UV-VIS-NIR ABSORPTION FEATURES OF HEATED PHYLLOSILICATES AS REMOTE-SENSING CLUES OF THERMAL HISTORIES OF PRIMITIVE ASTEROIDS

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Abstract: Powder samples of five kinds of phyllosilicates (antigorite, lizardite, clinochrysotile, chlorite, and saponite) have been heated in vacuum at 200, 300, 400, 500, and 600°C, and their UV-Vis-NIR reflectance spectra have been measured to test the hypothesis that the empirical correlation between the UV and 3-μm absorption strengths of primitive asteroids and CI/CM chondrites are due to the presence of phyllosilicates (T. Hiroi *et al.*, Meteorit. Planet. Sci., **31**, 321, 1996). The chlorite sample showed virtually no change in absorption strengths. Only the saponite sample showed a clear positive correlation between the UV and 3-μm absorption strengths, whose reason being yet to be studied. Heating experiments with coexisting carbon (graphite rod) at 600°C have given no systematic trend. Although an apparent conclusion would be that saponite is the cause of the correlation between the UV and 3-μm absorption strengths, it may not be true because saponite is not as abundant as serpentines in CM chondrites (M.E. Zolensky *et al.*, Geochim. Cosmochim. Acta, **57**, 3123, 1993).

1. Introduction

The C, G, B, and F asteroids have been generally believed to be similar to carbonaceous chondrites because their reflectance spectra are mostly dark and featureless, and thus they are often called primitive asteroids. As one of the first attempts to confirm such an idea, reflectance spectra of some of the primitive asteroids were shown to have similar absorption bands to some carbonaceous chondrites, especially CMs (Vilas and Gaffey, 1989). Later, varying degrees of thermal metamorphism of primitive asteroids were suggested based on their UV absorption strengths and overall spectral profiles (Hiroi *et al.*, 1993, 1994), and later based on their 0.7 and 3 μm band strengths (Hiroi *et al.*, 1996) in our previous studies comparing reflectance spectra of primitive asteroids and the CI and CM chondrites. Especially, a positive correlation between the UV and 3-μm absorption strengths noted by Feierberg *et al.* (1985) was confirmed for the 20 C, G, B, and F asteroids and 23 CI/CM chondrites including heated ones (Hiroi *et al.*, 1996). Because Fe (both Fe^{2+} and Fe^{3+}) and OH in phyllosilicates are believed to be mainly responsible for the UV, 0.7-μm, and 3-μm absorption features, the cause of such a correlation was assumed to be the presence of phyllosilicates. In this paper, the changes in those absorption strengths due to the heating process are examined in order to test the above assumption and to help detecting

evidence of heating through remote sensing.

2. Sample Description

Samples of antigorite from Eden Mills, VT, U.S.A., lizardite from Cornwall, England, clinochrysotile from Thetford, Quebec, Canada, chlorite from Calaveris County, CA, U.S.A., and saponite from unknown location were obtained for this research.

Chemical compositions of the above phyllosilicate samples were measured using a Cameca SX100 electron microprobe with natural mineral standards. The results are listed in Table 1.

Table 1.   Chemical compositions of unheated phyllosilicate samples.

Wt% (Average of 3)	Na$_2$O	K$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	CaO	TiO$_2$	Cr$_2$O$_3$	MnO	FeO	Total
Antigorite	0.00	0.01	40.77	0.58	45.88	0.02	0.01	0.06	0.03	1.35	88.70
Lizardite	0.01	0.01	33.97	1.94	43.13	0.10	0.05	0.22	0.12	5.20	84.75
Clinochrysotile	0.00	0.00	39.62	0.36	44.17	0.01	0.00	0.00	0.08	1.53	85.79
Chlorite	0.00	0.00	29.60	18.40	31.20	0.01	0.07	0.02	0.09	7.72	87.13
Saponite	0.09	0.03	22.81	4.43	49.29	0.36	0.02	0.01	0.02	0.69	77.76

3. Heating Experiments

Each of the antigorite, lizardite, clinochrysotile, chlorite, and saponite samples was separated into five fractions for the heating experiments at 200, 300, 400, 500, and 600°C. The pyrex tubes for the heating experiments were pre-cleaned, and the tubes for 300, 400, 500, and 600°C were preheated at 200, 300, 400, and 450°C for one hour, respectively, during which all the mineral samples were evacuated. The pre-heating was done to minimize oxidative effects of evolved volatiles. All tubes were sealed under vacuum and were heated to their final temperature for one week. Despite these precautions, some considerable water was noted with chrysotile at 500°C, and lizardite and antigorite at 600°C. In addition, the saponite 600°C tube gave off a sulfur oxide smell upon opening. Heating experiments at 600°C except the saponite sample were also done with a coexisting graphite rod in order to simulate the heating condition of carbonaceous chondrites where carbon particles coexist. There was not enough saponite sample to perform this experiment.

4. X-ray Diffraction Measurements

We performed X-ray powder diffractometry on all unheated minerals, being careful to chop up the samples (with a razor) to minimize turbostratic effects (Fig. 1). This work verified the identity of all minerals based on the standard minerals X-ray diffraction patters provided by the Joint Committee for Powder Diffraction Standards. The only unusual result was that the lizardite contains a minor amount of the amphibole actinolite, which should not significantly affect the results of this study.
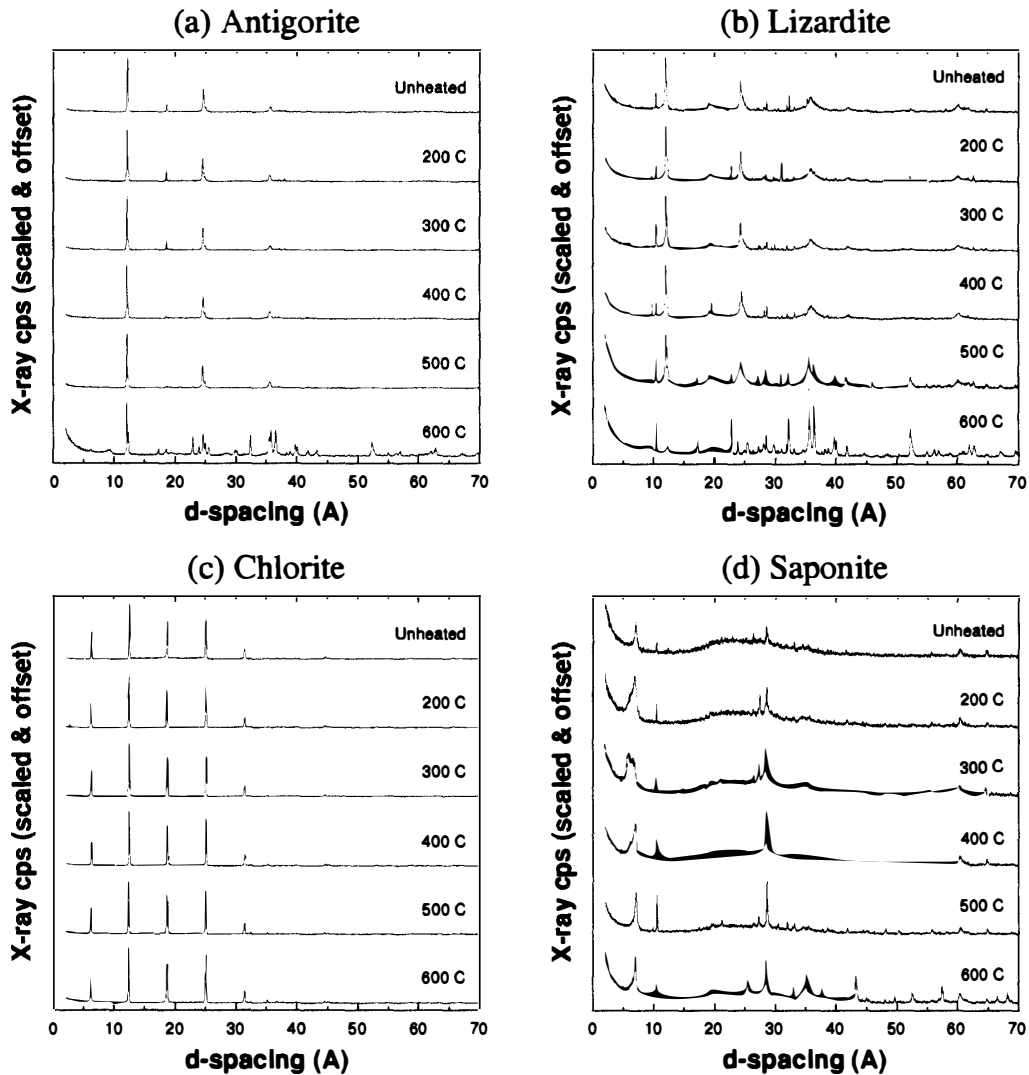
(a) Antigorite

(b) Lizardite

(c) Chlorite

(d) Saponite

Fig. 1. *X-ray power diffractometry patterns of unheated and heated phyllosilicate samples. Each pattern height is normalized by the strongest peak height and offset from one another for clarity.*

We also completed X-ray diffractometry on four of the five studied, minerals, the exception being clinochrysotile. For the four minerals, we are now able to compare the diffraction patterns at each heating step, as a first step in charting the structural changes that have occurred upon heating. These results should enable future workers to better estimate the degree of natural heating witnessed by meteorites. Examples of utility are given :

For Lizardite, a low temperature diffuse peak located at 36 A d-spacing becomes resolved into two sharp peaks upon heating. A sharp diffraction peak appears in saponite at 44 A upon heating to 600 degrees. For the same mineral a diffraction peak doublet occurs near 28 A upon heating at 200 degrees, but the peak heights are significantly changed upon further heating. These diffraction effects should be most apparent in X-ray diffraction, but may also carry over to electron diffraction, as only

future work may show.

5. Reflectance Spectra Measurements

All the mineral samples were ground and dry-sieved into powders of $< 125\,\mu$m (except for clinochrysotile which was fibrous and measured as was), and their UV-Vis-NIR diffuse reflectance spectra were measured at 30° incidence and 0° emergence angles at wavelengths from 0.3 to 2.6μm using the RELAB bidirectional spectrometer (PIETERS, 1983). Reflectances were then divided by those of halon at the same viewing geometry and the ratios were corrected based on absolute reflectances of halon. Biconical IR diffuse reflectance spectra of the samples were measured at 30° incidence and emergence angles at wavelengths from 1.8 to 26μm using the Niclet 740 FT-IR spectrometer with diffuse gold as the standard. The UV-Vis-NIR spectra and FT-IR spectra were connected at 2.5μm. In this study, only the 0.3–3.6μm portion was used for analysis from the measured full-range spectrum (0.3–26μm).

All the measured reflectance spectra are shown in Fig. 2.

The antigorite samples show only small changes in their overall spectral shapes except for the 600°C sample which shows very blue and rounded visible spectrum and a sharp 2.7μm band. Brightness, which is measured by the reflectance at 0.55μm and listed near the visible portion of each spectrum in Fig. 2, decreases until 500°C and increases again at 600°C. The 1.4μm band and the complex bands around 2.3–2.5μm steadily decrease as the heating temperature increases, while the 2.7μm band strength stays about the same. The 600°C sample with carbon shows a very different spectral shape from the others with strong UV and 3-μm absorption.

The lizardite samples show very systematic changes as heating temperature increases. The brightness decreases until about 400°C and increases again. The 0.7, 0.9, and 1.1μm bands keep weakening until they disappear around 400°C. The 1.4 and 2.3–2.5μm bands steadily decrease, while the 2.7μm band weakens only slightly before 600°C where the band weakens dramatically and becomes very sharp. The 1.4μm band seems to disappear at 600°C. The 600°C spectrum shows a very blue and smooth visible profile, similar to the antigorite 600°C sample. The 600°C sample with carbon shows a very different spectrum from the others with strong UV and 0.5-μm absorption.

The clinochrysotile samples also show very systematic changes. The 0.7, 0.9, and 1.1μm bands disappear around 400°C, the 1.4 and 2.3–2.5μm bands steadily decrease until 600°C and completely disappear for the 600°C sample with carbon, and the 2.7μm band seems to become sharper. The brightness keeps decreasing until 500°C.

The chlorite samples do not show much systematic change. The brightness seems to decrease until 400°C and begins increasing again. Visible spectral slope seems to have changed at 400°C but has reversed at 500°C. Strengths of other bands do not seem to have changed through the heating process up to 600°C. The 600°C sample with carbon seems to show the weakest 0.7-μm band among all.

The saponite samples show drastic and systematic changes. The brightness decreases until 400°C and begins increasing again. The 1.4, 1.9, 2.3, and 2.4μm bands keep weakening steadily, and the 2.7μm band keeps becoming sharper. The UV-visible spectral profile keeps flattening.

(a) Antigorite

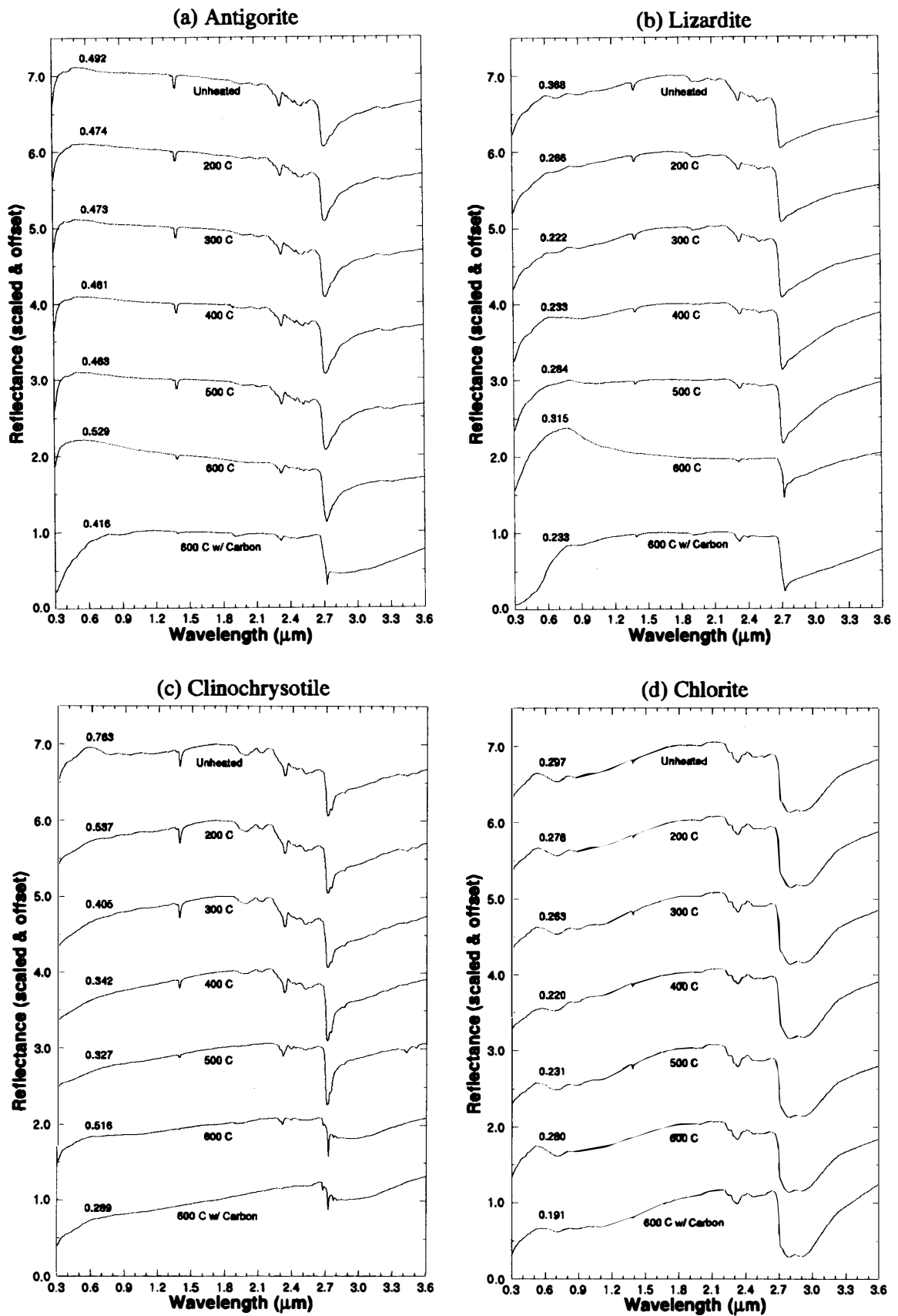## (b) Lizardite

(c) Clinochrysotile
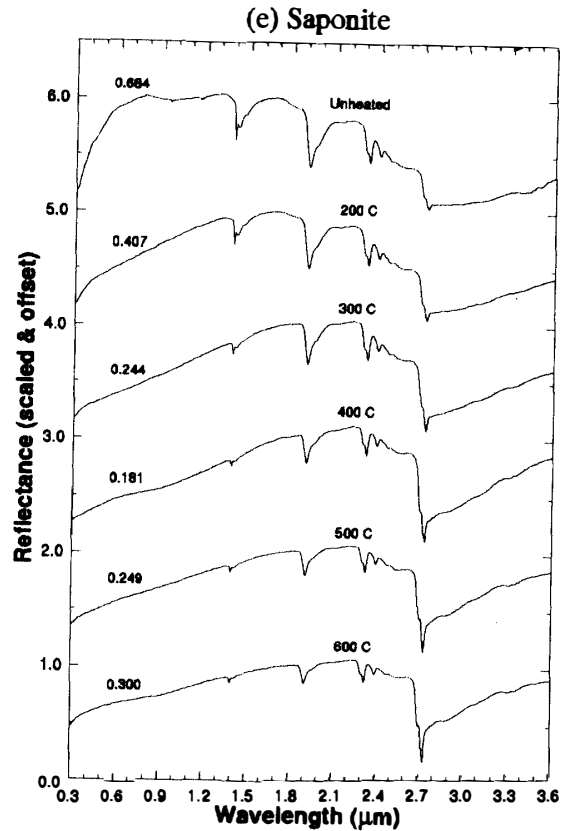
(d) Chlorite

Fig. 2.

Fig. 2 (opposite). *Reflectance spectra of unheated and heated phyllosilicate samples. Each spectrum is scaled at an appropriate wavelength and offset from one another for clarity.*

Fig. 2 (continued).

6. Albedo and UV, 0.7-μm, and 3-μm Absorption Strengths

In order to quantify and compare the above spectral features with telescopic measurements of primitive asteroids, the albedo and the UV and 0.7-μm absorption strengths are defined by simulating the filters used in the Eight-Color Asteroid Survey (ECAS) by ZELLNER et al. (1985). And the 3-μm band strength is defined so that even low-quality IR spectra of asteroids could be used. More concretely, the albedo and the absorption strengths are defined in the same way as in HIROI et al. (1996):

Albedo: R (0.550)
UV absorption strength: $\ln R$ (0.337) $- \ln R$ (0.550)
0.7-μm band strength: $\ln R$ (0.701) $- [0.152 \ln R$ (0.550) $+ 0.151 \ln R$ (0.853)]$/0.303$
3-μm band strength: $\ln R$ (2.9 ~ 3.0) $- \ln R$ (2.3 ~ 2.5)

where R (x) and R (x ~ y) indicate reflectance through an ECAS filter centering at $x\,\mu$m and average reflectance from x to $y\,\mu$m, respectively.

The above four quantities for all the phyllosilicate samples were calculated and plotted against heating temperatures in Fig. 3. If we exclude the samples heated at 600°C with carbon, the following points are observed. The albedo tends to decrease
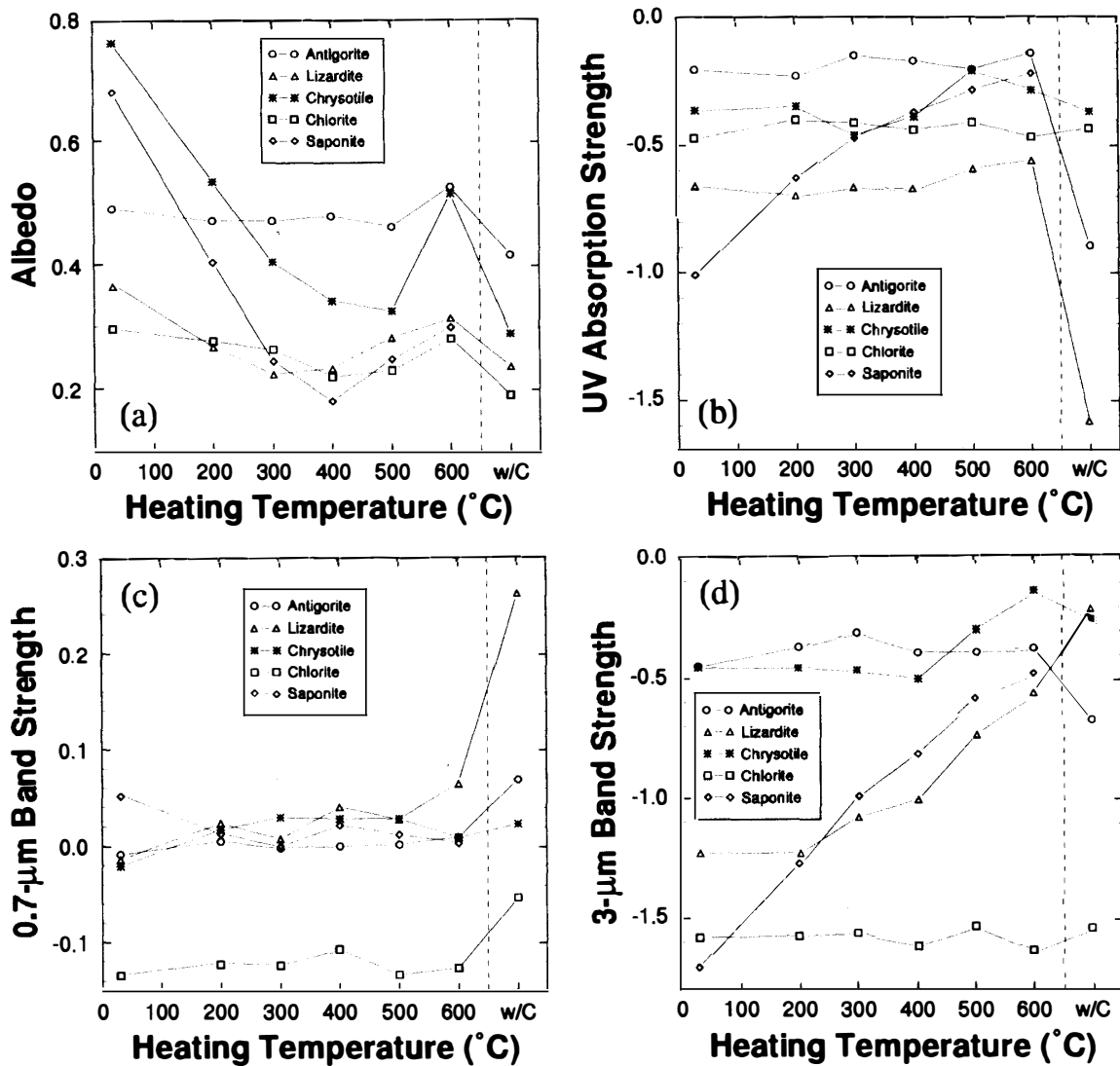
Fig. 3.   Plots of albedo and UV, 0.7-μm, and 3-μm absorption strengths of unheated and heated
          phyllosilicates samples.

until 300–500°C and begin increasing again, which suggests that the transitional prod-
ucts of heating are darker than both the original phyllosilicates and the final products.
Only saponite shows a clear trend of decreasing UV absorption strength as the heating
temperature becomes higher.   The 0.7-μm band for some samples disappear around
400°C, whereas that of chlorite sample survived until 600°C.   Saponite and lizardite
show steady decrease of the 3-μm band strength as they are heated at higher tempera-
tures.   The correlation between the UV and 3-μm absorption strengths claimed in HIROI
et al. (1996) is examined in Fig. 4.   The correlation is very clear for saponite samples
because saponite shows a very positive correlation between the heating temperature and
both the UV and 3-μm absorption strengths.   Lizardite also shows a slight correlation
between the UV and 3-μm absorption strengths, and the other phyllosilicate samples do
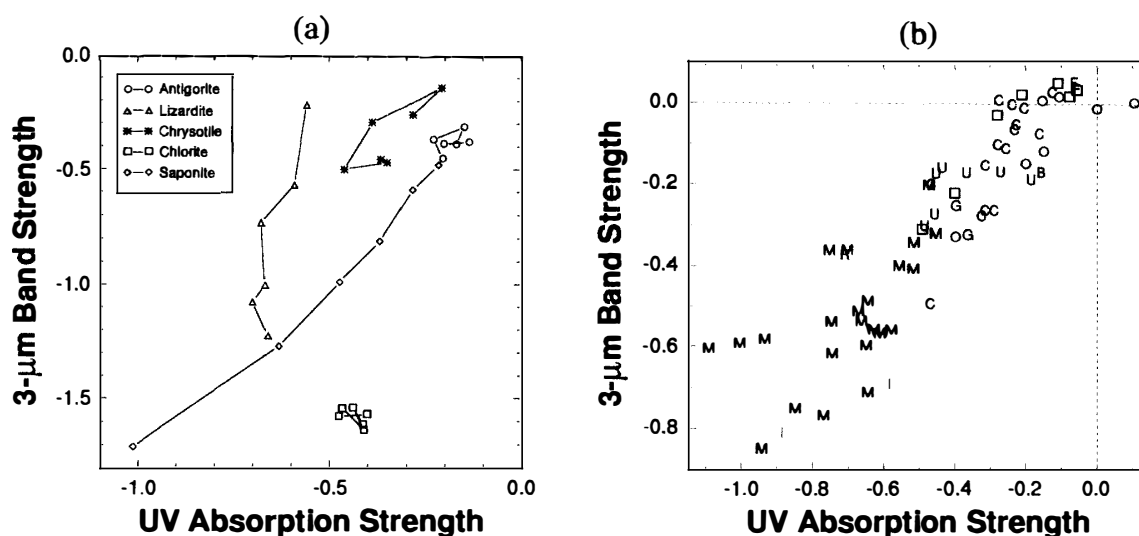not show any clear correlation.

Fig. 4. Plot between the UV and 3-μm absorption strengths. (a) The unheated and heated phyllosilicate samples excluding the 600°C samples with carbon. (b) The C, G, B, and F asteroids and CI/CM chondrites including the heated ones (HIROI et al., 1996).

7. Summary and Discussion

The results that the albedo decreases until 300-500°C and begins increasing afterward and that the 0.7-μm band disappears around 400°C are in accordance with our previous studies concerning the heated Murchison samples (HIROI et al., 1993, 1994). However, neither the correlation between the UV absorption strength and heating temperature nor the correlation between the UV and the 3-μm absorption strengths was found for serpentine samples although they were found for the heated Murchison samples and serpentine is the most important mineral in carbonaceous chondrites in its abundance, variety, and sensitivity against heating.

Because of the presence of the 0.7 and 0.9 μm bands in some primitive asteroid reflectance spectra (VILAS and GAFFEY, 1989), it is likely that a significant amount of serpentine exists on such asteroids as in the CM2 chondrites. Therefore, if these heating experiments are a good simulation of heating events on the present primitive asteroids or inside their parent body which was subsequently broken up to smaller pieces, they should have both serpentine and saponite by significant amounts to produce both the 0.7 and 0.9 μm bands and the correlation between the UV and 3 μm absorption strengths.

However, it is highly possible that our heating experiments are not simulating the heating processes of primitive asteroids. For example, the reason that coexisting carbon rod was not effective in suppressing absorption bands may be that a carbon rod was not as effective in suppressing absorption bands as intimate mixing of fine carbon powder as in the CM and CI chondrites. It is also possible that grain size distribution of phyllosilicates in the CM chondrites is centered at significantly smaller values than our phyllosilicate samples ($< 125 \mu$m), making it much easier for phyllosilicates in the

CM chondrites to lose water upon heating. Atmospheric control including oxygen fugacity control may also have some effects to the extent of water loss of the heated phyllosilicate samples.

In spite of some uncertainties of our experiments described above, insensitivity of chlorite against heating imposes a question of judging the degree of heating only from the 0.7 and 3 μm absorption bands because heating even at 600°C would not eliminate the features if chlorite is dominating the features. On the contrary, if saponite is dominant, it may be relatively easy to estimate the heating degree. If other things such as grain size distributions are similar among the phyllosilicate samples in this study, amount of water loss by heating must be highly dependent on kind of mineral and possibly chemical composition.

Although this kind of study should be further continued to clarify the true reason of the behaviors of reflectance spectra of the CI and CM chondrites and primitive asteroids, our present study has shown that just having a significant amount of phyllosilicates does not guarantee such a spectral behavior to be observed.

Acknowledgments

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