concept that we support with our new data.

RECENT WORK

Modal analysis of lunar and terrestrial material using an electron microprobe has been in practice for some time (e.g., Albee et al., 1973; Chodos et al., 1973; Dymek et al., 1975; Rooney and Basu, 1994). The technique has been recently refined and adapted to conduct modal analyses of lunar soils to determine the proportions of single phases in lunar mare soils (Taylor et al., 1996). Identification of specific phases is dependent on windows of chemical compositions set up by the operator. Once such windows are set up, phase-identification is automatically assigned based on the chemical composition of any pixel of the target as determined by an automated energy or wavelength dispersive x-ray analysis software. Automatic summation of analyzed spots of similar composition quantitates the abundance of each phase in the sample. Presumably, each analyzed spot is submicron in size although the excitation volume under the electron beam may be 3-5μm larger. Thus, relative proportions of phase distributions in lunar soils are determined at least at 2-3μm scales. Taylor et al. (2001) have found, by defining agglutinitic glass chemically, that in any "given soil and with decrease in grain size, the abundances of the agglutinitic glasses always increase" from 45μm to below 10μm (unless specified otherwise the size of a grain is expressed as the size of the sieve opening through which the grain passed). The principle of this method of modal analysis of lunar soils is identical to that of the Gazzi-Dickinson method used for optical modal analysis of terrestrial clastic sediments (Gazzi, 1966; Dickinson, 1970; Gazzi et al., 1973; Ingersoll et al., 1984; Suttner and Basu, 1985; Zuffa, 1985; Rooney and Basu, 1994). The method renders the results independent of the size of soil grains (e.g., Ingersoll et al., 1984; Zuffa, 1985). This means that if the proportion of one or more phases changes in different grain-size fractions of the same material, and especially if the change is systematic, then there must be a systematic addition or removal of the phase from appropriate grain-size fractions.

Cintala et al. (1993) conducted comminution experiments on two terrestrial natural glasses (tephra and obsidian) and found that they are weaker than olivine, pyroxene, and feldspar. Therefore, preferential comminution of agglutinitic glass is a likely process to concentrate agglutinitic glass in finer sizes. Consequently, the new data (Taylor et al., 2001, 2002) are compatible with the results of apparently the only experimental study (Cintala et al., 1993). The data are also compatible with the less likely possibility that more agglutinitic glass is produced in <10μm sizes than in larger sizes. Note that on recycling (i.e., as smaller fragments of previously formed agglutinates are incorporated in newer larger agglutinates) agglutinitic glass is added to larger sizes (McKay et al., 1974). This process acts in the opposite direction of preferential comminution. It is likely that agglutinitic melts form in the region of 10μm, binding clasts including previously formed agglutinates, to form larger agglutinates. The latter, upon comminution, systematically adds to the population of agglutinitic glass in finer fractions.

It is reasonable to accept that hypervelocity impacts of micrometeorites on the lunar regolith produce melts that scavenge nearby grains, congeal rapidly (indigenous microcrystallites are extremely rare in agglutinitic glass), and form agglutinates (McKay et al., 1972). At the point of hypervelocity impact (i.e., at the peak shock stress the target vaporizes); however, it is likely that some of the impacts on the lunar regolith are made by projectiles that do not have sufficient velocity to create significant vapor, but may still produce a melt. Away from the point of impact, shock stress attenuates, melting occurs followed by fracturing of the target at lower shock stresses. Calculations and modeling based on physical properties of matter, as well as some experimental work (Cintala, 1992), show that impacts (e.g., at 15km/s) into the lunar regolith generate 7x as much liquid as vapor. The volume of liquid produced (i.e., the melt volume) may range from 10 to 50x the volume of the projectile depending on the physical properties of the projectile (e.g., diabase or Fe-mehal). Whereas these model-dependent numbers are not absolute for all atmosphere-free planetary bodies at different distances from the asteroid belt (and the Sun), production of significant amounts of impact vapor is a robust result. Part of this impact vapor possibly escapes the gravitational field of the Moon; part may be trapped in vesicles in agglutinitic glass; the rest must condense back on surfaces of exposed lunar material (e.g., Christofferson et al., 1996; Keller and McKay, 1993, 1997). Cintala (1992) additionally shows, as have many others (e.g., Kieffer, 1971, 1975; Schaal et al., 1979), that porous targets melt and vaporize at lower shock pressures than non-porous targets. A corollary: for identical impacts, porous targets (e.g., regolith) would produce more melt (and vapor) than a non-porous large target (e.g., a rock fragment). Porosity in this case has to be understood in terms of the size of the projectile relative to the target. For example, to a 10μm projectile, a collection of loosely packed 10μm grains as target is porous but a target of 10cm rock fragment is non-porous.
CURRENT WORK

Many features of agglutinates are submicron in size. Resolution of optical microscopes with normal lenses stands at ~1 μm at high magnification, which can be improved by a factor of 2 or 3 with oil-immersion lenses under favorable conditions. We have followed up our optical microscopic observations with BSE microscopy and imaging of agglutinates and their interiors at about 5–10 nm resolution. We have examined and collected ~1500 BSE images of the interiors of ~75 agglutinates from 20 soils using a JEOL FEG-scanning electron microscope (SEM) at the Johnson Space Center. Observations and images provide higher resolution than that obtainable with optical microscopes or with older SEMs, which refine and add to our previous observation. Although new results do not lead us to fundamentally revoke our previous inferences, they provide direct evidence for non-F2 melting. We confirm that agglutinative glass, in general, consists of small (<<10 μm) domains of homogeneous entities. Margins of these domains commonly show concentrations of micron-scale clasts, vesicles, and Fe0 globules, which define flow lines (Figs. 1 and 2). Many vesicles and Fe0 globules tend to attach themselves to edges of larger clasts (e.g., around pyroxene in Fig. 1b, ilmenite in Fig. 2b) or larger vesicles (e.g., upper right in Fig. 1b).

DISCUSSION

Agglutinative glass is a preserved product of shock melting by micrometeorite impacts. Recent work indicates that agglutinative glass (defined chemically) is preferentially concentrated in sizes <10 μm (Taylor et al., 2001). Given Cintala's model, one infers that the size of the majority of micrometeorites responsible for producing agglutinates must also be <10 μm. From a study of impact pits on Gemini windows, Zook et al. (1970) estimated that the modal size of micrometeoroids at 1 AU to be ~8 μm. Whereas this is the mode of the numbers of micrometeorites, most of the mass of micrometeorites is carried by those that peak at ~100 μm (Zook et al., 1970; Grun et al., 1985). If so, the major numerical flux of micrometeorites is responsible for producing agglutinative melt on the Moon and the larger micrometeorites may be responsible for producing large glassy objects (See et al., 1983). However, note that a part of the melt produced on impact into soils will jet out in a spray, incorporating dust and then quench in flight. Botryoidal surfaces of most whole agglutinates (Figs. 3.8 and 3.9 in Taylor, 1975) attest to the availability of free space during quenching. Much of the melt may be injected into surrounding subsurface soils to produce clast-rich agglutinates or simply bond soil grains within the regolith. If so, domains of glass preserved in single agglutinates could be only a fraction of the total melt generated per impact. Regardless, the inference from current work is that micrometeoritic impacts produce agglutinative melt in very small quantities accompanied by a significant proportion of vapor.

FIG. 1. Backscattered electron (BSE) images of compositional domains in agglutinates: (a) at least three domains of molten material (medium gray, light gray, and white) in vesicular agglutinative glass; (sample 15221); (b) small (some <1 μm) domains of different glass compositions and partly melted to apparently unmelted mineral clasts, 75081; note the heterogeneity in the distribution of Fe0 globules within the glass.

Compositions of such small domains of melt provide clues to their origin. Electron probe microanalyses of 1–2 μm sized or smaller spots on agglutinative glass range in composition from being feldspar-like to being pyroxene-like (Charette and Adams, 1975; Gibbons et al., 1976; Basu and Bower, 1976; Via and Taylor, 1976; Hu and Taylor, 1977, 1978; Basu and McKay, 1985). Optical and BSE microscopy shows that glass in any agglutinate is commonly comprised of compositional domains (Fig. 1). The domains are commonly <<10 μm in size. Multiple analyses within small domains of glass in single agglutinates are similar to each other; however, the domains differ in composition from each other within a single agglutinate. In fact, the widths of domains analyzed by Basu and McKay (1985)
were of the order of 1 μm; analyses were done on a spot-mode at the highest magnification of an SEM in which the spot was no more than 100 nm in diameter (we note that the excitation volume is larger, perhaps up to a maximum of 10×, than the actual spot size). Quantitative analysis at finer resolution requires transmission electron microscopic (TEM) techniques and much thinner sections.

Indiscriminate Melting

In view of recent results, we consider the initial agglutininitic melt to be intrinsically inhomogeneous (i.e., does not necessarily represent only the finest fraction in the target). In this scenario, indiscriminate melting of a very small target, be it a collection of micron-scale grains or the surface of a single large mineral grain, produces a melt the compositional variability of which is ideally identical to that of the target. If the target is homogeneous, the melt is homogeneous; if the target is inhomogeneous, the melt is inhomogeneous. If there is sufficient turbulence in the melt and if there is sufficient time before quenching, the melt or some of its initial domains may homogenize. If melting is accompanied by differential volatilization or fractional vaporization, the composition of the melt will be rendered different from that of the target (e.g., Nancey et al., 1976; Delano et al., 1981), which may not directly affect the degree of homogeneity but may contribute to turbulence. Whereas impact melts may be produced instantaneously, the melt takes some finite time to quench into glass. During this time, the melt may flow and penetrate between cold soil grains. Clasts of random compositions and random sizes are incorporated into or attached to the melt. These clasts aid in quenching the melt in its heterogeneous state. Many observations show that heterogeneous glass at micron and smaller scale is common in most agglutinates (Figs. 1 and 2). The scenario given above is compatible with such observation. However, many agglutinates contain glassy segments that are larger than 10 μm. This observation needs an explanation.
Recycling

Recycling of lunar soils and soil grains is a well-documented process (e.g., McKay et al., 1974, 1977; Mendell and McKay, 1975; Basu and Meinschein, 1976; Basu, 1990). Not only can fragments of older agglutinates be incorporated into newer agglutinates (Fig. 3), older agglutinitic glass can also be remobilized to mix, but not necessarily homogenize with new melts (Simon et al., 1986b). The process of recycling, thus, not only alters the degree of homogeneity of agglutinitic glass, but also increases the total quantity (and proportion) of glass in agglutinates (Basu, 1977; McKay and Basu, 1983). Our observations indicate that most of the whole agglutinates we see in lunar soils, especially in mature ones, are products of recycling. The glass in these agglutinates is heterogeneous in composition, occurs in regions $\gg 1 \mu m$, and commonly comprises $> 10\%$ of the whole grain.

Fusion of the Finest Fraction (F$^3$)

Papike (1981) proposed the F$^3$ model. The model invokes a mechanism of preferential melting of the finest fraction of lunar soils upon micrometeoritic impact. Walker and Papike (1981) stated that "finer size fractions ... melt more efficiently because of their higher surface area: volume ratios". Their absolute small sizes also contribute to preferential melting. Cintala (pers. comm., 2001) cites three reasons: first, "a given heat pulse would engulf its smaller fragment much more quickly and thoroughly than a larger one", second, "the smaller the particle, the less [is] the distance the shock pulse has to decay", and third, smaller grains being products of comminution have already suffered shock damage that has "depressed [the] heat of fusion for such small particles". Relatively low-temperature pressure experiments appear to indicate that such is the case (Hörz et al., 1984; Simon et al., 1985, 1986b). All contribute to a "greater ease in melting" of the finest fraction. Additionally, the modal size of micrometeorites (about 8–10 $\mu m$; Zook et al., 1970; Zook, 1975) is smaller by orders of magnitude relative to the clasts in the lunar regolith. Large clasts, say >1 cm, would not behave as a porous target even if a layer of submicron dust covers them; however, a collection of smaller grains, say <50 $\mu m$, would behave as a porous target that would likely contribute to preferential melting (Kieffer, 1975; Kieffer et al., 1976; O'Keefe and Ahrens, 1977; Hörz and Schaal, 1981; Cintala, 1992). Lunar soils, (<1 cm fractions of the lunar regolith) are very fine grained with a mean grain size between 40 and 50 $\mu m$ and most are finely skewed (i.e., the median is finer than the mean) (Graf, 1993). This implies that finer grains of lunar soils are more readily available as targets of micrometeoritic impacts than larger grains. Additionally, the Rosswall principle requires that the topmost layer (only a few grains in thickness) of the lunar regolith have an excess of the finest grains (Chayes, 1956; Criswell, 1975). Electrostatic forces that accompany the terminator region of the Moon would also elevate and deposit the finest fraction of lunar soils at the very surface of the Moon (Criswell, 1972, 1975; Rennilson and Criswell, 1974; Criswell and De, 1977). Thus, any micrometeoritic impact on the lunar regolith would melt the finest grains because they are more abundant in general and especially so in the topmost layer of the lunar regolith.

The Prediction—Given the above arguments, "The F$^3$ model predicts that the composition of agglutinate glass will fall on a mixing line between the composition of the <10 $\mu m$ fraction and the bulk composition of the soil in which it formed" (Papike, 1981, p. 806; Papike et al., 1981, p. 412). This implies that the composition of agglutinitic glass in any given soil should vary, with a few exceptions, only within a short range.

The Test—The model was explained and defended in a series of papers (Walker and Papike, 1981; Simon et al., 1981; Laul...
et al., 1981; Papike et al., 1981). Walker and Papike (1981) and several others (see the bibliography in Simon et al., 1986a,b for a complete list) have shown, statistical protestations notwithstanding, that the average composition of agglutinitic glass in several agglutinates in a given soil is biased towards that of the finest fraction relative to the bulk composition of the soil. Our analyses of some 600 submicron spots on several agglutinates bear out the above (Basu and McKay, 1985). Based on finding a depletion of ilmenite in the finest fractions of lunar mare soils and a concomitant depletion of TiO₂ in agglutinitic glass, Taylor et al. (2001, 2002) have also supported the model. Note that it is the average composition of glass in several agglutinates in a soil that shows this bias. If the proportion of agglutinitic glass (defined chemically) increases with decreasing grain size (Taylor et al., 2001), it is only expected that the composition of agglutinitic glass in any size fraction would be biased towards that of finer sizes. Thus, the evidence put up in favor of the F² model is somewhat compromised. For example, if a size fraction (say "x") of a soil were to consist of only agglutinitic glass, the composition of agglutinitic glass in any size fraction in that soil would mimic the composition of size fraction "x". Yet, given the theoretical considerations listed above and experimental studies by Cintala et al. (1993), Hörz et al. (1984) and Simon et al. (1985, 1986b), there should be overwhelming support for F³.

Exceptions—The range of agglutinitic glass composition is extremely large within single agglutinates, agglutinates in any single soil, and in general (see plots in Gibbons et al., 1976; Via and Taylor, 1976; Hu and Taylor, 1977, 1978; Basu and McKay, 1985). For example, Hu and Taylor (1977) find that MgO varies from ~0% to ~12%, FeO from ~0% to ~14%, and Al₂O₃ from ~14% to ~34% in agglutinitic glass in soil 61241. Analyses of agglutinitic glass in four different agglutinates in soil 12033 show different ranges and different averages (Fig. 3 of Basu and McKay, 1985). In the literal sense of the F³ model, the range and averages of agglutinitic glass compositions in different agglutinates in the same soil should be similar, if not identical, to each other and to that of the finest fraction of the
soil. That is not the case. Rather, compositional differences between glass domains in and between single agglutinates are common.

Modification—We propose an addition to the concept of the F model, which we believe brings our understanding of agglutinatic glass closer to reality. We envisage that indiscriminate melting of the target will take place in the zone of peak shock pressure from a hypervelocity impact, irrespective of the composition and the size of the target grain(s). Preferential melting of the finest fraction will occur principally in the volume of the target where shock pressures are lower and for reasons mentioned above, especially because of their preponderance at the lunar surface. Additionally, not all grains will melt fully, especially if the target is orders of magnitude larger than the micrometeorite. The inhomogeneity of the target is likely to persist in the melt that may not have the time to mix completely before quenching. Thus the total melt produced by a micrometeoritic impact is not only that of the finest fraction nor is it a product of modal melting. It is a combination of both indiscriminate melting and preferential melting.

We illustrate the above with an image of an agglutinate in the 90–150 μm fraction of soil 76321 (Fig. 4a,b). We see an ilmenite grain melted in part to produce Fe-Ti-rich agglutinatic glass, the entity of which is distinct in the otherwise Si-Al-rich glass of the agglutinate (Figs. 4c,d are energy dispersive spectra of the two phases). The Fe-Ti-rich glass contains a string of FeO globules and is clearly agglutinatic in origin. The average composition of all agglutinates in this grain may well be on a mixing line between those of the bulk composition soil 76321 and its <10 μm fraction. However, the glass is heterogeneous and some, specifically the one illustrated in Fig. 4, can be easily traced to its primary parent mineral clast. We infer that an impact on an ilmenite grain with a veneer of dust resulted in a total indiscriminate melt of the dust and a part of the ilmenite grain to produce the Fe-Ti-rich agglutinatic glass.

**SUMMARY**

Agglutinatic glass is the quenched melt produced by the impact of micrometeorites on lunar soils. The melt is, on average, a product of the fusion of the finest fraction (F), *a la* the model proposed by Papke (1981). Agglutinatic glass, however, is intrinsically inhomogeneous in composition even at submicron scale. We, therefore, recommend an addition to the F model suggesting that agglutinatic glass is an incomplete mixture of the indiscriminate total melt of the target in the zone of peak pressure and fusion of the finest fraction in the immediate surrounding.

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**REFERENCES**


