# An investigation of the presence and nature of phyllosilicates on the surfaces of C asteroids by an analysis of the continuum slopes in their near-infrared spectra

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Abstract-To understand the nature of C asteroid surfaces, which are often related to phyllosilicates and C chondrites, we report near-infrared spectra for a suite of phyllosilicates, heated to 100-1100 °C in 100 °C intervals, and compare the results for telescope IRTF spectra for 11 C asteroids. As C asteroids have relatively featureless spectra, we focus on "continuum plots" (1.0-1.75 µm slope against 1.8-2.5 µm slope). We compare the continuum plots of the 11 C asteroids and our heated phyllosilicates with literature data for C chondrites. The CI, CR, CK, and CV chondrite meteorites plot in the C asteroid field, whereas CM chondrites plot in a close but discrete field. All are well separated from the large phyllosilicate field. Heating kaolinite and montmorillonite to  $\geq$ 700 °C moves their continua slopes into the C asteroid field, whereas chlorite and serpentine slopes move into the CM chondrite field. Water losses during heating are generally 10-15 wt% and were associated with a 20-70% albedo drop. Our data are consistent with surfaces of the C asteroids consisting of the dehydration products of montmorillonite whereas the CM chondrites are the dehydration products of serpentine and chlorite. The presence of opaque minerals and evaporites does not provide quantitative explanations for the difference in continua slopes of the phyllosilicates and C asteroids. The CM chondrites can also be linked to the C asteroids by heating. We suggest that the CM chondrites are interior samples, and the presence of a 3 µm feature in C asteroid spectra also indicates the excavation of material.

# INTRODUCTION

It has been assumed for decades that the C chondrites are related to the C asteroids, but the details are unclear (Johnson and Fanale 1973; Burbine et al. 2002; Gaffey et al. 2002). The C chondrites are very rare in terrestrial collections, presumably because of their friability, but C asteroids are very abundant in the asteroid belt so it is not clear that the few C chondrites are representative of their asteroid cousins. The reflectance spectra of both C chondrites and C asteroids show only weak absorption features, so compositional fingerprinting is difficult. C chondrites are noted for their high water contents, up to approximately 10 vol%

for CM chondrites and up to approximately 20 vol% for CI chondrites (Wiik 1969; Jarosewich 1990). Maybe one-half of the C asteroids contain evidence for water in the form of a 3  $\mu$ m feature, but measurements are difficult because of absorption by atmospheric water and weak signals. The 3.0  $\mu$ m feature (actually an O-H feature) has been observed on Ceres (Lebofsky 1978), and a number of C asteroids (Lebofsky 1980; Feierberg et al. 1985; Jones et al. 1990). Vilas and Gaffey (1989) found broad features at 0.7  $\mu$ m, with a depth of up to 5%, that matched similarly weak features in CM chondrites, which they ascribed to hydrated iron oxides associated with phyllosilicates. Vilas (1994) observed a correlation between the 0.7  $\mu$ m feature and the 3.0  $\mu$ m feature for a number of C asteroids, and found evidence for water in about half of the 31 asteroids she considered. Fornasier et al. (1999) similarly compared CM chondrites with C asteroids and suggested that 65% of the 34 C asteroids they observed contained the 0.7  $\mu$ m feature.

The meteorite classes most closely resembling the solar photosphere in composition are the CI and CM chondrites. These meteorites are very fine grained and the CM chondrites are inclusion and chondrule-bearing breccias displaying wide variety in the degree of aqueous alteration. Much of the fine-grained matrix in these meteorites is amorphous. Brearley (2006) recently reviewed the topic, describing the CI chondrites as complex with a dark, fine-grained matrix comprised largely of phyllosilicates (serpentine interlayered with saponite) with magnetite, sulfides, carbonates, and sulfates embedded within it (DuFresne and Anders 1962; Böstrom and Fredriksson, 1966; Nagy, 1966; Tomeoka and Buseck 1985). The CM chondrites are fine-grained serpentines and amorphous/nanocrystalline material, nanometer- to micrometer-sized sulfides, tochilinite  $[6Fe_{0.9}S \quad 5(Fe,Mg)(OH)_2]$ , intergrown the Fe<sup>3+</sup>-rich serpentine, and cronstedtite (e.g., Tomeoka and Buseck 1985). These intergrowths have commonly been called "spinach" or "poorly characterized phase." Given the bulk composition of the C chondrites, being high in volatile elements and water, and their apparently low formation temperatures, it seems reasonable that C asteroids could consist primarily of phyllosilicates. In fact, a number of primitive small solar system objects such as interstellar grains, interplanetary dust particles, and micrometeorites, are known to consist in part of phyllosilicates (Zaikowski and Knacke 1975; Rietmeijer 1991; Genge et al. 1997). So why do the spectra of C asteroids look so unlike those of phyllosilicates?

In fact, the spectra of the C chondrite meteorites bear little similarity to those of the phyllosilicates, despite frequent references to phyllosilicates in these meteorites. The spectra of C chondrites are virtually flat and featureless when compared to those of terrestrial phyllosilicates, which contain deep absorption bands attributable to a variety of water-related bonds (e.g., Hiroi et al. 1993). In addition, the albedo of the C chondrites is very low (approximately 0.06), compared phyllosilicates (approximately 0.4). Is it the to abundance of minor phases, particularly the opaque phases, which flattens the spectra while decreasing the albedo? Or is it that silicates in these meteorites are largely dehydrated and the water in the meteorites is mostly associated with other phases, such as the abundant carbonates? Perhaps, it is both the form of the silicates and the abundance of opaque phases that is responsible for the flat, featureless, low albedo spectra of C chondrites. Then, we also have the issue of how the phyllosilicates and the C chondrites relate to the C asteroids. Hiroi and colleagues have shown that laboratory heating experiments on CM chondrites will change the slope of their continua and make them resemble those of the C asteroids (Hiroi et al. 1993; Hiroi and Zolensky 1999), so why is this the case and how do these data relate to phyllosilicates? The purpose of this study is to explore these relationships.

Phyllosilicates are minerals consisting of silicate sheets, the layers being made of tetrahedral and octahedral unit cells. Depending on the number and pattern of these sheets, the phyllosilicate structures are referred to as 1:1, 2:1, and 2:1:1. Compositionally, phyllosilicates can be quite diverse. The octahedral sheets commonly contain Fe(II), Fe(III), Al, or Mg, whereas the tetrahedral sheets contain Si, Al, and sometimes Fe(III). Their layered structure and ionic environment mean that they are capable of adsorbing variable amounts of water that can usually be removed by heating to 500–700 °C (Grim 1968, chapter 9).

It is clear from many images of asteroid surfaces, in fact the surfaces of most airless solar system bodies, that impact, thermal processing, and regolith gardening have been important in determining the present nature of their surfaces. Thus, Hiroi and his coworkers have performed laboratory heating experiments on C chondrites and suggest that CM chondrites heated to 1000 °C provide a reasonable match in the shape of the continuum (including the UV wavelengths) for the spectra of five C asteroids (Hiroi et al. 1993). On the basis of analogous heating studies of five terrestrial phyllosilicates, but heating only to 600 °C, Hiroi and Zolensky (1999) suggested that the phyllosilicate on C asteroid surfaces was saponite (a smectite) but were uncomfortable with this conclusion because this mineral is rare in CM chondrites.

In this study, we report heating experiments—over the temperature range 100-1100 °C-on five terrestrial phyllosilicates, chosen to represent a variety of compositions and structures, and we compare the results with spectra of 11 C asteroids and with C chondrites. We have obtained spectra for meteorites and terrestrial phyllosilicates from online databases, and we have obtained spectra for C asteroids using the NASA Infrared Telescope Facility (IRTF) which are discussed elsewhere (Ostrowski et al. 2010). We place an emphasis on continuum slopes in our work, because we argue that they provide a new quantitative way of comparing spectra and looking for genetic links. There is no reason to assume every C asteroid is represented in our meteorite collections, and in any event the meteorites are probably not representative of their parent

location	Nominal composition	Structure	Typical terrestrial occurrence
Kaolinite, 46E0995, Edgar, Florida	$Al_2Si_2O_5(OH)_4$	1:1	Weathering and decomposition of rocks containing feldspathic minerals (Kruckeberg 2002; Best 2003; Evans 2004)
Serpentine, 46E7263, Eden Mills, Vermont	$Mg_3Si_2O_5(OH)_4$	1:1	Metamorphic and aqueous alteration of forsterite and pyroxene, replacement other magnesium silicates (Lagasse et al. 2008)
Nontronite, 49E5108, Cheney, Washington	Na <sub>0.3</sub> Fe <sup>+3</sup> <sub>2</sub> Si <sub>3</sub> AlO <sub>10</sub> (OH) <sub>2</sub> ·4(H <sub>2</sub> O)	2:1	Weathering of biotite and basalts, precipitation from iron and silicon rich hydrothermal fluids (Bischoff 1972; Eggleton 1975)
Montmorillonite, 46E0438, Panther Creek, Colorado	(Na,Ca) <sub>0.3</sub> (Al,Mg) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>10</sub>	2:1	Aqueous alteration product of volcanic tuff and ash, pegmatite dikes, wall rocks. Alkaline conditions of poor drainage (Early et al. 1953; Deer et al. 1962; Gaines et al. 1997)
Chlorite, 46E1923, Madison Co., North Carolina	$(Mg,Fe^{+2})_5Al(Si_3Al)O_{10}(OH)_8$	2:1:1	Alteration product of mafic minerals such as pyroxenes, amphiboles, and biotite, low-grade metamorphism (Hurlbut and Klein 1985)

Table 1. Phyllosilicates used in this study with relevant information.

<sup>a</sup>Catalog numbers of the Ward's Natural Science.

asteroids. They are a random selection of the tougher ejecta. As we discussed above, meteorites are also highly complex and take some disentangling to understand their history. To improve our understanding, the least we can do is take likely minerals and treat them in the laboratory in a manner likely to reproduce some aspect of their history on an asteroid surface. Hiroi's phyllosilicate heating experiments had an upper temperature limit of 600 °C (Hiroi and Zolensky 1999), which is too low for impact processes that result in craters, glasses, breccias, etc. Our results clearly link certain phyllosilicates to certain asteroids for which meteorite data are consistent but not definitive. Preliminary reports of this project were made at several conferences (Ostrowski et al. 2008a, 2008b; Sears et al. 2008a, 2008b).

# EXPERIMENTAL

The phyllosilicates we used for this work are listed in Table 1, with source, composition, structure, and typical terrestrial occurrence. Samples were sieved to a grain size  $< 63 \mu m$  using a #230 U.S. Standard Testing Sieve attached to a Humboldt MFG Co. shaker. Two gram samples of the phyllosilicates were placed in a ceramic tube and preheated to 100 °C in an oven to release adsorbed water. Samples were then heated to 300, 400, 500, 600, 700, 800, 900 for 24 h and at 1000 and 1100 °C for 6 h. Two-sigma uncertainties on these temperatures throughout the experiment were approximately 1%. Water loss was determined by weight difference. Samples were placed in desiccators for cooling. Most samples were heated and allowed to cool in air, but since some of the samples changed color and albedo, we also performed a series of heating experiments on chlorite in an argon atmosphere flowing at 135 mL min<sup>-1</sup>.

After the heat treatments, many of the samples sintered and caked slightly, and were gently crushed a second time. They were then mounted in holders and their reflectance spectra obtained over the range 0.8-2.5 µm using a Nicolet 6700 FTIR (Thermo Electron Corporation, Madison, WI) in diffuse reflectance mode with an incident and emergence angle of 90°. A flowing atmosphere of dry nitrogen kept the samples dry during spectroscopy, and 150 scans were summed providing a final resolution of  $2 \text{ cm}^{-1}$ . Titanium dioxide was used as a reflectance standard. The phase angle of the phyllosilicate reflectance measurements, 90°, is much less than that used to measure the asteroids, generally 15-50°. Measurements of reflectivity as a function of phase angle for the Allende meteorite, which we assume to be typical of dark carbonaceous chondrites, have shown this effect to be insignificant at these angles (Gradie and Veverka 1982).

We focus on the spectral range from 0.8 to  $2.5 \,\mu\text{m}$  because this is the range of the IRTF and because it is the range of most relevance to mineralogy. Representative spectra are shown in Fig. 1a. We quantify the curves by comparing the continuum slope



Fig. 1. a) Representative spectra for an asteroid (45 Eugenia), meteorite (Orgueil CI chondrite), and a terrestrial phyllosilicate (serpentine), displaced on the vertical scale for clarity. Note the numerous absorption bands in the phyllosilicate and weak to absent bands in the meteorite and asteroid. b) Illustration of way in which we determine "continuum slopes" for these spectra over the two wavelength intervals. For the purposes of determining slopes, the spectra are normalized to 0.875 µm.

between 1.0 and 1.75 µm with the continuum slope between 1.8 and 2.5 µm (Fig. 1b). As the slope depends on the wavelength used for normalization, we normalized all the spectra to 0.875 µm. The difference in the reflectance values at 1.0-1.75 µm was divided by 0.75 and the difference in the reflectance values at 1.8-2.5 µm was divided by 0.70 to obtain the slopes in the two regions. We refer to the graphs of the  $1.0-1.75 \,\mu m$ continuum slope against the 1.8-2.5 µm continuum slope as "continuum plots." Based on multiple measurements of a given sample, we estimate a 5% uncertainty in both the 1.0-1.75 µm continuum slope and the 1.8-2.5 µm continuum slope. Of course, the uncertainty is greater for phyllosilicates with multiple absorption features, but even here we find reproducibility for a given silicate. In fact, these bands do cause scatter in the data, and the reduction of this scatter upon heating is a diagnostic feature of the data and it can be meaningfully compared with the scatter in asteroid and meteorite data.

An approximate estimate of albedo was determined from digital photographs using the Adobe Photoshop software (Adobe Systems, Inc., San Jose, CA). Our "albedo" value refers to the grayness of the sample normalized to the grayness of an adjacent and equal area of white paper. We recognize that this is not a very sophisticated method for determining albedo, lighting conditions, sample preparation, camera response, and even reproducibility of the whiteness of the paper, are not optimum, but the reproducibility and scatter of the data suggest that our albedo values are reasonable to about  $\pm 0.05$ .

# RESULTS

# Spectra of Heated Phyllosilicates

In Fig. 2, we show representative spectra for our heated phyllosilicates. For the sake of simplicity, we do not show all the spectra, but the others can be assumed to be reasonable interpolations of those shown. We see three changes occurring to the spectra as a result of heating that are fairly common to the samples (1) the absorption features at 1.4 and 2.3 µm weaken after heating to 300-400 °C and have almost disappeared after heating to 800-900 °C; (2) the long wavelength slopes (1.8–2.5 µm) go from negative to positive over the temperature range 600-1100 °C; and (3) the reflectance of the samples increases with heating up to about 600-800 °C, and thereafter falls so that the samples heated at 1100 °C are the darkest. These results are in general agreement with those of Hiroi and Zolensky (1999), although these authors limited their heating experiments on phyllosilicates to temperatures ≤600 °C.

Although the samples have the above responses to the heat treatment in common, their behavior is not identical. Kaolinite and montmorillonite show relatively little change in reflectance, whereas for serpentine and nontronite there was a large change. The chlorite sample heated in argon showed greater change in reflectance than the samples heated in air.

# Water Release on Heating Phyllosilicates

Our water release data are shown in Table 2 and Fig. 3. The patterns are fairly similar for the six cases, a 5-10% mass loss after heating to 100 °C, and a major mass loss after heating to 500 °C. The degree of the major mass loss varies from approximately 10% for montmorillonite, to approximately 15% for chlorite, chlorite in Ar and serpentine, kaolinite, and nontronite. These results are very similar to those described in Grim's (1968) textbook (see chapter 9).

#### Albedo Changes on Heating

With the exception of kaolinite all samples of terrestrial phyllosilicate experienced a lowering of albedo after these heating treatments (Fig. 4). The decrease in albedo for montmorillonite was 1.0–0.8, whereas for serpentine and chlorite the decrease was from 0.8–0.9 to 0.5–0.6. The decrease was greatest for nontronite, where a decrease from approximately 0.9 to approximately 0.3 was observed. These values are not as low as observed for C chondrites, but they are certainly significant decreases. The argon atmosphere in the

chlorite sample seems to have made little difference to the albedo change, suggesting that it is not related to an oxidation process.

# DISCUSSION

We are primarily interested in determining the surface composition of the C asteroids and will discuss our data with this in mind. We first note the spectral similarities of the C asteroids and the C chondrites. However, neither the C asteroids nor the C chondrites have spectra resembling the phyllosilicates which are often thought to be the major mineral phase in the C chondrites and are expected to be the major mineral phases in C asteroids. We will first discuss the continuum plots for terrestrial phyllosilicates, and we will compare these with similar data for C asteroids we obtained and discuss the C chondrite data from the literature. We then discuss our data for the heated phyllosilicates samples and the extent to which heated phyllosilicates resemble the C asteroids and can explain their surface compositions. We conclude with a discussion of the C chondrites and remaining challenges in understanding the spectra and surface composition of C asteroids.

# The Value and Limitations of Continuum Slopes and Absorption Features

We are not the first researchers to consider continuum slope in the analysis of asteroid spectra, although we are probably the first to focus on this property. The Bus (1999) taxonomy makes use of a Principal Components Analysis of visible spectra which identifies the continuum slope, absorption at approximately 0.8 µm, and absorption in the UV as important discriminators. This results in three complexes: C. X. and S. and 26 individual taxonomic classes. DeMeo et al. (2009) extended the Bus scheme into the near-IR, continuing to rely strongly on slope. Similarly, Hiroi et al. (1993, 1996b) performed spectral matching between heated phyllosilicates, C chondrites, and C asteroids that are generally featureless so that his method amounts to slope comparison.

Although continuum slopes are implicit in major asteroid spectra studies, some authors remain skeptical about their use. For example, Bus and Binzel (2002, p. 147) stated that, "It (taxonomy) should be based only on spectral (absorption) features, as these are the most reliable indicators of an asteroid's underlying composition," but it is clear that spectra-based taxonomies, and thus asteroid characterization, are heavily dependent on continuum slopes (DeMeo et al. 2009). In fact, most of the C, X, and similar classes



Fig. 2. Representative spectra for five terrestrial phyllosilicates in the unheated states and after heating in air for 6–24 h at the temperatures indicated, and a sample of chlorite heated in an inert atmosphere. a) Kaolinite. b) Serpentine. c) Nontronite. d) Montmorillonite. e) Chlorite. f) Chlorite in argon. At higher temperatures, absorption features disappear, albedo changes (first increasing and then decreasing), and continuum slopes, as defined in Fig. 1b, change, sometimes increasing, sometimes decreasing. The albedo changes in the sample of chlorite heated in an inert atmosphere were greater than the sample heated in air, but otherwise the results are very similar.

described by DeMeo et al. (2009) are defined by slope (see their table 5). Absorption features are generally weak or absent in C asteroids, and even papers ostensibly based on absorption features, such as Hiroi and Zolensky (1999), repeatedly rely on slopes. The  $3 \mu m$  absorption feature has long been used to



Fig. 3. Mass loss as a result of heating the present terrestrial phyllosilicates for 6–24 h. These are not stepwise heating experiments, but individual experiments in which independent samples were heated in the manner indicated. Thus, the apparent mass gain occasionally observed reflects sample heterogeneity and, in the case of the low-temperature step (100 °C), variations in the amount of surface adsorbed water, which depend on the nature of adsorption (number of molecular layers, silicate morphology, etc.). The amount of surface adsorbed water is typically approximately 5% by mass. After heating to temperatures above 500 °C, chemically bound water is lost and this water amounts to 10-15% by mass.

demonstrate the presence of water on asteroid surfaces, although this observation requires careful correction for atmospheric water (Lebofsky 1980; Jones et al. 1990; Lebofsky et al. 1990). Vilas (1994) showed that an absorption feature at 0.7  $\mu$ m, also observed in C chondrites (Vilas and Gaffey 1989), and which correlates with the 3  $\mu$ m feature, could also be used to

1.4 1.2 1 0.8 0.0 9.0 **Albedo** 0.4 Kaolinite ■ Montmorillonite ▲ Nontronite ▼ Serpentine 0.2 Chlorite Chlorite in A 0 200 600 800 400 1000 1200 Heating temperature (°C)

Fig. 4. Albedo plotted against heating temperature for five phyllosilicates. For this purpose, albedo was determined by dividing the grayness of the sample by the grayness of an adjacent sheet of white paper measured under the same conditions and quantified using digital images and Photoshop software. Heating was performed in air, but for chlorite an additional heating series was performed with the samples in an inert atmosphere. Experimental uncertainties can be judged from the scatter and are typically approximately  $\pm 0.05$  (1 $\sigma$ ). There is little or no change for the kaolinite samples, but for montmorillonite and serpentine there is a drop of approximately 20%. For chlorite and nontronite, the decrease in albedo is greater, for chlorite (regardless of the heating atmosphere) decrease is approximately 40% whereas for nontronite the decrease seems to be approximately 60%, ending albedos being approximately 0.3.

deduce the presence of water. The similarity of this feature in C chondrites and C asteroids suggests the presence of Fe-rich phyllosilicates on the asteroids. The strength of the UV absorption correlates with the

Table 2. Water loss on heating five phyllosilicate minerals<sup>a</sup>.

Temperature (°C) <sup>b</sup>	Kaolinite (wt%)	Serpentine (wt%)	Nontronite (wt%)	Montmorillonite (wt%)	Chlorite (wt%)	Chlorite in argon (wt%)
100	0.28	0.99	7.50	8.46	0.50	
300	$0.50^{\circ}$	2.49	2.50	3.54	1.99	1.99
400	4.52	1.49	4.46	5.47	3.00	3.50
500	7.43	1.50	6.50	4.48	5.97	4.48
600	13.50	8.08	5.00	7.00	9.00	9.95
700	14.07	11.94	6.97	7.00	11.44	13.93
800	13.93	11.50	10.95	7.07	12.94	13.93
900	14.57	13.86	13.00	9.45	12.44	12.38
1000	14.50	13.93	12.38	9.50	12.12	12.44
1100	15.00	14.43	10.45	9.00	14.00	13.93

<sup>a</sup>The wt% figures refer to weight loss relative to original weight. Heating times were 24 h for all but 1000 and 1100  $^{\circ}$ C, which were heated for 6 h. Separate samples were used at each temperature, so these are not stepwise heating experiments. There is a 0.4% uncertainty in the weight percent calculations.

<sup>b</sup>The uncertainty in the temperature measurements is  $\pm 1\%$  of the reported value.

°The kaolinite 300 °C sample was actually heated to 350 °C.

strength of the 3  $\mu$ m band and indicates that this too provides an indication of the presence of water on the asteroids (Hiroi et al. 1996b). None of these features were observed in this study, and a maximum absorption intensity of approximately 5% was observed by Vilas and Gaffey (1989) for the 0.7  $\mu$ m band; most of the bands in their work were considerably weaker.

Some of the caution over the use of slopes results from the idea that there are many experimental factors that affect continuum slope, such as placement on the slit, differential refraction, diffraction, and atmospheric variations. The asteroids and solar analog stars in this study were all observed no more than 15° from the meridian to minimize differential refraction effects, which could in principle affect the continuum slope of the reduced spectrum if not carefully minimized. The spectrograph dispersion direction was normal to the slit, so when the target was kept near the meridian the atmospheric dispersion was along the slit. The entire signal along the slit was detected and combined during the reduction of the spectrograms. Automatic guiding, combined with tracking at the predicted rate and in the predicted direction, was utilized to keep the asteroid carefully centered on the slit. The 0.8 arcsec slit was typically slightly overfilled by the diffracted image of the asteroid or star. We corrected for atmospheric variations by using the models of Vacca et al. (2003) at the specific zenith distance of the object during the reduction of each spectrogram. We are convinced that these steps remove significant continuum slope errors in the reduced spectrograms.

Most important, we consider the clustering of slope data and the resolution of various groups of objects (C asteroids and CM chondrites, for instance), and the reproducibility of the slope data when determined by different research groups, as the most meaningful indication that these spectral continuum measurements have merit. These will become apparent in our later discussion. Thus, while we recognize the value of absorption features in studying asteroid spectra, we think that the weakness and scarcity of these peaks and the implicit use of continuum slope in prior work, means that a detailed study of heated phyllosilicate, C asteroid, and C chondrite continuum slopes is worthwhile.

#### **Continuum Slopes of Terrestrial Phyllosilicates**

Figure 5 presents the continuum plot for terrestrial phyllosilicates for spectra in the USGS Digital Spectral Library (Clark et al. 2007). The data are not well clustered, and placement on the plot does not depend on structure or composition. There is also no correlation between the continuum slopes in the two spectral ranges. The large number of broad and intense



Fig. 5. Continuum plots for nine terrestrial phyllosilicates (including the five used in this study), with the structure indicated by symbols, and with the nominal composition indicated by formulae. We see no obvious correlation between position on this plot and structure or composition. A 5% uncertainty exist for both the x and y values for each of the points in the continuum plot.

absorptions due to OH-metal cation interactions (predominantly  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Mg^{2+}$ ,  $Al^{3+}$ ) controls the slope of the continuum at long wavelengths (Grim 1968), while the slope between 1.0 and 1.75 µm is determined by a very broad absorption effect at 1.0-1.2 µm due to charge transfer involving  $Fe^{2+}$  or  $Fe^{3+}$  (Cotton and Wilkinson 1962). It is therefore reasonable that there should be no correlation between the slopes in the two regions or simple correlation with structure or composition. What is important, however, is that all of the terrestrial phyllosilicates that were examined had strong absorptions at long wavelengths and therefore negative slopes in their 1.8–2.5 µm continuum.

# Continuum Slopes of Terrestrial Phyllosilicates Compared with Asteroids

Figure 6 shows the continuum plot for phyllosilicates compared with asteroids. We show the data for the 11 C asteroids obtained recently by our group (Ostrowski et al., unpublished data). The asteroid data plot in a relatively well-constrained field that is discrete from the phyllosilicates. This tight clustering is an indication of the value of continuum slopes in characterizing these objects. The C asteroid field has slightly positive slopes in the 1.8-2.5 µm spectral region and a narrow range of slopes in the 1.0-1.75 µm spectral region (Fig. 6). The tight clustering suggests similarity in the surface compositions of the asteroids and the discreteness of the fields suggests that either phyllosilicates are not important on the surfaces of asteroids or that if they were present at one time, they have undergone considerable alteration.



Fig. 6. Continuum plot for the terrestrial phyllosilicates (reproduced from Fig. 5) compared with similar data for the 11 C asteroids observed by Ostrowski et al. (unpublished data). Bounding ovals are indicated that cover the fields occupied by these two data sets. While the terrestrial phyllosilicates show considerable spread on this plot, the C asteroids occupy a relatively well-defined field with more positive slopes in the 1.8–2.5  $\mu$ m region and they plot to the upper left side of the terrestrial phyllosilicate region. This suggests both the uniformity of the C asteroids and fundamental differences in the mineralogy of the C asteroids and the phyllosilicates. A 5% uncertainty exist for both the *x* and *y* values for each of the points in the continuum plot.

# Continuum Slopes of Terrestrial Phyllosilicates Compared with C Chondrites

Figure 7 compares the terrestrial phyllosilicate field, and the C asteroid field shown in Fig. 6, with data for C chondrites from the papers of Hiroi et al. (1993, 1996b) and Gaffey (2001). The C chondrites plot in a field more highly constrained than the phyllosilicates. but the clustering is not quite as tight as it is for the C asteroids. In fact, while the CM chondrites plot above the phyllosilicates and to the right of the C asteroids, there is overlap between the C asteroids and a variety of C chondrites which have been termed CI/ CM chondrites (Belgica-7904, Yamato-82162 [Y-82162] and Y-86720), CK (Y-693), CV (Allende), CI (Orgueil, two samples, and Ivuna), and CR (Renazzo). Another CI (Alais) plots well outside this field and in the phyllosilicates field. This is a highly diverse group of chondrites that have little in common besides the bulk compositional parameters that define them as C chondrites.

The challenge, therefore, is to understand the relationship between the objects in Figs. 6 and 7 and what processes cause the samples to plot in different

regions of the plot, particularly what discriminates the fields defined above. Options for moving about on the diagram are (i) the addition of minor phases, such as carbon-bearing species, sulfides, and fine sulfide-metal intergrowths and (ii) thermal treatments that in some way replicate the major alteration processes on the surfaces of asteroids. The space environment is essentially an impact environment in which heating and dehydration are the major processes. We will assume that radiation damage, microscale evaporation and condensation, and associated processes, that are collectively considered "space weathering," are relatively minor processes that cannot explain the differences between phyllosilicates and the meteorites and asteroids shown in Fig. 7. We will argue that the alteration processes responsible, and seen, for example, in meteorites, are macroscopic parent-body processes that are best replicated by laboratory heat treatments that can be monitored by spectral changes in the near-IR.

#### **Continuum Slopes of Heated Terrestrial Phyllosilicates**

Our continuum plots of heated terrestrial phyllosilicates are shown in Figs. 8 and 9. All are on



Fig. 7. The continuum plot shown in Fig. 6 with the C asteroid and phyllosilicates fields indicated as ovals, compared with similar data for C chondrites of various classes. The CM chondrites define a relatively well-constrained field within the oval labeled "CM meteorite field" while the other classes of C chondrites plot slightly to the left of the CM chondrite field and mostly in the C asteroid field. The distinction between the phyllosilicates and the C chondrites is marked, even though CM and CI chondrites are known to consist largely of phyllosilicates; the exception is the CI chondrites, do not contain phyllosilicate field. It should be noted that some of the C chondrites, such as the CV and CK chondrites, do not contain phyllosilicates but plot in the C asteroid field. A 5% uncertainty exists for both the x and y values for each of the points in the continuum plot. See Ostrowski et al. (unpublished data) for a more detailed study of C chondrites relationship to all the asteroid types in the C complex.

the same axes to facilitate comparison, the unheated samples indicated by a larger, open symbol and the data for the heated samples labeled with the heating temperature. The fields for terrestrial phyllosilicates, C asteroids, and C chondrites (Fig. 7) are also shown. We will first discuss our serpentine results and compare them with similar plots derived for three serpentines that were the subject of heat treatment by Hiroi and Zolensky (1999) (Fig. 8) and then we will discuss each plot in Fig. 9 in turn.

#### Serpentine

In Fig. 8, we compare the data resulting from our heating experiments with those of Hiroi and Zolensky (1999) to assess the level of reproducibility in these data for a given mineral. We only show our data up to 600 °C for ease of comparison with these authors who terminated their experiments at this point. Our serpentine sample, purchased from Ward's Natural Science (Rochester, NY), was said to have come from Eden Hills, Vermont, while Hiroi and Zolensky (1999) examined three serpentines, antigorite (also from Eden

Hills, and probably the same as our "serpentine"), lizardite (from Cornwall, UK), and clinochrysotile (from Thetford, Quebec). The clinochrysotile and lizardite samples are displaced slightly to the right of the serpentine and antigorite samples and 500 and 600 °C have left the phyllosilicate field, and moved into the CM chondrite and C asteroid fields, respectively. These data indicate that, at least to 600 °C, compositionally and structurally similar phyllosilicates have similar spectra and similar response to these heat treatments, notwithstanding an occasional anomalous point. The agreement between our serpentine and Hiroi and Zolensky's (1999) antigorite samples is particularly good.

Figure 9 shows our data for the present five phyllosilicates over the range 100–1100 °C. We briefly discuss each mineral in turn.

#### Kaolinite

The results for kaolinite start at the bottom of the terrestrial phyllosilicates field and move directly upwards on the plot, leaving the phyllosilicates field at 500 °C



Fig. 8. Continuum plots for unheated and serpentines heated to 600 °C, compared with the phyllosilicate, C asteroid, and CM meteorite fields. a) Serpentine from this study. b) Chlinochrysotile, c) antigorite, and d) lizardite which are various serpentines from the work of Hiroi and Zolensky (1999). The fields for the C asteroids, CM chondrites, and terrestrial phyllosilicates are as indicated in Fig. 7. Open diamond symbols are for unheated samples, filled diamonds are for samples heated to temperatures up to 600 °C. Based on source localities, we suspect our "serpentine" is the same material as Hiroi and Zolensky's antigorite. There is very good agreement between serpentine and antigorite data where the heating to 600 °C does not significantly affect the data on this plot. The lizardite and clinochrysotile samples behave similarly on this plot, remaining in the phyllosilicate field until heating above 400–500 °C at which point they move into the general region of the C asteroid and CM meteorite fields. A 5% uncertainty exists for both the x and y values for each of the points in the continuum plot.

and plotting in the C asteroid field at temperatures above 600 °C, mostly in the left half of the C asteroid field (Fig. 9a). During our heating experiments, kaolinite began to lose its water at 500 °C and had essentially suffered complete water loss by 600 °C (Table 2; Fig. 3). It is the destruction of the OH–cation bonds through the loss of water that moves the data out of the phyllosilicates field and moves them into the C asteroid field. With no Fe<sup>2+</sup> charge transfer bands in the 1.0  $\mu$ m region to be lost during heating, the continuum slope in the 1.0–1.75  $\mu$ m region does not change significantly. We might infer from this evidence that spectra of C asteroids are consistent with their surface being dehydrated kaolinite and that temperatures experienced by the surface were approximately 600 °C or above.

#### Serpentine

With heating, our serpentine result moves along the top of the phyllosilicates field and at 800 °C moves into the CM chondrite field (Fig. 9b). The increase in continuum slope in the 1.0–1.75  $\mu$ m region appears to be due to an increase in absorption over the interval 0.8–1.2  $\mu$ m, and thus is not readily explained by the loss of water and the disruption of metal-OH interactions. Serpentine was one of the phyllosilicates in this study to lose only approximately 12.5% mass during our heating experiments, and most of the water was lost at approximately 500 °C. It is therefore not clear what moved the data to the right, but it is clear that this causes the data to move into the CM field rather than the C asteroid field. Fe oxidation could cause these



Fig. 9. Continuum plots for the present five phyllosilicates. a) Kaolinite, b) serpentine, c) nontronite, d) montmorillonite, e) chlorite, and f) chlorite heated in an argon atmosphere. The fields for the C asteroids, CM chondrites, and terrestrial phyllosilicates are as indicated in Fig. 7. In general, heating to 500–600 °C moves the data on these plots but keeps them within the phyllosilicate field. Again, in general, heating above 600 °C, moves the samples out of the phyllosilicate field and into the C asteroid field (kaolinite and montmorillonite), or the CM chondrite field (serpentine and chlorite), or above the CM chondrite field (nontronite and chlorite in an argon atmosphere). Clearly, heat treatment is a means of moving samples from the phyllosilicates field to the other fields. A 5% uncertainty exists for both the x and y values for each of the points in the continuum plot.

spectral changes, assuming there are small amounts of Fe in our serpentines, but if Fe oxidation were important it is difficult to understand our data for chlorite (see Figs. 9e and 9f).

#### Nontronite

The natural nontronite sample result plots in the bottom-middle of the phyllosilicates field and moves to center right of the field with heating up to 700 °C

(Fig. 9c). Above 700 °C, the samples make a large jump to the right of the CM chondrites field, and move leftwards at 1100 °C. Again, the jump out of the phyllosilicates field coincides with the loss of long wavelength absorption features and the loss of structural water, which begins at 400 °C and is complete by 700 °C. There is no evidence in these data that the surface of the C asteroids consists primarily of nontronite heated by impact.

### Montmorillonite

The montmorillonite trajectory on Fig. 9d is fairly similar to that of kaolinite, essentially showing an upwards movement in which the data leave the terrestrial phyllosilicates field at 600 °C and then enters the C asteroid field and remains there upon further heating. Hiroi and Zolensky (1999) performed heating experiments on saponite (a member of the montmorillonite group) and the data agree well with our results although the earlier data show more scatter and their experiments terminated at 600 °C. Our montmorillonite samples lose the least water in our experiments, only approximately 10% of their original mass, but the water is lost by 600 °C when the data enter the C asteroid field. These data are also consistent with the loss of water participating in the OH-metal absorption bands at approximately 2.4 µm. These results would be consistent with the C asteroids having heated montmorillonite on their surface.

#### Chlorite

The behavior of chlorite is quite different from the previous cases since it starts on the right end of the terrestrial phyllosilicates field, then at approximately 500 °C moves to the upper center of this field, and then moves into the CM chondrite field at 700 °C (Fig. 9e). Hiroi and Zolensky (1999) performed heating experiments on chlorite and the data agree well with our results although their earlier data show more scatter and their experiments terminated at 600 °C. The chlorite in this work loses approximately 15% of its mass when heated to 600 °C also suggesting that these spectral changes are related to loss of metal-OH interactions. We suggest that loss of the OH-cation interactions in the 2.4 µm region causes the leftward trend within the phyllosilicates field and loss of the Fe<sup>2+</sup> charge transfer bands at approximately 1.0-1.2 µm causes the upward trend into the C asteroid field. These data are consistent with the surfaces of the CM chondrites consisting of heated chlorite.

However, we observed that our chlorite sample underwent significant color changes during heating which we thought might reflect atmospheric oxidation of  $Fe^{2+}$ . As oxidation of iron can be seen in the

infrared spectra as a very broad feature between 1.0 and 1.2  $\mu$ m, it would cause the slope in the 1.0–1.75  $\mu$ m region to increase and the data points to move to the right on the continuum plots. In fact, they move to the left inferring that oxidation of Fe is not important in determining these slopes.

# Chlorite in an Argon Atmosphere

We therefore repeated our heating experiments under an inert atmosphere. We found that the behavior of chlorite on this plot was very similar to that of chlorite heated in air, although samples heated above 900-1100 °C plotted further outside the CM chondrite field than the chlorite samples heated in air (Fig. 9f). In other words, the data points move in the opposite direction to that expected if oxidation were affecting the data in Fig. 9e. In short, we do not believe the differences in Figs. 9e and 9f are significant and thus oxidation is not affecting our data.

The decrease of albedo of the heated samples does not reduce to that observed for the C chondrites. In general, this does not affect the continuum slope significantly, because its main effect is on the resolution of weak features. The higher albedo of the samples might allow for weak features at the higher temperatures to still be present and if so this could lower the reflectance of parts of the continuum slope. The effect would be to move affected samples' data points on the continuum plot closer to 0,0 position and into the C asteroid field. This is not expected to be a major factor because it only affects weak features which are not observed when the heated samples start to match that of the C chondrites and C asteroids.

#### **Continuum Slopes of Heated C Chondrites**

Figure 10 shows data from Hiroi et al. (1993, 1996a) for the Murchison CM chondrite and the Ivuna CI chondrite, respectively. Murchison initially plots on the lower limit of the CM chondrite field and remains in this field until heating to 900 and 1000 °C. Similarly, Ivuna is initially at or close to the lower limit of the C asteroid field and remains in the C asteroid field with heating, although the 500 °C point plots close to two CI/CM chondrites (Y-82162 and B-7904, see Fig. 7) at the interface of the C asteroid and CM chondrite field. It is significant that the CI and CM chondrites, with their abundant water do not plot initially with the phyllosilicates. Heat treatments sufficient to dehydrate these samples, and which caused some phyllosilicates to move into the C asteroid and CM fields, do not move CI chondrite data out of their field of origin and only when 900 and 1000 °C are reached do the CM chondrite data move into the asteroid field.



Fig. 10. Continuum plots for a) the CM chondrite Murchison, and b) the CI chondrite Ivuna from work of Hiroi et al. (1993, 1996a), respectively. The fields for the C asteroids, CM chondrites, and terrestrial phyllosilicates are as indicated in Fig. 7. Hiroi et al. (1996a) provided data for two unheated samples of Ivuna, while for Murchison one data point is from Hiroi's work and one is from Gaffey (2001). In the case of Murchison, heating to 800 °C keeps the data in the CM chondrite field, while higher temperatures move the data into the C asteroid field. In the case of Ivuna, the data are essentially unchanged, remaining in the C asteroid field. A 5% uncertainty exists for both the x and y values for each of the points in the continuum plot.

# Relationships between Phyllosilicates, C Asteroids, and C Chondrites

# Predicted Primary C Asteroid Materials

We presume that C asteroid surfaces were predominantly phyllosilicates when they formed. Thermodynamic calculations, often expressed in terms of the "condensation sequence" of solids forming from an initially hot cooling primordial solar nebula, predict that at temperatures low enough for condensed water, the silicates would be predominantly phyllosilicates with minor amounts of organics, hydrated Fe oxides, and Fe sulfides (Grossman and Larimer 1974). In any event, the coexistence of water and silicates on the parent body would soon produce phyllosilicates (Brearley 2006). To a reasonable approximation, this mineral assemblage is similar to that observed in CI and CM chondrites that are widely assumed to be the most "primitive" (i.e., solar-like) meteorites (Brearley 2006). There is an abundance of water in CI and CM (Wiik 1969; Jarosewich 1990), and water features are observed in about half of the C asteroids (Vilas 1994). The CI and CM chondrites often contain phyllosilicates (Barber 1981; Zolensky and McSween 1988; Browning et al. 1996), and there are occasional spectral features in C asteroids attributed to phyllosilicates (Vilas and Gaffey 1989).

#### Asteroid Surface Processes

Superimposed on our expectations based on thermodynamics and CI and CM chondrites, is the effect of long-term exposure to the space environment, and sometimes great impact activity (Clark et al. 2002). The surfaces of all airless bodies in the solar system examined to date are heavily cratered, often to the point of saturation. Spacecraft imagery shows the surface of asteroids to be heavily cratered (Chapman 2002).

Our best data on the nature of surface processes on airless bodies are provided by the lunar samples. Samples returned from the Moon contain abundant evidence for heating (Taylor et al. 1991). Virtually all are breccias, diverse fragments lithified as glass, most of which show evidence for violent shock. Impact melt spherules are common, as are agglutinates formed when melts impacted the surface prior to solidification (Symes et al. 1998). Grains in the regolith have amorphous coatings, due partly to the recondensation of elements evaporated during impact (Keller and McKay 1993).

However, it is to be expected that there are quantitative differences between regolith processes on the Moon and asteroids (McKay et al. 1989). From models based on impact-melts in ordinary chondrites, it is possible for asteroid surfaces to be collisionally heated to just over 1200 °C (Rubin 1995). It seems to us that most of the surface of the asteroids should have been drastically thermally processed, multiple times, mostly from micrometeorite impact and to some of the higher temperatures tested in this study. What is remarkable is the presence of water and hydrated phases that have been detected on the asteroid surfaces. There is also considerable gardening on asteroids, and interior material is constantly brought to the surface. Many of these properties, a consequence of the exposure to the space environment, are referred to as "space weathering," especially for microscale processes (Clark et al. 2002).



Fig. 11. Continuum plot that summarizes the effect of heat treatment on the phyllosilicates in this study. The symbols  $\Delta K$ ,  $\Delta M$ ,  $\Delta S$ ,  $\Delta C$ ,  $\Delta N$ , refer to the locations of samples of kaolinite, montmorillonite, serpentine, chlorite, and nontronite heated above 600 °C. Also shown are the fields for phyllosilicates, C asteroids, and CM chondrites as indicated in Fig. 7. Heating kaolinite and montmorillonite produces samples in the C asteroid field, whereas heating chlorite and serpentine (although originally well separated on this plot) and to some extent montmorillonite produces data in the CM chondrite field. Nontronite does not produce data in the CM or C asteroid fields. We note that various authors have suggested that the CM chondrites consist of serpentine or chlorite, whereas some authors have suggested that the CI chondrites and certain CM chondrites consist of montmorillonite. A 5% uncertainty exists for both the x and y values for each of the points in the continuum plot.

# A Priori Predictions

If these processes were all that was involved, we could relate terrestrial phyllosilicates (the presumed primary phyllosilicates of asteroids) to present asteroid surfaces via Fig. 11. We suggest that it is possible to describe meaningful trajectories-driven by thermal processing-that relate the phyllosilicates to the asteroids and that it might be possible to use these trajectories to make suggestions about the nature of the asteroid surfaces. For instance, the C asteroid field seems to be consistent with thermally altered kaolinite or montmorillonite, while the CM chondrite field could be interpreted as thermally altered serpentine or chlorite. On the basis of these data, there appear to be no asteroids consistent with nontronite surfaces. Meteorites that plot in the C asteroid field, CI chondrites aside, are generally not thought of as predominantly containing phyllosilicates. The major mineralogy of the CR, CV, and CO classes consists of olivines. pyroxenes, feldspars, and occasionally anhydrous refractory inclusions associated with high temperatures (Weisberg et al. 2006).

We have not characterized the mineralogical changes produced by our heat treatments because these are well documented in texts such as Deer et al. (1962) and Grim (1968), and recent work in our laboratory using some of the same phyllosilicates is consistent with observations these (Gavin and Chevrier 2009). Decomposition of the monmorillonite group occurs between 800 and 900 °C and forms spinel, quartz, or cristobolite, depending on initial composition. For the kaolinite group, decomposition occurs between 650 and 800 °C and produces metakaolinite, a highly disordered anhydrous phase, and at higher temperatures 900-1000 °C produces alumina, cristobolite, and mullite, also depending on initial compositions. Some of these phases have not been observed in the C chondrites, because most of the matrix of these meteorites is amorphous. Serpentine forms olivine at 600 °C, and variants of serpentine form olivine at slightly different temperatures. Chlorite similarly decomposes, through stages involving brucite, into olivine. While these minerals can sometimes be detected, especially at higher temperatures and even more so when melting occurs, in

Table 3. Carbon and H<sub>2</sub>O content of C chondrites mentioned in this work, where available.

Meteorite	Class	C (wt%)	H <sub>2</sub> O (wt%)	References
Orgueil	CI	2.80	16.90	Fredriksson and Kerridge (1988)
Alais	CI	3.19	19.45	Wiik (1969)
Ivuna	CI	2.09	18.64	Wiik (1969)
Y-86720	CI/CM		6.40	Ikeda (1992)
B-7904	CI/CM	1.12	2.60	Shimoyama et al. (1987);
				Haramura et al. (1983)
Y-82162	CI/CM		11.95	Ikeda (1992)
Bells	CM			
Cold Bokkeveld	CM	1.30	15.17	Wiik (1969)
Mighei	СМ	2.48	12.85	Wiik (1969)
ALH 83100	CM	1.46	13.38	Jarosewich (1990)
Nogoya	CM	5.20		Bunch and Chang (1980)
Murchison	CM	1.85	10.09	Jarosewich (1990); Fodor et al. (1971)
Renazzo	CR	1.44	5.62	Wiik (1969)
Allende	CV3	0.29	< 0.1	Clarke et al. (1970)
Y-693	СК		0.18	Shima et al. (1973)

general after the release of chemically bound water at 600–800 °C and the collapse of the phyllosilicate structure, they produce an amorphous anhydrous material, and the purpose of this study is to see whether the IR continuum slope is diagnostic of the precursor phyllosilicate. The sort of minerals expected from the decompositions of these phyllosilicates is very similar to the present mineralogy of the CR, CV, and CO chondrites. The CR, CV, and CO chondrites are "primitive" in the sense that they have escaped the large amounts of aqueous alteration characteristic of the CI and CM chondrites, although phyllosilicates have been found in CV and CO chondrites (Rubin 1997).

# CM Chondrites

What is remarkable, given our expectation about the nature of solids produced in the asteroid belt, and our understanding of the nature of the surfaces of asteroids, is that C chondrites with 10-20% water reach the Earth's surface (Table 3). Clearly, the water-rich CI and CM chondrites are samples from the interior of their parent bodies, buried too deep to be affected by surface processes, yet occasionally being capable of being excavated by major impact that would send them on their way, ultimately, to Earth. It is as if the water was introduced subsequent to the regolith dehydration processes (thus the C chondrites do not plot with the terrestrial phyllosilicates) and it is now present in a form other than chemically bound within the phyllosilicate structure. It is clear that aqueous alteration has played a major part in determining the properties of at least some of the C chondrites, notably the CM chondrites (Browning et al. 1996; Brearley 2006), including the formation of opaque phases. There may also be considerable water trapped as water of

Table 4. Hydrates of ionic solids in carbonaceous chondrites<sup>a</sup>.

Hydrate	Formula	Occurrence
Sulfates		
Blodite	Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	CI
Epsomite	MgSO <sub>4</sub> ·7H <sub>2</sub> O	CI
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	CI
Hexahydrite	MgSO <sub>4</sub> ·6H <sub>2</sub> O	CI
Oxalates		
Whewellite	CaC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	CM
3TE	CD 1: (1005)	

<sup>a</sup>From the compilation of Rubin (1997).

crystallization associated with the evaporite minerals in these meteorites (Table 4).

#### Evaporites

Evaporites are abundant in CI chondrites and present in CM chondrites, and sometimes appear as thick macroscopic veins passing through CI chondrites. Water introduced into the asteroid surfaces from the interior of the asteroid would almost certainly have been mineral-rich, and these liquids would have been quickly evaporated to produce crystals with considerable water of crystallization (for instance, MgSO<sub>4</sub>·7H<sub>2</sub>O; DuFresne and Anders 1962). Assuming that the 1.7-2.2 wt% S (Wiik 1969; Jarosewich 1990) in these meteorites is as MgSO<sub>4</sub>·7H<sub>2</sub>O, then 6.7–8.6 wt%, (about half) of the water in these meteorites is in the evaporites and not in the phyllosilicates. There is considerable uncertainty in this calculation, because there are other phases to host sulfur and there are other inorganic solids to host the water, but it is reasonable that much of the water in the CI and CM and meteorites and by implication the C asteroids, is not



Fig. 12. Spectra for serpentine and epsomite, normalized at  $0.875 \ \mu\text{m}$ , with continuum slopes as defined in Fig. 1b superimposed. While both samples show absorptions due to water in various locations in the solid phases, the slopes are complementary and form a trapezium suggesting that a mixture of the two phases would produce a relatively featureless spectrum with a negative slope.

associated with the phyllosilicates. Figure 12 compares the spectra of serpentine and epsomite (MgSO<sub>4</sub>·7H<sub>2</sub>O) and a numerical sum resulting from a 40% epsomite and 60% serpentine mixture. We show this because this is the mixture that produces the most featureless spectrum. We can calculate the expected proportions of these phases in a CI chondrite from the bulk composition of Orgueil and assuming S is distributed between FeS or (Fe,Ni)S and epsomite and Mg is distributed between epsomite and serpentine. The values are 17-27 wt% epsomite in the meteorites and 30-26 wt% serpentine, the range depending on the amount of Ni assumed to be in the sulfide. Thus, our mixture in Fig. 12 is reasonable and we can see that this mixture will cause the loss of several strong absorption features but it still retains a negative slope (Ostrowski et al. 2010). The coexistence of serpentine- and epsomite-like minerals would explain some of the featureless nature of the C chondrite spectra, but not the zero slope of their spectra.

#### Opaques and Albedo

As summarized in the Introduction, the matrix of the C chondrites is complex, fine grained, often amorphous, highly heterogeneous with a mixture of components, and requires TEM to characterize. This is a highly localized technique that only occasionally locates unambiguous characteristics of a readily identifiable phyllosilicate (Table 5). Much of the fine-grained material is a complicated mixture of Fe-rich phyllosilicates produced by aqueous alteration of metal and sulfides, tochilinite,  $Fe^{2+}_{5-6}(Mg,Fe^{2+})_5[(OH)_{10}S_6]$ , montmorillonite, or cronstedite (Barber et al. 1983;

Table 5. Phyllosilicates reported in carbonaceous chondrites<sup>a</sup>.

Silicate	Formula	Occurrence
Chlorite group		
Chamosite	$(Fe^{+2}, Mg, Fe^{+3})_5 Al(Si_3Al)O_{10}(OH, O)_8$	CM, CI
Clinochlore	$(Mg,Fe^{+2})_{5}Al(Si_{3}Al)O_{10}(OH)_{8}$	CM, CV, CO
Serpentine group		
Amesite	Mg <sub>2</sub> Al(SiAl)O <sub>5</sub> (OH) <sub>4</sub>	CM
Antigorite	$Mg_3Si_2O_5(OH)_4$	CM
Berthierine	$(Fe^{+2}, Fe^{+3}, Mg)_{2-3}(Si, Al)_2O_5(OH)_4$	CM
Chrysotile	$Mg_3Si_2O_5(OH)_4$	CM
Cronstedtite	$Fe^{+2}Fe^{+3}(SiFe^{+3})O_{5}(OH)_{4}$	CM
Ferroan Antigorite	$(Mg,Fe,Mn)_3(Si, Al)_2O_5(OH)_4$	CM
Greenalite	$(Fe^{+2}, Fe^{+3})_{2-3}Si_2O_5(OH)_4$	CM
Lizardite	$Mg_3Si_2O_5(OH)_4$	CM
Smectite group		
Saponite	$(Ca,Na)_{0.3}(Mg, Fe^{+2})_3(Si, Al)_4O_{10}(OH)_2 \cdot 4H_2O$	CM, CV
Montmorillonite	(Na,Ca) <sub>0.3</sub> (Al,Mg) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ·nH <sub>2</sub> O	CI, CV
Sobotkite	(K,Ca) <sub>0.3</sub> (Mg <sub>2</sub> Al)(Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>2</sub> ·5H <sub>2</sub> O	CM
Mica		
Clintonite	$Ca(Mg,Al)_3(Al, Si)_4O_{10}(OH,F)_2$	CV
Margarite	$CaAl_2(Si_2Al_2)O_{10}(OH)_2$	CV
Other		
Sodium-phlogopite	$(Na,K)Mg_3(Si_3Al)O_{10}(F,OH)_2$	CV
Talc	$Mg_{3}(Si_{4}O_{10})(OH)_{2}$	СМ

<sup>a</sup>From the compilation of Rubin (1997).

Mackinnon and Zolensky 1984; Tomeoka and Buseck 1985). Thus, there are a great many nano-scale opaque minerals, finely integrated with the silicates, that can have a profound effect on the spectra of these materials.

Several workers have suggested that the effect of these opaque phases on the spectra of phyllosilicates can be investigated by the addition of carbon black, or other opaque phases such as ilmenite (Clark 1983; Cloutis et al. 1990; Milliken and Mustard 2007a). Of course, while meteorites can contain up to 4 wt% C, it is virtually all in the form of organics (mostly an insoluble polymer, but some as volatile colorless compounds), so free carbon is essentially absent, but it is assumed that the carbon black can reproduce most of the physical effects of any finely dispersed opaque phase. However, it remains clear from these studies that the primary effect of opaque phases is to weaken the features and decrease albedo. It is not clear that opaque phases on their own are sufficient to obliterate absorption features (Cloutis et al. 1990), but they can reduce albedo to values approaching those of C asteroids. On the other hand, dehydrated phyllosilicate products can have albedo from one-half to one-third those of their hydrated equivalents (Fig. 4), so if asteroid surfaces contain heat-alteration products this too would contribute to their low albedo.

So what is the effect of the addition of opaque phases on the continuum slopes? The data from two research groups are presented in Fig. 13 (Clark 1983; Milliken and Mustard 2007a). The data from these authors are in good agreement. Coating the surface of the grains with a black material causes the data to move up and left on the diagram (the slope at shorter wavelengths decreasing whereas the slope at longer wavelengths increases) in a fairly linear fashion. Thus, we can argue that the presence of opaque phases could move only nontronite and chlorite into the asteroid fields (Fig. 11): however, these are not reasonable candidates for the phyllosilicates on asteroids. While many asteroid astronomers believe carbon black is a reasonable proxy for the opaque phases on asteroids, it has been suggested that certain opaque phases (maybe organics, metals, and sulfides) might produce slightly reddened spectra, especially if fine grained and well dispersed (Pieters and McFadden 1994). This effect has vet to be explored.

Britt and Pieters (1994) also showed that ordinary chondrites can have flat and relatively featureless reflectance spectra when they have been severely shocked. During such intense events, the metal and sulfide melts are finely disseminated throughout the rock making it appear black. The gas-rich ordinary chondrite regolith breccias are also known for the darkness of their matrix, which encloses normal



Fig. 13. Continuum plot for samples of montmorillonite to which various amounts of carbon black have been added. Also shown are the previously described fields for the C asteroids, CM chondrites, and terrestrial phyllosilicates. The addition of carbon black affects both the short and long wavelengths of the spectra, with a greater effect on the long wavelength region. In fact, as the amount of carbon increases, the data show a negative linear trend in which at short wavelengths the slope decreases from 0.0 to -0.1, whereas the slope at long wavelengths increases -0.6 to -0.1. This is in contrast to the effect of heating on terrestrial phyllosilicates in which the trends on this plot are essentially positive, except for chlorite.

ordinary chondrite clasts. (This is often referred to as the light-dark structure.) The origin of the dark matrix involves shock blackening, and the introduction of C and inert gases by the adsorption of solar wind. It should therefore be borne in mind that some C or X asteroids could be related to such ordinary chondrite material, but they are anhydrous and will not be further discussed here.

# Grain Size Effects

Grain size affects the reflectance spectra of these bodies. As grain size decreases the absolute reflectance of the material increases and the ability to resolve absorption features decreases (Milliken and Mustard 2007b). Figure 14 shows a compilation of the data for Murchison grain size separates. We first note that for samples of similar grain size, the data obtained by the different groups are very similar, suggesting that continuum slopes are reproducible. (These data were obtained by Mike Gaffey, Takahiro Hiroi, and Carle Pieters and are posted at the NASA RELAB Laboratory at Brown University.) Second, the smaller grain size fractions plot within the CM chondrite field and it is only when especially large grain size fractions are involved that the data move into the C asteroid field. This would imply that if the C asteroids are mineralogically similar to CM chondrites, their surfaces



Fig. 14. Continuum plot for samples of the Murchison CM chondrite compared with the previously described fields for C asteroids and CM chondrites. The Murchison bulk data point is from Hiroi et al. (1993, 1996a, 1996b), while the grain size fractions are from spectra acquired by Mike Gaffey, Tahi Hiroi, and Carle Pieters at the NASA RELAB Laboratory at Brown University. While grain size seems to affect the continuum slope at the shorter wavelengths, there is little or no effect on the continuum slope at the longer wavelengths. The finer grain fractions (<63 and <125  $\mu$ m) plot in the CM chondrite field whereas the coarser fraction (<200  $\mu$ m) plot in the C asteroid field.

are covered with coarser grains, a reasonable conclusion if one assumes that the finer material would be lost to space under the microgravity conditions on the asteroid. This of course is only based on infrared spectra. The grain size of the phyllosilicates in the C chondrites is much smaller, on the order of micron to submicron, than the grain size of the phyllosilicates used in this study, but what matters is not the size of individual grains but the size of particles on the surface, which will be grain aggregates. It has been calculated that asteroid 253 Mathide has a surface regolith grain size of  $< 150 \ \mu m$  (Clark et al. 1999), at the more coarse end of the size range in Fig. 14. The meteorite measurements shown in Fig. 7 were not made on sorted powders and were in most respects similar, so we doubt that grain size is relevant in determining the location of meteorites in the continuum plot.

# C Chondrites and C Asteroids

It seems equally clear that there is no evidence that C chondrites of any class came from the surface of their asteroid parent bodies. There are no impact regolith breccias among the C chondrites, although several ordinary chondrites contain small clasts of dehydrated CM-like material suggesting that CM chondrites are abundant impactors (Bischoff et al. 2006). In addition, the regolith diffusion and desorption rates for water—even from phyllosilicates—are fast at near-Earth asteroid surface temperatures (Zent et al. 2001; Bryson et al. 2008; Chevrier et al. 2008). The fact that water features have been observed in spectra from asteroid surfaces suggests that gardening of material from the interior is important. This suggestion is plausible because over the life of the asteroids the vacuum and impact environment would have dehydrated the surface of the asteroids (e.g., Kieffer and Simonds 1980).

We conclude that the surfaces of the C asteroids are serpentine or chlorite (CM field) or montmorillonite or kaolinite (CI chondrites field) that have been dehydrated by heating above approximately 600 °C. It is clear that the C chondrites we now observe have never been heated above 800 °C because they are waterrich. However, as we argued earlier, this implies aqueous alteration as a secondary process. In other words, we argue that (1) surface dehydration processes moved the data from the terrestrial phyllosilicates field and into the CM chondrites field, whereupon (2) the meteorites were buried and water was introduced as a secondary process. Finally, (3) major impact excavated this material and sent it to Earth.

#### Implications for Asteroid History

Table 1 includes a summary of the environments in which these phyllosilicates are found on Earth. Of course, conditions in the early solar system and on an asteroid are very different from these terrestrial environments, but the chemical constraints will be common to both bodies; i.e., whether on Earth or on asteroids, the right bulk compositions must be present and not all phyllosilicates can be produced from chondritic precursors. Serpentine and chlorite are metamorphic and aqueous alteration products of mafic minerals, the mafic minerals being predicted by cosmic abundances and found in ordinary chondrites. They are therefore reasonable phyllosilicates to be found in meteorites and on asteroids. Nontronite and montmorillonite are aqueous alteration products of basaltic materials, expected for differentiated bodies, such as V asteroids. Kaolinite is an aqueous alteration product of feldspar, which-while found in ordinary chondrites at the 5% level-again would be expected to be a major component only in differentiated bodies like the lunar uplands. In summary, the trajectories and the associations suggested in Fig. 11 are reasonable, excluding kaolinite, nontronite, and possibly montmorillonite although it has been observed by TEM studies.

#### CONCLUSIONS

We have obtained reflectance spectra of 11 C asteroids using NASA's IRTF and conducted heating

experiments on a suite of terrestrial phyllosilicates. Further, as C asteroid and C chondrite spectra are essentially featureless, it is appropriate to discuss their spectra in terms of "continuum plots," plots of the continuum between 1.0 and 1.75 μm against the continuum between 1.8 and 2.5 µm. The use of continuum slopes is implicit in existing asteroid taxonomies (Bus and Binzel 2002) and in several studies that interpret asteroid spectra by spectrum matching (e.g., Hiroi et al. 1993). We acknowledge that the continua of spectra are affected by a number of instrumental factors, but argue these are minor. We point out that the existence of discrete and well-defined clusters of C asteroids and C meteorites on the continuum plot and the reproducibility of measurements on the Murchison CM chondrite suggest that this method of spectral characterization is meaningful.

In confirmation of earlier studies (Hiroi and Zolensky 1999), we have found that heating five phyllosilicates of diverse composition and structure causes features in their IR to weaken and disappear and, with one exception, their albedo to decrease by as much as 70%. These responses are associated with water loss and mineralogical changes.

Terrestrial phyllosilicates of a variety of structures and compositions have a wide range of continuum slopes and there is no systematic relationship between these parameters and location in the continuum plot. However, they are discrete from the C asteroids and C meteorites because of the large negative slopes at long wavelengths reflecting the presence of considerable structural water.

The C chondrites of CI, CV, CK, and CR classes plot in a discrete field on the continuum plot that overlaps the C asteroid field. The CM chondrites also plot in a tight, discrete field, well separated from the terrestrial phyllosilicates, but also discrete from the C asteroid/C chondrite field. A group of meteorites identified as CI/CM chondrites plot on the interface between the C chondrite and the CM chondrite fields.

Heat treatments on five terrestrial phyllosilicates (also chosen to bracket compositions and structures of meteorites) cause the positions of the samples to move on the continuum plot. Heating to temperatures below 700 °C causes the samples to move within the terrestrial phyllosilicate field. Heating to temperatures above 700 °C moves montmorillonite and kaolinite into the region occupied by the C asteroids and C chondrites, while heating serpentine and chlorite >700 °C moves their data into the CM chondrite field. Heating nontronite >700 °C moves the data away from the C asteroid/C chondrite and CM chondrite fields. We observed that the chemically bound water is lost between 500 and 700 °C and undoubtedly it is the loss of this water and collapse of the phyllosilicate structure that explains the spectral changes we observe. The data are consistent with the surfaces of the C asteroids being composed of dehydrated phyllosilicates, serpentine or montmorillonite. These phyllosilicates have been observed in C chondrites.

The data are also consistent with CM chondrites containing heated serpentine and chlorite, and again these minerals have been reported in CM chondrites. Literature data show that CM chondrites can be moved into the C asteroid field on the continuum plot by heating > 800 °C (Hiroi et al. 1993, 1996a, 1996b). CM chondrites are also water-rich suggesting that these meteorites were excavated from the interior of the asteroid since exposure for prolonged times on the surface would have caused them to become dehydrated. The presence of 3 µm absorption features on many C asteroids infers that excavation of interior material occurs.

Our data provide insights into the nature of asteroid surfaces and the relationship between the C asteroids and phyllosilicates. Dehydration of the clay minerals studied causes the albedo to decrease to values almost as low as observed for the C asteroids, the presence of opaques would lower the albedo further and the presence of hydrated ionic solids would help remove absorption bands, although it does not affect slope. In summary, while we think opaques and hydrated ionic solids play a part in explaining the spectra of asteroids, most of their properties can be understood in terms of the dehydrated phyllosilicates, montmorillinote and kaolinite.

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