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How to cite:

Hanna, R. D.; Hamilton, V. E.; Haberle, C. W.; King, A. J.; Abreu, N. M. and Friedrich, J. M. (2020). Distinguishing relative aqueous alteration and heating among CM chondrites with IR spectroscopy. *Icarus*, 346, article no. 113760.

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Version: Accepted Manuscript

Link(s) to article on publisher's website:
<http://dx.doi.org/doi:10.1016/j.icarus.2020.113760>

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1 **Distinguishing Relative Aqueous Alteration and Heating among CM Chondrites with IR**
2 **Spectroscopy**

3

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16

17 **Abstract**

18 Using infrared (IR) spectroscopy of thin sections, we characterize the relative degree of
19 aqueous alteration and subsequent heating of a suite of CM chondrites to document spectral
20 indicators of these processes that can contextualize observations of carbonaceous asteroids. We
21 find that IR spectroscopy reveals the subtle progressive alteration of the CMs in two different
22 ways. The low-wavenumber region ($1200\text{--}400\text{ cm}^{-1}$; $8\text{--}25\text{ }\mu\text{m}$) records the increasing proportion
23 of Mg-Fe phyllosilicates relative to anhydrous silicates as aqueous alteration proceeds, with a
24 highly correlated shift of the Christiansen feature (CF) to lower wavenumber and the Si-O
25 bending band minimum to higher wavenumber, and an increase in depth of the Mg-OH band
26 ($\sim 625\text{ cm}^{-1}$). The strongest correlation ($R^2=0.90$) with petrologic subtype is the distance
27 between the CF and Si-O stretching minimum, which predicts the petrologic subtype of the
28 sample to within 0.1. The high-wavenumber region ($4000\text{--}2500\text{ cm}^{-1}$; $\leq 3.33\text{ }\mu\text{m}$) probes the
29 variation in abundance and composition of Mg-Fe serpentine and tochilinite among the altered
30 CMs. All moderately to highly altered CMs (≤ 2.3) have an OH/H₂O band emission maximum
31 of 3690 cm^{-1} ($2.71\text{ }\mu\text{m}$) indicative of Mg-bearing serpentine, and mildly aqueously altered CMs
32 (≥ 2.5) have a wider band with a complex shape that results from contributions of Fe-bearing
33 serpentine and tochilinite. Among weakly heated CMs, the low-wavenumber region exhibits
34 spectral features resulting from the dehydration and dehydroxylation of phyllosilicates that
35 include broadening of the Si-O stretching band and a shift of its minimum to lower wavenumber,
36 and the disappearance of the Mg-OH band. The location of the Si-O bending band minimum
37 appears to be unaffected by mild heating. Among extensively heated CMs, the low-wavenumber
38 region is dominated by the spectral features of secondary, Fe-bearing olivine and low-Ca
39 pyroxene. The OH/H₂O band of all heated CMs is broad and rounded with an emission peak at

40 higher wavenumbers ($\leq 3636 \text{ cm}^{-1}$; $\geq 2.75 \text{ }\mu\text{m}$) than in unheated CMs. However, spectral and
41 petrographic evidence suggests that our heated CMs have been compromised by terrestrial
42 rehydration. Our study confirms that thermal metamorphism effects are concentrated within the
43 matrix and suggests that the matrix of the CM WIS 91600 had a CI-like mineralogy prior to
44 heating.

45

46 **Keywords:** spectroscopy; meteorites; geological processes; asteroids, composition

47

48 **1. Introduction**

49 The CM carbonaceous chondrites are a group of meteorites that show variation in the effects
50 of the earliest stages of metamorphism, specifically aqueous alteration and thermal processing,
51 through their physical and chemical characteristics. Detailed investigations of this group provide
52 an opportunity to extract information on how and when primitive Solar System material was
53 geologically altered from a more pristine state, and as such they have been studied in great detail.
54 It has long been recognized that aqueous alteration of the CMs is a progressive sequence of
55 mineralogical and chemical changes resulting in the destruction of metal and chondrule glass
56 mesostasis, serpentinization of anhydrous silicates (olivine, pyroxene), and the mobilization of
57 Fe and Mg to form initially Fe-bearing and then Mg-rich serpentine (Tomeoka et al., 1989;
58 Zolensky et al., 1993; Browning et al., 1996; Zolensky et al., 1997; Lauretta et al., 2000; Rubin
59 et al., 2007; Howard et al., 2015; Leroux et al., 2015). A subset of CMs have also experienced
60 post-aqueous alteration heating (i.e., thermal metamorphism) (e.g., Lipschutz et al., 1999;
61 Nakamura, 2005; Tonui et al., 2014). The degree of heating experienced by a CM chondrite can
62 be identified based on mineralogical changes, primarily the dehydration and dehydroxylation of

63 phyllosilicates and eventual formation of secondary olivine and pyroxene from phyllosilicates
64 (Lipschutz et al., 1999; Nakamura, 2005; Tonui et al., 2014), as well as the modification and
65 structural changes of organic material within it (Quirico et al., 2014; Quirico et al., 2018).

66 There has been great interest in characterizing CMs using spectroscopic methods to allow for
67 direct comparison of their spectra to those of asteroids from telescopic and spacecraft data (e.g.,
68 Gaffey, 1976; Hiroi et al., 1996; Sato et al., 1997). More recent efforts have endeavored to relate
69 the spectral signatures of CMs to their degree of aqueous alteration or heating to more accurately
70 interpret the spectra of C-complex asteroids, which may host CM or CM-like material (Gaffey et
71 al., 1993a; Beck et al., 2010; Cloutis et al., 2011; Cloutis et al., 2012; Takir et al., 2013; Beck et
72 al., 2014; McAdam et al., 2015; Garenne et al., 2016; Beck et al., 2018). Data acquisition and
73 sample preparation methods among these previous studies have varied, and in some cases their
74 applicability to ground- or spacecraft-based spectral observations is limited. First, these studies
75 collected spectral data of particulate samples that were ground from meteorite chips. This
76 complicates the comparison of the laboratory data to asteroid observations as particle size effects
77 can substantially modify the depth, shape, and/or position of spectral bands in the IR (e.g., Lyon,
78 1964; Salisbury, 1993). Further, IR spectra of silicates with fine particle sizes ($<75 \mu\text{m}$) display
79 scattering (transparency) features in wavelength regions where their absorption coefficients are
80 extremely low (e.g., Vincent and Hunt, 1968; Salisbury and Walter, 1989), and the recent arrival
81 of spacecraft to carbonaceous asteroids (162173) Ryugu and (101955) Bennu has revealed that
82 their regolith is dominated by coarse particulates and rocks (Hamilton et al., 2019; Okada et al.,
83 2019). In addition, the petrographic context of the material is lost other than the general ‘bulk
84 composition’ of the stone that was ground. Another complication of grinding CM chondrites in
85 the laboratory is contamination of the powders with adsorbed terrestrial water, which modifies

86 the shape and position of the “3- μm ” water band (referred to as the OH/H₂O band in the
87 remainder of the manuscript) that is diagnostic of hydrated minerals within CM chondrites (Beck
88 et al., 2010; Takir et al., 2013). Many spectral studies have heated chondrite powders to
89 minimize this effect, but it is unclear if all terrestrial adsorbed water is being removed and
90 whether heating could be modifying the native water band through thermal modification of the
91 phyllosilicate or hydrated Fe sulfide (tochilinite), the latter of which breaks down at temperatures
92 as low as 120°C (Fuchs et al., 1973; Zolensky et al., 1997). Finally, grinding of phyllosilicates
93 [which are the dominant mineralogy in CMs (Howard et al., 2009)] in the laboratory has been
94 shown to damage their structure and change their spectral character (e.g., Drief and Nieto, 1999).

95 The Origins, Spectral Interpretation, Resource Identification, and Security–Regolith Explorer
96 (OSIRIS-REx) mission to asteroid (101955) Bennu is equipped with the OSIRIS-REx Thermal
97 Emission Spectrometer (OTES) that collects spectra in the 1750–100 cm^{-1} wavenumber region
98 (5.71–100 μm) (Christensen et al., 2018). Because OTES is measuring emitted energy, previous
99 spectral studies that have collected IR data of CM chondrites in transmission (Beck et al., 2010;
100 Beck et al., 2014) or bidirectional reflectance (Beck et al., 2018) are not directly applicable to
101 OTES measurements. Although McAdam et al. (2015) collected bi-conical reflectance of CMs
102 [which are equivalent to emissivity through Kirchhoff’s Law (Salisbury, 1993)], the samples
103 were powdered ($\sim 35 \mu\text{m}$) and the spectra are dominated by transparency features. Other recent
104 IR emission and diffuse reflectance studies of CM and CI chondrites are likewise dominated by
105 transparency features due to fine particle sizes (Donaldson Hanna et al., 2019; Bates et al., 2020)
106 thereby complicating direct comparison to some asteroid regolith surfaces such as Ryugu and
107 Bennu that do not appear to contain abundant fine-grained material (DellaGiustina et al., 2019;
108 Grott et al., 2019). Initial results from the OSIRIS-REx mission indicate that Bennu’s surface is

109 dominated by a hydrous mineralogy consistent with a low petrologic type-2 CM lithology, and
110 the average OTEs spectrum does not show strong transparency features attributable to fine-
111 particulate silicates (Hamilton et al., 2019).

112 The primary goal of our study is to identify IR spectral trends that are correlated with degree
113 of aqueous alteration and heating among CM chondrites. Ultimately, the knowledge gained from
114 these laboratory-based observations will be used to remotely characterize aqueous alteration and
115 possible heating of CM material on Bennu from OTEs and OSIRIS-REx Visible and InfraRed
116 Spectrometer (OVIRS) data. We anticipate that our results also will be useful in the
117 investigation of other asteroids that may have CM material on their surfaces, as well as for rapid
118 characterization of CMs in the laboratory using bulk samples or thin sections. We do not aim to
119 relate spectral features to modal mineral abundances or specific chemical compositions of
120 minerals within CMs [which can vary within a petrologic subtype (Rubin et al., 2007; Howard et
121 al., 2015)]; rather, we identify broad spectral trends that are correlated with mineralogical and
122 compositional changes resulting from aqueous alteration and heating. Additionally, microscopic
123 Fourier transform infrared (μ -FTIR) spectroscopy, which can collect spectral data of samples
124 mounted in thin section, provides an in situ view of spectral trends while retaining spatial
125 context, allowing insights into the details of aqueous alteration and heating within CM
126 chondrites. Both topics will be explored in this paper.

127

128 **2. Methods**

129 *2.1 Samples*

130 We analyzed 13 CMs that represent a range of aqueous alteration [2.0–2.7 on the Rubin et al.
131 (2007) scale] and degree of heating [Stages II–III/IV; (Nakamura, 2005)], as well as one CI

132 (Alais) to use as a comparison to the most altered CMs (Tables 1–2). While some isotopic data
133 suggest that WIS 91600 may be better classified as an ungrouped carbonaceous chondrite rather
134 than a CM (Alexander et al., 2007; Yabuta et al., 2010; Tonui et al., 2014), we include it here as
135 the latter but explore this classification issue in the discussion section. All samples apart from
136 Murchison and Alais are Antarctic finds. Five of the unheated CMs (LAP 04514, LAP 02333,

137 **Table 1.** Altered CMs and CI examined for this study

	Section number	Petrologic subtype ^a	Weathering grade	PSF ^b	Alteration Index ^c	Equivalent Petrologic Subtype ^d	Olivine (vol%)	Pyroxene (vol%)	Magnetite (vol%)	Fe-sulfide (vol%)	Calcite (vol%)	Gypsum (vol%)	FeNi metal (vol%)	Fe-rich phyllosilicate (vol%)	Mg-rich phyllosilicate (vol%)	Total (vol%)	Petrologic Subtype Reference	PSD-XRD Data Reference
LAP 04514	6	2.7	B	0.74	1.6	2.5	10.9	14.2	2.3	1.3	0.9	0.0	0.0	42.8	27.4	99.8	e	f
LAP 02333 ^j	2	2.6	B	0.73	1.5	2.4	9.6	10.2	1.9	1.2	0.95	0	0	23.6	52.5	100.0	e	g, f
Murchison	USNM 5487-3, USNM 5487-1	2.5	n.a.	0.49	1.5	2.4	15.1	8.3	1.1	1.8	1.2	0.0	0.0	50.3	22.2	100.0	a	g
LAP 031214	7	2.3	B	0.63	1.6	2.5	18.2	5.9	2.3	1.1	1.0	0.3	0.0	30.8	40.4	100.0	e	h
LEW 90500	60	2.2	B	0.67	1.5	2.4	15.2	4.9	1.9	3.1	1.0	3.7	0.0	27.7	41.7	99.2	e	g
ALH 85013	13	2.2	A	0.76	1.3	2.2	9.8	3.4	1.6	1.6	4.0	1.9	0.0	37.1	40.7	100.1	e	g
LAP 031166	16	2.1	B	0.91	1.2	2.1	5.0	1.5	2.0	1.4	0.9	2.4	0.0	21.5	65.3	100.0	e	h
LAP 02277	38	2.0	A	0.93	1.2	2.1	5.3	0.0	1.9	2.2	1.7	0.0	0.0	20.6	68.3	100.0	a, e	h
CI Alais	P10910	n.a.	n.a.	1.00	n.a.	n.a.	0.0	0.0	7.0	4.0	3.0	0.0	0.0	0.0	83.0	97.0	n.a.	i

138 ^aRubin et al. (2007) scale139 ^bPSF of g calculated from XRD values in this table140 ^cFrom PSF of this work141 ^dUsing Equation (2) of g142 ^eFriedrich et al. (2018)143 ^fMason et al. (2018)144 ^gHoward et al. (2015)145 ^hKing et al. (2017)146 ⁱKing et al. (2015)147 ^jPSD-XRD data average of g and f

148

149

Table 2. Heated CMs examined for this study

		Sample number for PSD- XRD	Heating Stage ^a	Weathering grade	Olivine (vol%)	Pyroxene (vol%)	Magnetite (vol%)	Fe- sulfide (vol%)	Calcite (vol%)	Gypsum (vol%)	FeNi metal (vol%)	“Rusts” (vol%)	Feldspar (vol%)	Fe-rich Phyllosilicate (X-ray amorphous) (vol%)	Mg-rich Phyllosilicate (X-ray amorphous) (vol%)	Total (vol%)	Decomposed/ Dehydrated/ Phyllosilicate	Secondary Olivine	Heating Stage Reference
WIS 91600 ^b	22	76,9	II	A/B	10.1	1.5	7.8	3.7	0.6	0.0	0.0	0.0	0.0	3.8	74.4	101.7	yes	no	c, d, e
EET 87522	30	51, 2	II	Be	15.3	6.6	1.9	0.7	0.4	0.2	0.1	0.0	0.0	34.8	40.0	100.0	yes	no	c, e
EET 96029	23	57, 21 [§]	II	A/B	12.2	15.7	3.1	2.4	1.0	1.0	0.3	0.0	0.0	24.7	40.0	100.4	yes	no	c, g
PCA 91008	6	37, 5	III	B/C	76.7	16.9	2.5	0.8	0.0	2.7	0.0	0.4	0.0	0.0	0.0	100.0	yes	yes	c, d, e, a, h
PCA 02010	11	24, 2	III/IV	B	75.2	16.1	0.0	3.8	1.3	0.0	0.4	0.0	3.2	0.0	0.0	100.0	yes	yes	f, h, i

150

Italics: This work

151

^aNakamura (2005) scale

152

^bPSF XRD data average of Howard et al. (2015) and this work, sample number refers to this work [Howard et. al (2015) reported 73.5% Mg-rich phyllosilicate as crystalline for their sample]

153

^cQuirico et al. (2018)

154

^dTonui et al. (2014)

155

^eNakato et al. (2009)

156

^fGarenne et al. (2014)

157

[§]PSD-XRD from Lee et al. (2016)

158

^hBeck et al. (2014)

159

ⁱAlexander et al. (2013)

160

161

162 LAP 031214, LAP 031166, ALH 85013) are the same sample sections analyzed by Friedrich et
163 al. (2018), and the two Murchison sections are from the sample analyzed and described in Hanna
164 et al. (2015). Two samples with the same petrologic subtype (2.2; ALH 85013 and LEW 90500)
165 were selected to examine intra-subtype variability in the μ -FTIR spectra. In all cases, the same
166 sample section was used for both μ -FTIR spectroscopy and electron microscopy. For the
167 Antarctic finds, all samples are weathering grade A, A/B, or B (apart from PCA 91008, which
168 has been assigned a B/C) (Table 1), indicating minor to moderate terrestrial weathering of the
169 samples. We checked all sections for indications of terrestrial weathering [rust, evaporites,
170 sulfate or carbonate veins (Bland et al., 2006)] and noted weathering effects where apparent
171 below. In addition, we determined the modal mineralogy of separate aliquots of the heated CM
172 chondrites WIS 91600, EET 87522, PCA 91008, and PCA 02010 using position sensitive
173 detector X-ray diffraction (PSD-XRD) to verify the previously assigned heating stage and check
174 for terrestrial weathering products (Table 2).

175

176 *2.2 Electron microscopy*

177 We used scanning electron microscopy (SEM) to provide mineralogical and textural context
178 for the μ -FTIR spectra and to verify the relative degree of alteration and heating among the CM
179 samples. For the five CM sections previously analyzed by Friedrich et al. (2018), the
180 backscattered electron (BSE) image and energy dispersive (EDS) X-ray data collection are
181 described in that work. Likewise, BSE imagery and EDS analysis of the Murchison sections are
182 described in Hanna et al. (2015). For the five heated CMs (Table 2) and the unheated CM LEW
183 90500, we collected whole-section BSE and EDS mosaics on a FEI XL 30 ESEM at the Electron
184 Microbeam Analysis Laboratory at the Jackson School of Geosciences at the University of Texas

185 (UT) at Austin. Sections were not carbon-coated, thus all data collection was done at low
186 pressure (0.1 Torr) with H₂O gas with a 20.0 kV beam and a working distance that varied
187 slightly per session (9.9–10.1 mm). EDS X-ray elemental maps were generated using major
188 element K α peaks. For LAP 02277, we collected whole-section BSE and wavelength dispersive
189 (WDS) X-ray mosaics on a JEOL JXA-8200 Electron Microprobe (EPMA) at the same UT
190 facility. The section was carbon-coated, and data were collected at 15 kV and 38 mA with a
191 dwell time of 4 ms (focused beam). We collected all BSE, EDS, and WDS data after IR
192 reflectance measurements.

193

194 *2.3 PSD-XRD analysis*

195 Meteorite chips (~50 mg) were powdered using an agate mortar and pestle, then analyzed
196 using an INEL XRD equipped with a curved 120° PSD at the Natural History Museum, London.
197 XRD patterns were collected for 16 hours from the meteorite samples and for 30 minutes from
198 standards of all minerals present in the meteorites. Differences in the incident beam flux
199 throughout the experimental run were monitored by analyzing a polished block of Fe metal at the
200 start of each day.

201 Mineral abundances were determined using a profile-stripping method that has previously
202 been applied to both unheated and heated CM chondrites (e.g. Howard et al., 2015; King et al.,
203 2015). The XRD pattern of a mineral standard was scaled to the same length of time as the
204 meteorite analyses (i.e. $\times 32$), then reduced in intensity by a factor to match its intensity in the
205 XRD pattern of the meteorite sample. The standard pattern was subtracted to leave a residual
206 meteorite pattern, and this process was repeated for all phases identified in the meteorite until
207 there were zero counts left in the residual and the sum of the fit factors was one. The fit factors

208 for the mineral standards were then corrected for relative differences in X-ray absorption to give
209 a final volume fraction in the meteorite. Uncertainties on the measured abundances are 2–4% for
210 crystalline anhydrous phases and 3–5% for fine-grained, poorly crystalline phyllosilicates.

211

212 *2.4 μ-FTIR*

213 We collected IR reflectance spectra (4000–400 cm⁻¹, 2.5–25 μm) of all samples with a
214 Thermo Scientific iN10 FTIR microscope (μ-FTIR) equipped with an extended range, liquid
215 nitrogen-cooled mercury cadmium telluride (MCT) detector, and potassium bromide (KBr)
216 beamsplitter. Samples were mounted as polished thin sections (no carbon coat), and individual
217 spectra were acquired as the average of 256 scans at a spatial resolution of 300 μm per pixel and
218 spectral sampling of 2 cm⁻¹. Except as noted below, all data were collected as maps using the
219 attached, automated sample stage. Collected map sizes for each sample are reported in Tables 3
220 and 4. Measured radiance was converted to biconical reflectance using a polished gold plate
221 mounted on the stage as the background. A background was collected every 15–30 minutes
222 during mapping to account for any variability in atmospheric conditions or instrument drift over
223 time. Because the spectrometer has a permanently aligned, 15X 0.7 N.A. (half angle range 20°
224 to 43.5°) visible/IR objective and condenser, the solid angle is sufficiently small that band-
225 broadening effects, typically associated with biconical reflectance systems, are not observed
226 (Hamilton, 2018). Therefore the reflectance spectra have equivalence with emission and are
227 converted to emissivity using Kirchhoff's Law $E = 1 - R$, where E is the emissivity and R is the
228 reflectance (Salisbury, 1993). This conversion enables a more direct comparison of our
229 laboratory data to IR emissivity datasets from instruments such as OTEs (Christensen et al.,
230 2018).

Table 3. Altered CMs and CI spectral parameters

	Petrologic subtype ^a	Sample area for μ FTIR (x90000 μm^2)	Christiansen feature (cm^{-1})	Si-O stretching band minimum (cm^{-1})	Separation of CF and Si-O stretching band minimum (cm^{-1})	Si-O stretching band symmetry	Mg-OH band minimum (cm^{-1})	Mg-OH band depth	Si-O bending band minimum (cm^{-1})	OH/H ₂ O band maximum (cm^{-1})	OH/H ₂ O band maximum (μm)	OH/H ₂ O band center (cm^{-1})	OH/H ₂ O band center (μm)	OH/H ₂ O band depth
LAP 04514	2.7	532	1155	948 (2)	207	0.95 (0.06)	619 (3)	0.0071 (0.0001)	432 (0)	3671 (2)	2.724 (0.002)	3667 (4)	2.727 (0.003)	0.0052 (0.0000)
LAP 02333	2.6	522	1176	946 (3)	231	1.01 (0.06)	615 (6)	0.0065 (0.0002)	427 (2)	3623 (1)	2.760 (0.001)	3622 (2)	2.761 (0.002)	0.0079 (0.0001)
Murchison	2.5	796	1147	944 (2)	204	0.97 (0.04)	620 (4)	0.0095 (0.0001)	430 (7)	3626 (3)	2.758 (0.002)	3643 (4)	2.745 (0.003)	0.0069 (0.0001)
LAP 031214	2.3	436	1136	959 (2)	177	0.81 (0.03)	619 (3)	0.0164 (0.0004)	438 (4)	3686 (4)	2.713 (0.003)	3661 (5)	2.731 (0.004)	0.0083 (0.0002)
LEW 90500	2.2	354	1120	952 (1)	168	0.86 (0.02)	619 (2)	0.0153 (0.0001)	442 (1)	3685 (3)	2.714 (0.002)	3679 (4)	2.718 (0.003)	0.0072 (0.0001)
ALH 85013	2.2	534	1126	966 (4)	160	0.75 (0.06)	618 (2)	0.0159 (0.0003)	440 (1)	3686 (3)	2.713 (0.003)	3665 (5)	2.729 (0.004)	0.0075 (0.0002)
LAP 031166	2.1	495	1128	984 (9)	144	0.69 (0.14)	625 (2)	0.0248 (0.0004)	446 (1)	3693 (3)	2.708 (0.002)	3693 (5)	2.708 (0.004)	0.0075 (0.0000)
LAP 02277	2.0	195	1111	970 (3)	141	0.80 (0.05)	625 (1)	0.0297 (0.0002)	442 (4)	3693 (3)	2.708 (0.002)	3693 (3)	2.708 (0.003)	0.0080 (0.0002)
CI Alais	n.a.	114	1126	1008 (2)	119	0.40 (0.03)	600 (12)	0.0131 (0.0008)	450 (2)	3691 (2)	2.710 (0.001)	3690 (7)	2.710 (0.005)	0.0061 (0.0001)
LAP 04514 matrix	2.7	11	1117	970 (3)	147	0.70 (0.05)	627 (0)	0.0127 (0.0000)	443 (3)	3671 (4)	2.724 (0.003)	3668 (6)	2.726 (0.004)	0.0066 (0.0003)
LAP 02333 matrix	2.6	10	1136	977 (2)	159	0.66 (0.03)	630 (2)	0.0148 (0.0017)	441 (1)	3629 (4)	2.756 (0.003)	3626 (4)	2.758 (0.003)	0.0118 (0.0004)
Murchison matrix	2.5	16	1122	964 (2)	159	0.77 (0.03)	624 (2)	0.0167 (0.0003)	440 (4)	3628 (3)	2.756 (0.002)	3652 (3)	2.738 (0.002)	0.0084 (0.0001)
LAP 031214 matrix	2.3	11	1124	979 (5)	145	0.58 (0.07)	617 (2)	0.0186 (0.0002)	440 (1)	3686 (3)	2.713 (0.002)	3665 (5)	2.729 (0.004)	0.0097 (0.0001)
LEW 90500 matrix	2.2	12	1107	967 (3)	140	0.72 (0.03)	617 (1)	0.0170 (0.0002)	445 (0)	3686 (3)	2.713 (0.002)	3684 (8)	2.714 (0.006)	0.0085 (0.0002)
ALH 85013 matrix	2.2	11	1120	984 (4)	137	0.58 (0.05)	618 (2)	0.0161 (0.0003)	444 (2)	3685 (4)	2.713 (0.003)	3679 (11)	2.718 (0.008)	0.0091 (0.0002)
LAP 031166 matrix	2.1	10	1136	993 (5)	142	0.62 (0.09)	628 (2)	0.0428 (0.0004)	448 (4)	3693 (1)	2.707 (0.001)	3692 (4)	2.709 (0.003)	0.0082 (0.0000)
LAP 02277 matrix	2.0	10	1115	970 (4)	144	0.82 (0.09)	627 (0)	0.0554 (0.0000)	445 (4)	3693 (0)	2.708 (0.000)	3693 (3)	2.708 (0.003)	0.0080 (0.0002)

232 2σ uncertainty in parentheses233 ^aRubin et al. (2007) scale

Table 4. Heated CMs spectral parameters

	Sample area for μ FTIR ($\times 90000 \mu\text{m}^2$)	Christiansen feature (cm^{-1})	Si-O stretching band minimum (cm^{-1})	Separation of CF and Si-O stretching band minimum (cm^{-1})	Si-O stretching band symmetry	Si-O bending band minimum (cm^{-1})	OH/H ₂ O band maximum (cm^{-1})	OH/H ₂ O band maximum (μm)	OH/H ₂ O band center (cm^{-1})	OH/H ₂ O band center (μm)	OH/H ₂ O band depth
WIS 91600	534	1149	982 (7)	167	0.53 (0.07)	445 (4)	3643 (5)	2.745 (0.004)	3639 (4)	2.748 (0.003)	0.00336 ($3\text{e}10^{-5}$)
EET 87522	441	1165	934 (4)	230	1.17 (0.08)	426 (5)	3600 (4)	2.778 (0.003)	3592 (3)	2.784 (0.002)	0.00469 ($2\text{e}10^{-5}$)
EET 96029	330	1165	935 (4)	230	1.20 (0.08)	428 (3)	3591 (3)	2.785 (0.002)	3586 (2)	2.788 (0.002)	0.00441 ($3\text{e}10^{-5}$)
PCA 91008	276	1184	876 (3)	308	2.00 (0.14)	<i>n.d.</i>	3529 (2)	2.834 (0.002)	3531 (1)	2.832 (0.001)	0.00520 ($5\text{e}10^{-5}$)
PCA 02010	309	1180	878 (4)	302	1.50 (0.12)	<i>n.d.</i>	3495 (5)	2.861 (0.004)	3494 (6)	2.862 (0.005)	0.00344 ($6\text{e}10^{-5}$)
WIS 91600 matrix	33	1146	1001 (1)	145	0.42 (0.01)	451 (2)	3651 (2)	2.739 (0.001)	3647 (3)	2.742 (0.002)	0.00405 ($0\text{e}10^{-5}$)
EET 87522 matrix	11	1161	916 (5)	245	1.52 (0.10)	433 (5)	3593 (6)	2.783 (0.005)	3600 (3)	2.778 (0.002)	0.00623 ($2\text{e}10^{-5}$)
EET 96029 matrix	11	1174	990 (2)	184	0.46 (0.02)	433 (7)	3617 (3)	2.765 (0.002)	3609 (2)	2.771 (0.002)	0.00671 ($0\text{e}10^{-5}$)
PCA 91008 matrix	10	1167	873 (3)	294	1.53 (0.14)	<i>n.d.</i>	3535 (3)	2.829 (0.002)	3538 (3)	2.826 (0.002)	0.00883 ($1\text{e}10^{-5}$)
PCA 02010 matrix	15	1176	875 (4)	301	1.37 (0.13)	<i>n.d.</i>	3509 (2)	2.849 (0.002)	3508 (3)	2.851 (0.003)	0.00464 ($6\text{e}10^{-5}$)

235 2σ uncertainty in parentheses236 *n.d.*: not determined

237

238

239 Collection of μ -FTIR spectra from thin sections of chondrites has several advantages. First,
240 the *in situ*, spatially resolved spectral measurements can be directly compared to our other
241 spatially resolved measurements of the same section (BSE, EDS, and WDS). We used the
242 correlated datasets to exclude individual spectra that overlapped with areas of fusion crust and
243 terrestrial weathering and to isolate spectral measurements for matrix-only spectra. Second,
244 because all sections are of solid samples, spectral variations due to scattering by small particles
245 ($< \sim 65\text{--}75\ \mu\text{m}$) are not an issue. Third, unlike for powdered meteorite samples, which require
246 heating to drive off terrestrial adsorbed water that is introduced during the powdering process
247 (e.g., Beck et al., 2010; Takir et al., 2013; Takir et al., 2019), no sample heating is required.
248 Importantly, this preserves any native, interlayer molecular water that may be present within the
249 phyllosilicate minerals, as well as hydroxyl (OH^-) that is loosely bound due to mineral
250 deformation attributable to impact or regolith gardening on the parent body. Several experiments
251 have shown that phyllosilicate dehydroxylation is enhanced by mechanical deformation and
252 occurs at lower temperatures than heating alone (Drief and Nieto, 1999; Dlugogorski and
253 Balucan, 2014). Therefore, heating chondrite samples may influence the native spectral
254 character of the high-wavenumber region ($4000\text{--}2500\ \text{cm}^{-1}$; $2.5\text{--}4\ \mu\text{m}$) that probes molecular
255 water and hydroxyl and may affect the tochilinite, sulfates, and Fe-oxyhydroxides within the
256 sample. Finally, we note that the specialized protocol of the NASA Astromaterials Curation
257 Meteorite Thin Section Lab insures that Antarctic meteorite carbonaceous chondrites do not
258 come into contact with water during section preparation and are carefully polished to minimize
259 deformation of the surface (Harrington and Righter, 2017).

260 Two potential spectral artifacts associated with μ -FTIR spectra on thin sections are
261 interference fringes and spectral contributions from epoxy (Hamilton, 2018). The former is

262 caused by internal reflections between the parallel surfaces of the section, and are typically most
263 readily observed in areas of high transparency (i.e., low absorption). We removed any individual
264 spectra with strong evidence of fringes. Epoxy is commonly used during the preparation of
265 carbonaceous chondrite thin sections (e.g., Harrington and Righter, 2017). Various types of
266 epoxies are used, but all are variants of thermoplastic resins and have spectral features, mainly
267 associated with hydrocarbons, that are distinct from and much weaker than meteorite mineral
268 spectra in most wavenumber regions (Hamilton, 2018). The only exception is the spectral region
269 near 2900 cm^{-1} ($3.4\text{ }\mu\text{m}$) that contains strong absorptions due to organics in carbonaceous
270 chondrites (e.g., Kaplan et al., 2019). The strong C-H absorptions of the epoxy in this region
271 preclude detailed analysis of native organic spectral features in epoxy-impregnated meteorite
272 thin sections (Supplemental Materials; Fig. SM1).

273 For each sample map, we identified spectra that contain a substantial amount of epoxy, such
274 as around sample edges and within sample pore space and fractures, in the reflected light image
275 collected by the μ -FTIR instrument (and BSE and EDS maps when available), as well as on the
276 basis of their spectral character, and we deleted these spectra from the map. We averaged the
277 remaining spectra to obtain the average bulk emissivity spectrum of each sample. Some bulk
278 sample spectra still showed evidence of a minor contribution from epoxy in the form of a small,
279 distinctive features around 11150 , 1250 , and 1500 cm^{-1} (Hamilton, 2018) (Fig. SM1). This is
280 attributed to epoxy that has permeated these relatively porous samples, and we removed it by
281 subtracting a fractional amount of a pure epoxy spectrum from the bulk spectrum using the
282 equation:

$$283 \quad y = \frac{(y_i - y_e * x)}{(1 - x)} \quad (1)$$

284 where y is final bulk spectrum, y_i is the initial bulk spectrum, y_e is the pure epoxy spectrum, and x
285 is the fraction of epoxy to remove (values ranging from 0.05 to 0.30), which was determined by
286 visual verification of complete removal of the epoxy feature (Fig. SM1). We calculated the band
287 parameters (described below) of the spectra both with and without the fractional epoxy spectrum
288 removed and found no significant difference in the parameter values. Thus, even though the
289 manual subtraction of epoxy from our bulk sample spectra results in a purer spectral
290 representation of each chondrite sample, this additional data processing step has no influence on
291 the conclusions reached in our study.

292 For all CMs, we used the BSE and EDS data to select matrix-only μ -FTIR spots within each
293 spectral map. Matrix-only spots were identified based on an absence of chondrules, refractory
294 inclusions, and mineral fragments visibly larger (at the 0.6–0.9 $\mu\text{m}/\text{pixel}$ scale of the maps) than
295 the surrounding matrix. We plotted candidate matrix spectra individually to confirm the absence
296 of spectral features of overlooked mineral fragments (olivine, pyroxene, carbonate, or sulfide).
297 We then averaged the matrix spectra (10–33 per sample; Tables 3–4) to obtain the average
298 matrix spectrum for each sample. Similar to the bulk sample spectra, some of the matrix-only
299 spectra exhibited small contributions from epoxy, and these were removed using the fractional
300 epoxy subtraction method described above.

301 To calculate the band parameters (Tables 3–4) from the averaged bulk sample and matrix-
302 only spectra we first isolated the band and used the POLYFIT function in MATLAB to model it.
303 For all bands, the band minimum [or maximum, in the case of the OH/H₂O band in the high-
304 wavenumber region (4000–2500 cm^{-1} ; 2.5–4 μm)] was located by fitting a 6th degree
305 polynomial. For the OH/H₂O band, we also fit a 3rd degree polynomial to the band to determine
306 the band center. We fit seven separate polynomials for all bands by varying (by up to 10 spectral

307 channels) the bounds of the band. The reported band minimum, maximum, or center is the
 308 average of these fits, and the reported uncertainty is 2σ . This is similar to the method of Takir et
 309 al. (2013); Takir et al. (2019) for calculating uncertainties on spectral band fits. For the Si-O
 310 bending band, the bounds of the band fit were ~ 490 to $\sim 405\text{cm}^{-1}$; for the Si-O stretching band,
 311 the bounds were ~ 1050 to $\sim 850\text{ cm}^{-1}$; for the Mg-OH band, the bounds were ~ 715 to $\sim 550\text{ cm}^{-1}$;
 312 and for the OH/H₂O band, the bounds were ~ 3700 to $\sim 3600\text{ cm}^{-1}$ (see Fig. 5 for an example of
 313 the polynomial fit to find band center and maximum for the OH/H₂O band).

314 For all bands except the Si-O bending band, we also calculated band depth. The band depth is
 315 defined as the distance between the straight-line continuum bounding the band and the spectral
 316 emissivity at the band minimum or maximum. For the Mg-OH band, these local maxima were
 317 approximately at ~ 715 to $\sim 550\text{ cm}^{-1}$; for the Si-O bending band, ~ 1050 to 700 cm^{-1} ; and for the
 318 OH/H₂O band, ~ 3900 to $\sim 3200\text{ cm}^{-1}$. For additional characterization of the Si-O stretching
 319 band, we calculated two other parameters: the separation between the Christiansen feature (CF;
 320 defined as the maximum emissivity between 1300 and 400 cm^{-1}) and the band minimum, and the
 321 band symmetry. We define band symmetry as the ratio of the band area (below the straight-line
 322 continuum) on each side of the band minimum:

$$323 \quad \frac{[A(\bar{\nu})]_{\zeta_2}^m}{[A(\bar{\nu})]_m^{\zeta_1}} \quad (2)$$

324 where A is the area of the band between the designated wavenumbers $\bar{\nu}$ (m is the band minimum,
 325 and ζ are the continuum points; $\zeta_2 > \zeta_1$).

326

327 **3. Results**

328 *3.1 Unheated, aqueously altered CMs*

329 *3.1.1 Relative degree of alteration among samples*

330 Because we are investigating the use of IR spectroscopy to distinguish the relative degree
331 of aqueous alteration among CM materials, we also characterized the relative degree of aqueous
332 alteration among our samples using traditional petrographic techniques. We chose two alteration
333 classification schemes, the petrologic subtype of Rubin et al. (2007) and the alteration scale of
334 Howard et al. (2015), because both utilize petrographic and mineralogical data that are available
335 for all of our samples (either through this work or available in previously published studies;
336 Table 1). For five samples, the same sections were previously assigned a petrologic subtype by
337 Friedrich et al. (2018) (Table 1). For ALH 85013, on re-inspection of the section, we reclassified
338 it as a CM 2.2 [cf. CM 2.0 in Friedrich et al. (2018)]. Our section of LEW 90500 differs from
339 that examined by Friedrich et al. (2018), but we confirmed the petrologic subtype of 2.2 assigned
340 by that study. The two Murchison sections are derived from the sample previously examined in
341 detail by Hanna et al. (2015), and we confirmed the petrologic subtype (2.5) assigned by Rubin
342 et al. (2007) for this sample as well.

343 To determine the alteration scale of Howard et al. (2015) for our samples, we used PSD-
344 XRD data available from previous studies, averaging the data for LAP 02333 from two
345 independent studies (Table 1). We then calculated the phyllosilicate fraction (PSF) and
346 converted this value into the petrographic type as defined by Howard et al. (2015). Although
347 that study refers to this latter value as a “petrographic type”, we use the term “alteration index”
348 (Table 1) to discriminate it from the petrologic subtype scale of Rubin et al. (2007). We then use
349 equation 2 of Howard et al. (2015) to convert the alteration index to the equivalent Rubin et al.
350 (2007) petrologic subtype. In this way we can directly compare the relative degree of alteration
351 among the samples that is derived independently using both petrographic observations and bulk

352 mineralogical data (Fig. 1). Although the bulk mineralogy of CI Alais translates to a PSF of 1.0,
353 we refrain from assigning a petrologic subtype for direct comparison to the CMs, as other
354 observations suggest that the aqueous alteration of most CIs, including Alais, is not complete (as
355 required by PSF 1.0 on the Howard et al. scale) (King et al., 2015).

356 Although the two scales generally agree on the relative alteration between samples within
357 the small number of CMs studied here (eight), they are only moderately linearly correlated ($R^2 =$
358 0.60; Fig. 1). This is a weaker correlation than that found by Howard et al. (2015) ($R^2 = 0.88$)
359 for the same number of CMs. In addition, we find less distinction in the predicted degree of

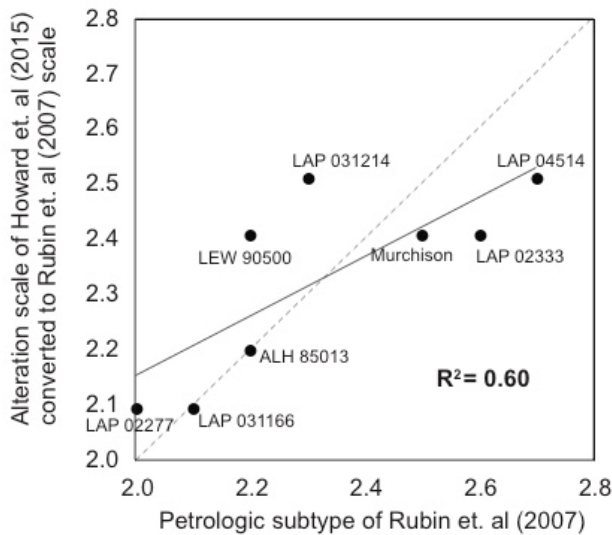


Figure 1. Comparison of CM alteration scales. Petrologic subtype of Rubin et al. (2007) compared to alteration index of Howard et al. (2015) [latter converted to the Rubin et al. (2007) scale using Eq. 2 of Howard et al. (2015)]. The two CM alteration scales are moderately correlated; however, the alteration scale of Howard et al. (2015) appears less sensitive to the relative degree of alteration among the CM suite presented here.

360
361 relative alteration among samples using the bulk mineralogy [PSF (Howard et al., 2015)]
362 approach, especially for the less altered CMs, compared to the petrographic observational
363 approach of Rubin et al. (2007). In other words, the Howard et al. (2015) classification scheme
364 appears less sensitive to the relative degree of alteration among the CM suite presented here.
365 Reasons for this discrepancy are explored in Section 4.3, but based on this analysis, we select the
366 relative alteration degree as determined by petrographic observations (i.e., petrographic subtype;

367 Rubin et al., 2007) as the basis of comparison for the IR spectra of the samples and their derived
368 spectral parameters.

369

370 *3.1.2 Spectral trends correlated with the degree of aqueous alteration*

371 Infrared spectra of the unheated CMs and CI indicate that several spectral trends are
372 correlated with petrologic subtype (Fig. 2). The CF ($\sim 1100\text{ cm}^{-1}$) shifts to lower wavenumbers
373 and the Si-O stretching band minimum ($\sim 950\text{ cm}^{-1}$) to higher wavenumbers with increasing
374 aqueous alteration. These shifts are linearly correlated ($R^2 = 0.82$ and 0.65 , respectively) with
375 petrologic subtype (Fig. 3A-B). The combination of these shifts also results in a strong

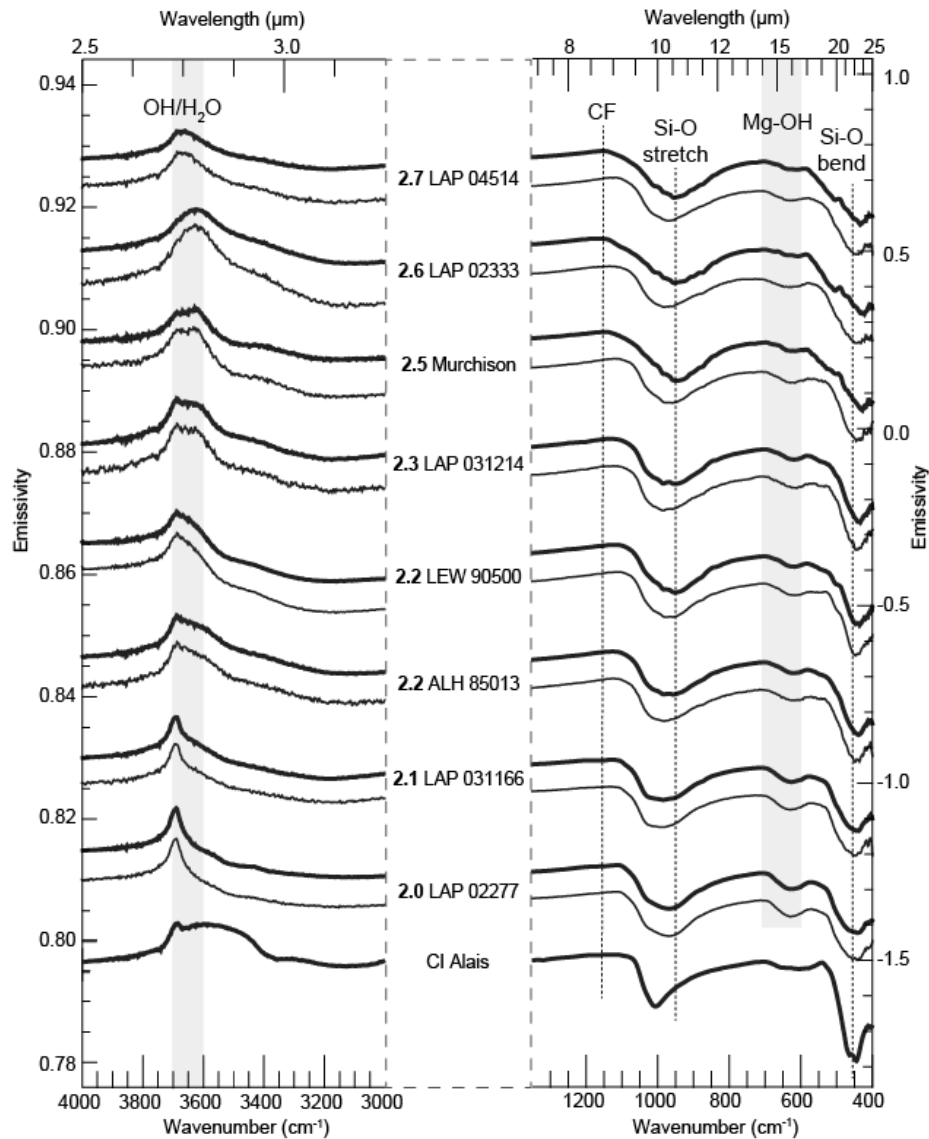


Figure 2. Average bulk sample spectra (thick lines) of eight CMs and 1 CI from least least (top spectrum; LAP 04514, 2.7) to most (bottom spectrum; CI Alais) aqueously altered. Matrix-only spectra (thin lines) of the CMs are also plotted. Spectra are offset (differently for each graph—note the different emissivity scales) and normalized for clarity. Grey boxes and dashed lines highlight spectral features discussed in the text.

376

377 correlation ($R^2 = 0.90$) between the separation distance of the CF and Si-O stretching center and
 378 petrologic subtype (Fig. 3C). With increasing alteration, the shape of the Si-O stretching band
 379 becomes increasingly asymmetric [Eq. (2)] about the band minimum with increasing petrologic

380 subtype ($R^2 = 0.71$; Fig 3D), and the bottom of the band becomes more rounded (Fig. 2). CMs
 381 with a petrologic subtype of 2.2 or above also have minor bands superimposed on the central part

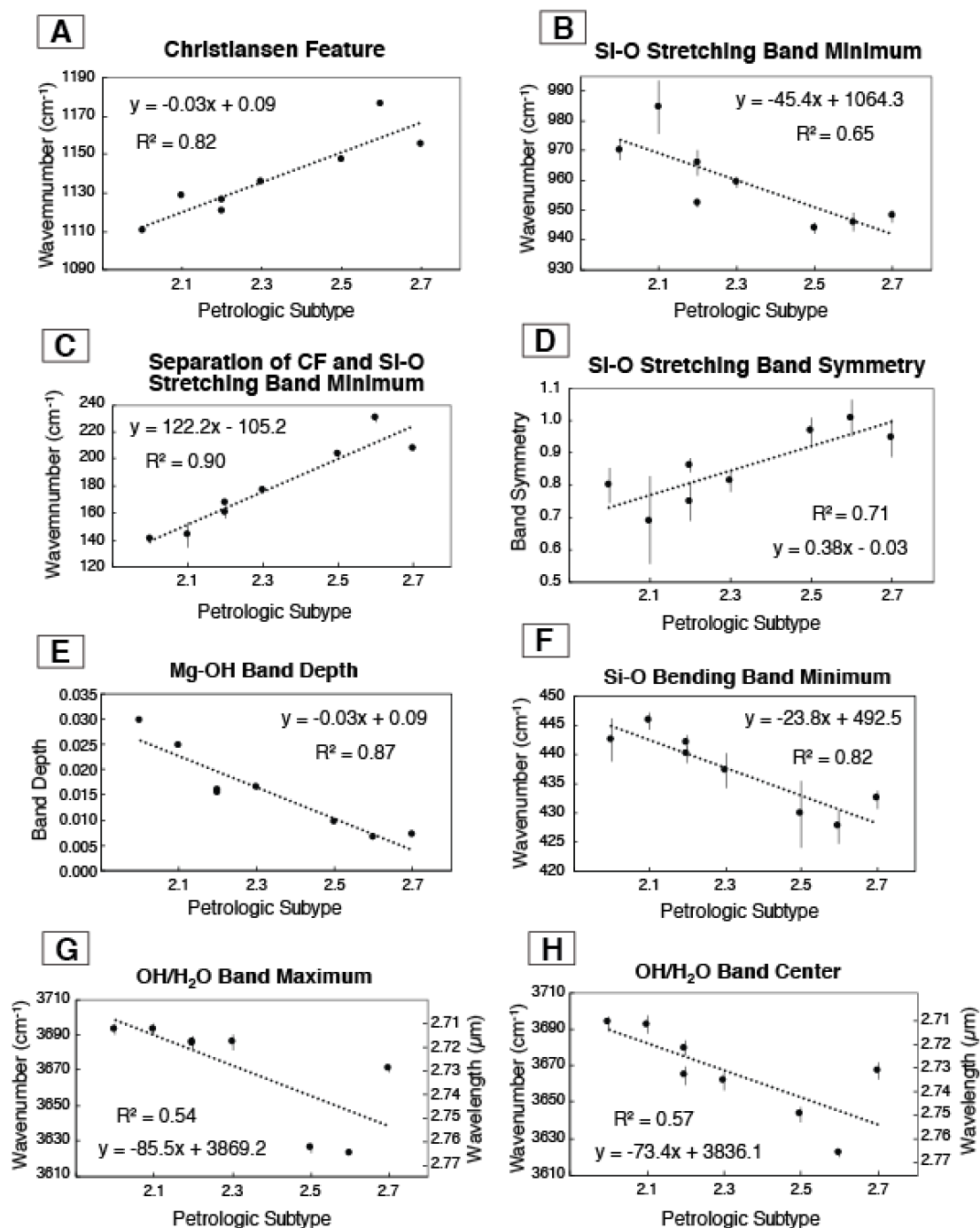


Figure 3. Band parameters of CM spectra in Fig. 2. Vertical bars indicate 2σ .

382

383 of the Si-O stretching band that result from the increased abundance of olivine in these samples
384 (Table 1 and Fig. 2). The shallow band centered around 625 cm^{-1} is attributed to a pair of weak
385 absorptions arising from librations (rotational vibrations) of the inner and surface hydroxyl ions
386 in the octahedral sheet of Mg-bearing serpentine, herein referred to as the Mg-OH band (Farmer,
387 1974; Michalski et al., 2006). The depth of this band increases as the degree of alteration
388 increases ($R^2 = 0.87$), although the spectrum of CI Alais does not follow this trend (Figs. 2 and
389 3E). The lowest wavenumber band has a minimum near 440 cm^{-1} and is a combination of the Si-
390 O bending, Mg-O-Si deformation, and Fe-O-Si deformation bands that overlap in this
391 wavenumber region (Farmer, 1974; Salisbury et al., 1987; Michalski et al., 2006), herein referred
392 to as the Si-O bending band. With increasing petrologic subtype, the Si-O bending band
393 minimum shifts to shorter wavenumbers ($R^2 = 0.82$; Fig. 3F) and broadens (Fig. 2). A local
394 emissivity maximum also appears on the high wavenumber side of the band near 490 cm^{-1} for
395 the least altered CMs (≥ 2.5 ; Fig. 2). Both the broadening of the band and this local emissivity
396 maximum are due to the increased abundance of forsteritic olivine, which has two major
397 absorptions in this wavelength region (Fig. 4) [see summary by Hamilton (2010) and references
398 therein]. In the most altered CMs (≤ 2.1), a large proportion olivine has been transformed to Mg-
399 Fe phyllosilicate (Table 1), and indeed the CM 2.0 LAP 02277 spectrum shows a strong
400 similarity to an Mg-Fe serpentine spectrum (Fig. 4). Although the CM 2.3 LAP 031214 and CM
401 2.2 LEW 90500 samples have abundant olivine (Table 1), the olivine maximum near 490 cm^{-1} is
402 subtle.

403 The other band present in the spectra of all samples, albeit at a greatly reduced spectral
404 contrast compared to the shorter wavenumber bands, is the $3700\text{--}3330\text{ cm}^{-1}$ ($\sim 2.7\text{--}3.0\text{ }\mu\text{m}$)
405 emission maximum (reflectance minimum) that is associated with OH^- and H_2O (Fig. 2),

406 referred to herein as the OH/H₂O band. The band shape varies among the samples, and in some
 407 cases the complexity of the shape means that the band maximum is not aligned with the band
 408 center (Fig. 5). Both the band maximum and center vary between 3690 cm⁻¹ (~2.71 μm) and

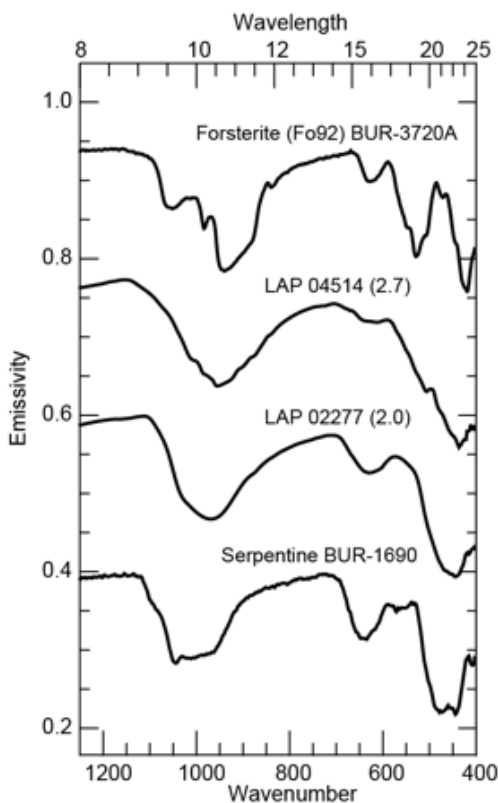


Figure 4. Emissivity spectra of LAP 04514 (CM 2.7) and LAP 02277 (CM 2.0) compared to forsterite (Fo92) and an MgFe serpentine spectra (Christensen et al., 2000). LAP 02277 has a strong similarity in overall spectral shape to the serpentine spectrum, with the same Christiansen feature location and broad, rounded Si-O stretching, Mg-OH, and Si-O bending bands. The LAP 04514 spectrum has a Christiansen feature location similar to a forsteritic olivine, and a long downward slope from ~17 to ~24 μm that likely results from an increased abundance of olivine, which has two strong absorptions in this wavelength region.

409
 410 3623 cm⁻¹ (~2.76 μm) and are only weakly correlated ($R^2 = 0.54$ and 0.57 , respectively) with
 411 petrologic subtype (Fig. 3G-H). Some of the samples also show increased emissivity on the low
 412 wavenumber side (< 3450 cm⁻¹; ≥ 2.9 μm), indicating that molecular H₂O is present (Aines and
 413 Rossman, 1984; Salisbury et al., 1987). This is most pronounced in CI Alais but is also
 414 discernable in the spectra of ALH 85013, LAP 031214, and LAP 02333. Because these spectra
 415 were collected from thin sections and not all sections show evidence of this molecular water, it is
 416 probably not the terrestrially adsorbed surface water that contaminates spectra of meteorite
 417 powders with much higher surface area (Beck et al., 2010; Takir et al., 2013). Rather, it is likely
 418 interlayer or mesopore water, which could be native to the meteorite or of terrestrial origin. To

419 check for the latter, we examined all unheated CM sections for a spatial correlation between
420 increased emissivity at 3450 cm^{-1} (defined as the difference in emissivity between 3800 and
421 3450 cm^{-1}) and the edges of the sample, especially when fusion crust was present.

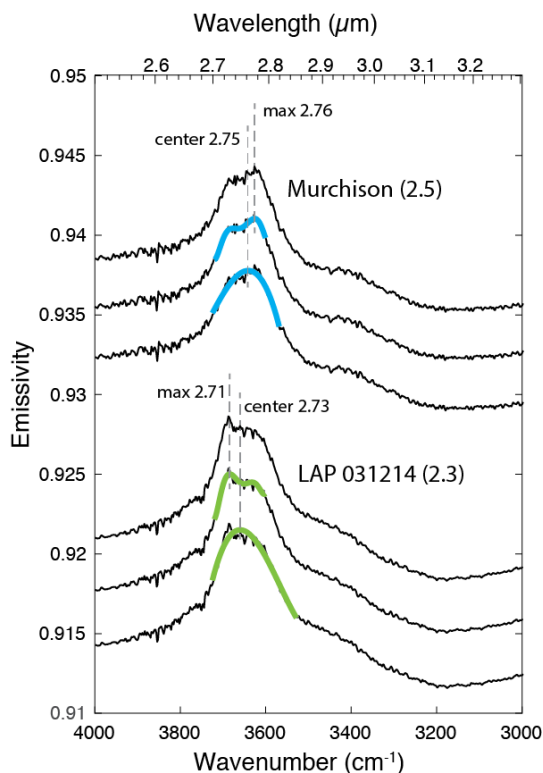


Figure 5. Band center and maximum for two CMs with complex OH/H₂O band shapes that result from a combination of Fe- and Mg-bearing serpentines. The OH/H₂O band of LAP 031214 (2.3) has an emissivity maximum at 2.71 μm indicative of Mg-rich serpentine. The longer wavelength maximum of Murchison (2.5) is consistent with a higher abundance of Fe-bearing serpentine, which has a longer wavelength peak than Mg-rich serpentine.

422
423 Both LAP 031166 and LAP 02277 display a clear increased emissivity at 3450 cm^{-1} in areas of
424 fusion crust and nearby regions with dehydration cracks, suggesting that molecular water from
425 terrestrial contamination is present near the sample surface. Because spectra of these areas were
426 excluded from the bulk sample spectra (Section 2.4), this increased emissivity at 3450 cm^{-1} is
427 not present in their bulk sample spectra. The absence of a correlation between increased
428 emissivity at 3450 cm^{-1} and sample edges for the other sections (especially ALH 85013, LAP
429 031214, and LAP 02333) does not necessarily indicate an absence of terrestrial water
430 contamination, but rather may be the result of the spectral map being located away from the
431 original sample surfaces. None of the sections, however, display any signs of terrestrial

432 weathering such as carbonate, sulfate, or iron oxide veins (Bland et al., 2006). Most importantly,
433 only CI Alais displays a characteristic molecular water band near 1630 cm^{-1} (Supplemental
434 Materials; Fig. SM2) due to H-O-H bending vibrations (Salisbury et al., 1987; Rossman, 1988),
435 implying that any molecular water within the unheated CM sections is minor and does not
436 substantively affect the shape and position of the OH/H₂O band, especially the position of the
437 band maximum. Finally, we note that most sections display a weak carbonate band near 1500
438 cm^{-1} that is consistent with its low abundance ($\leq 4\%$; Tables 1-2) within these samples (Fig.
439 SM2).

440 Samples of the same petrologic subtype (ALH 85013 and LEW 90500; both 2.2) have
441 very similar CF positions and overall spectral shapes, and their OH/H₂O band maximum and Si-
442 O bending minimum are within uncertainties of each other (Figs. 2 and 3; Table 3). Significant
443 differences between the two samples are in the OH/H₂O band center (lower wavenumber for
444 ALH 85013), Si-O stretching minimum (higher wavenumber for ALH 85013), Si-O stretching
445 symmetry (lower for ALH 85013), and Mg-OH band depth (higher for ALH 85013). The
446 difference in the OH/H₂O band center between the two samples is likely due to the increased
447 emissivity at $<3450\text{ cm}^{-1}$ for ALH 85013 that we attribute to the presence of molecular water.
448 The latter three differences all point to ALH 85013 being slightly more altered than LEW 90500,
449 based on the spectral trends among petrologic subtype outlined above and summarized in Figure
450 3. This is consistent with its higher phyllosilicate abundance and PSF compared to LEW 90500
451 (Table 1). While the Si-O stretching band minimum and symmetry differences are higher than
452 the average difference between the subtypes, these spectral parameters also have the lowest
453 correlations ($R^2 \leq 0.71$) with subtype. On the other hand, the difference in Mg-OH band depth is
454 much less than the average difference between subtype, which is highly correlated to subtype (R^2

455 = 0.87). In summary, our analysis suggests that the spectral variability among samples of the
456 same petrologic subtype is less than the spectral variability between subtypes, especially in
457 regards to spectral parameters that readily distinguish subtypes (CF, Mg-OH band depth, Si-O
458 bending minimum).

459

460 3.1.3 *Matrix spectra of aqueously altered CM chondrites*

461 Matrix-only spectra are shown in Figure 2 along with their corresponding bulk sample
462 spectra. For individual samples, the averaged matrix spectrum at high wavenumbers ($> 3000 \text{ cm}^{-1}$)
463 is very similar to that of the bulk sample, with the same general shape and maxima location for
464 the OH/H₂O band, although the matrix-only spectra have a consistently larger OH/H₂O band
465 depth (Table 3), likely attributable to the exclusion of some anhydrous phases that would act to
466 reduce the contrast of this feature. At lower wavenumbers ($< 1200 \text{ cm}^{-1}$), the bulk sample and
467 matrix spectra are similar for the two most altered CMs (LAP 02277 and LAP 031166) but show
468 increasing differences among less altered CMs (≥ 2.3). First, for the matrix spectra, the CF is at
469 a lower wavenumber and the Si-O stretching band minima are at a higher wavenumber compared
470 to those of the associated bulk sample spectra. The matrix spectra do not show the $\sim 490 \text{ cm}^{-1}$
471 emissivity maximum associated with olivine that is evident in the bulk sample spectra of the less
472 altered CMs, and the $\sim 440 \text{ cm}^{-1}$ band of the matrix spectra is also broader with a higher
473 wavenumber minimum compared to the bulk sample spectra. Thus, the low-wavenumber
474 ($< 1200 \text{ cm}^{-1}$) matrix spectra do not display the spectral changes correlated with the degree of
475 aqueous alteration that are evident in the bulk sample spectra of these CMs. Rather, the matrix
476 spectra among the differently altered CMs are consistent and generally match the bulk sample
477 spectra of the most altered CMs (≤ 2.1).

478 Examination of the various band parameters of the matrix-only spectra with respect to
479 petrologic subtype supports these observations. The trend of petrologic subtype with the
480 maximum and center of the OH/H₂O band is essentially unchanged, with correlations of $R^2 =$
481 0.54 and $R^2 = 0.63$, respectively (Supplemental Materials; Fig. SM3). This is expected, as the
482 OH/H₂O band is similar between matrix and bulk sample spectra. For most bands at longer
483 wavelength, linear correlations are low ($R^2 < 0.44$; ; Fig. SM3), as expected. The only exception
484 is the depth of the Mg-OH band, where there is still a moderate correlation ($R^2 = 0.66$; ; Fig.
485 SM3), with petrologic subtype among the matrix-only spectra.

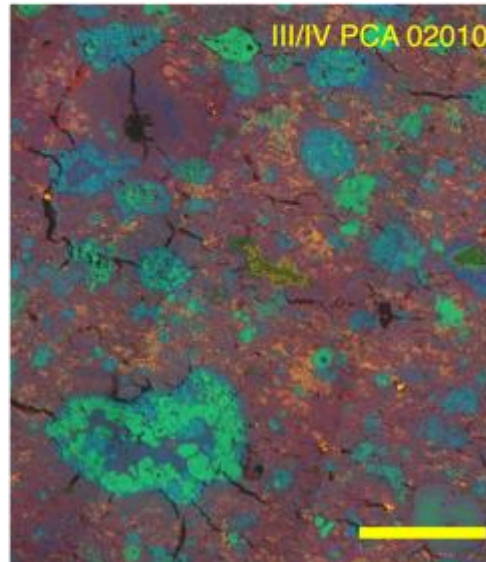
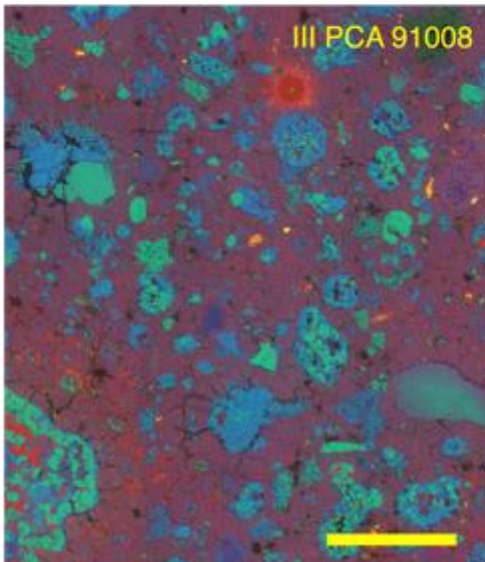
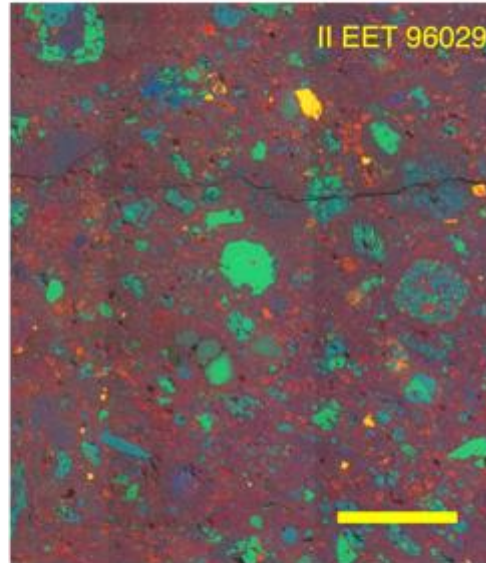
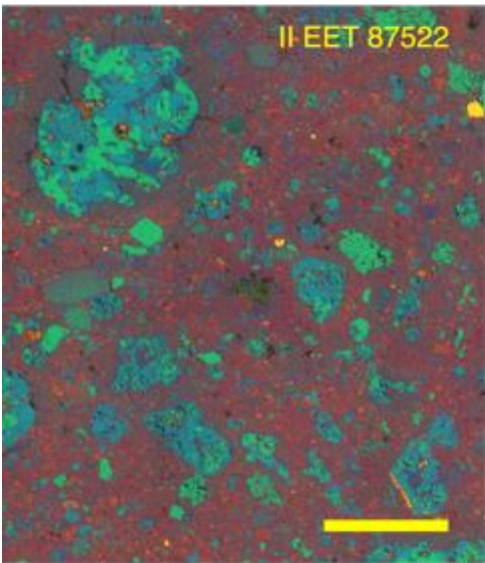
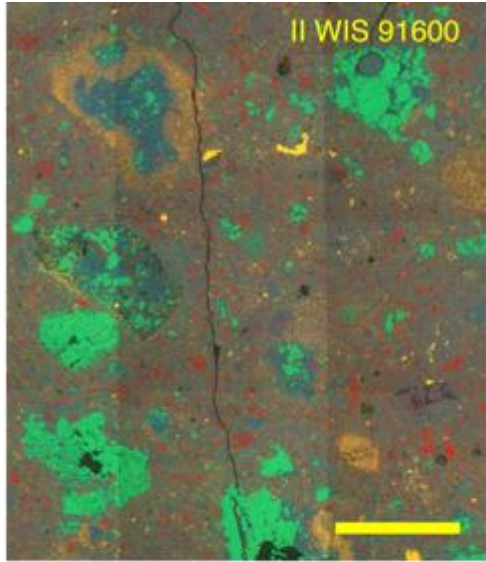
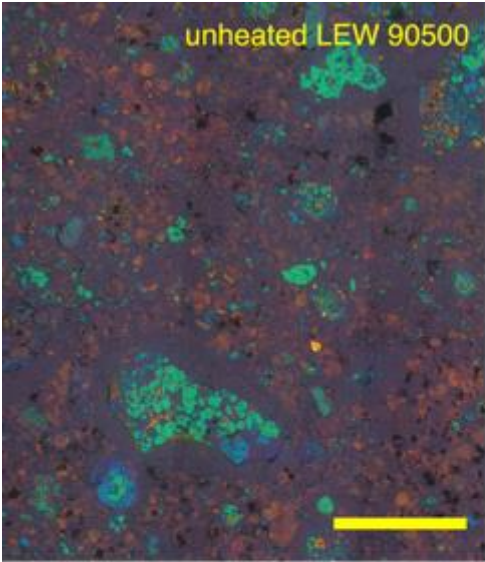
486

487 *3.2 Heated CMs*

488 *3.2.1 Petrographic trends associated with degree of heating*

489 Because some aqueously altered samples are known to have undergone subsequent
490 heating (e.g., Nakamura, 2005; Tonui et al., 2014), we also characterized the mineralogical,
491 chemical, textural, and spectral effects of such heating. In addition to the PSD-XRD data
492 presented here, we compiled all available mineralogical and PSD-XRD data for our suite of five
493 heated CMs (Table 2). We use the heating stage scale of Nakamura (2005) to rank the relative
494 heating degree among the samples; in addition, EDS X-ray compositional false-color maps
495 highlight the chemical and textural changes that occur with increased degree of heating (Table 2
496 and Fig. 6). PSD-XRD data indicates that the abundances of olivine and pyroxene increase and
497 the abundances of amorphous materials and magnetite decrease with increased heating stage
498 (Table 2). Compared to an unheated CM (LEW 90500), Stage II (300–500°C) samples show a
499 more homogenized matrix with an absence of well-defined tochilinite-cronstedtite intergrowths
500 (TCIs; orange-colored phase in LEW 90500 EDS map). The matrices of EET 87522 and EET

501 96029 are dominated by a dispersed red-colored (in the EDS false color map) phase that is likely
502 composed of Fe-bearing material that has resulted from the breakdown of Fe serpentine (i.e.,
503 cronstedtite) and tochilinite, which occurs in Stage II heating (Nakamura, 2005). For WIS
504 91600, this Fe liberation has resulted in the formation of magnetite and Fe sulfide (Table 2)—
505 which are visible in the map as discrete, bright red phases and diffuse, gold phases,
506 respectively—within the matrix and has been observed by other workers (Brearley, 2004; Tonui
507 et al., 2014). All three Stage II samples have a small proportion of chondrules (< ~10%) with
508 thin dehydration cracks within the fine-grained rims (FGRs) surrounding them. Among these
509 three samples, only WIS 91600 shows obvious mineralogical evidence of terrestrial weathering,



(prev page) Figure 6. EDS X-ray elemental false-color maps highlighting the various phases and textures among the heated CMs. Unheated LEW 90500 is shown for comparison. In all maps, Fe is red, Mg is green, Si is blue, S is yellow, and scale bars are 500 μm . The brightest green and blue phases within the chondrules in all maps are Mg-olivine and Mg-pyroxene, respectively. Fe sulfide and tochilinite are yellow to orange, and pure red phases are primarily magnetite with minor metal.

510

511 with a diffuse Mg-bearing, Si- and Fe-poor phase distributed in an elongated patch that is parallel
512 to the fusion crust. Isolated spectra of this phase show a band near 1600 cm^{-1} (Supplemental
513 Material; Fig. SM2) due to H-O-H bending vibrations (Aines and Rossman, 1984; Salisbury et
514 al., 1987), so we tentatively interpret this phase as a Mg-bearing, terrestrial hydrated evaporite
515 such as hydromagnesite (Bland et al., 2006).

516 The more highly heated [$> 500^\circ\text{C}$; (Nakamura, 2005)] CMs PCA 91008 and PCA 02010
517 display more pronounced textural changes, although the abundant secondary olivine that has
518 crystallized within their matrices (Table 2) is not visible at the scale of the EDS maps (Fig. 6).
519 The matrix of Stage III ($500 - 750^\circ\text{C}$) PCA 91008 is even more chemically and texturally
520 homogenized than that of the Stage II CMs, and dehydration cracks within FGRs are more
521 abundant (Fig. 6). A large magnetite nodule is evident at the top of the map and within the
522 chondrule at the lower left, which is consistent with the moderate abundance (2.7 vol. %) of
523 magnetite in this sample (Table 2). The X-ray map shows signs of Fe diffusion from the large
524 magnetite nodule into the surrounding matrix, likely caused by terrestrial alteration ['rusts' were
525 detected via PSD-XRD in another aliquot of this sample; Table 2)]. The most extensively heated
526 CM, Stage III/IV ($>750^\circ\text{C}$) PCA 02010, has abundant large dehydration cracks around
527 chondrules and within the matrix, and, similar to WIS 91600, diffuse patches of Fe-sulfide are
528 visible within the matrix (Table 2 and Fig. 6). The chondrules in PCA 02010 also appear
529 'blurred', a texture that has been previously noted in highly heated CMs, suggesting incipient
530 recrystallization and integration with the surrounding matrix (Tonui et al., 2014). Also visible in

531 the upper left corner is a thin crack filled with Fe oxide (rust) from terrestrial weathering; similar
532 cracks are seen elsewhere in this section and range in width from 8 to 20 μm . The detection of
533 feldspar (3.2%; Table 2) with PSD-XRD indicates that PCA 02010 may be a stage IV or even
534 higher, as feldspar is found within PCA 02012 [estimated to have been heated to 900°C (Nakato
535 et al., 2013)] and is also present in thermally metamorphosed type 3 chondrites (Grossman and
536 Brearley, 2010).

537

538 3.2.2 *Spectral trends associated with degree of heating*

539 The bulk sample IR spectra among the heated CMs show differences associated with
540 their relative heating stage (Fig. 7). Several band parameters also show a general correlation with
541 degree of heating (Table 4), although we did not test for a linear correlation due to the small
542 sample size, especially in regards to the heating stages represented. The CF shifts to slightly
543 higher wavenumbers and the Si-O stretching band minimum to lower wavenumbers for the Stage
544 III–III/IV than for the Stage II CMs. This translates to an increase in the separation distance
545 between the CF and Si-O stretching band minimum as heating proceeds (Table 4). The Stage
546 III–III/IV CMs also have a generally more symmetric Si-O stretching band shape than the
547 weakly heated samples. This is unsurprising as the Stage III and III/IV samples show a
548 markedly different band shape that is sharper with several overlapping bands not present in the
549 Stage II samples. These overlapping bands are most evident in PCA 02010 as two small
550 shoulder bands at 965 and 833 cm^{-1} on either side of the Si-O stretching minimum that are
551 consistent with the olivine that dominates this sample (Hamilton, 2010; Beck et al., 2014), some
552 of which is secondary (Table 2). These olivine shoulder bands are weaker in the PCA 91008
553 spectrum, consistent with this sample's lower olivine abundance (Table 2). The positions of

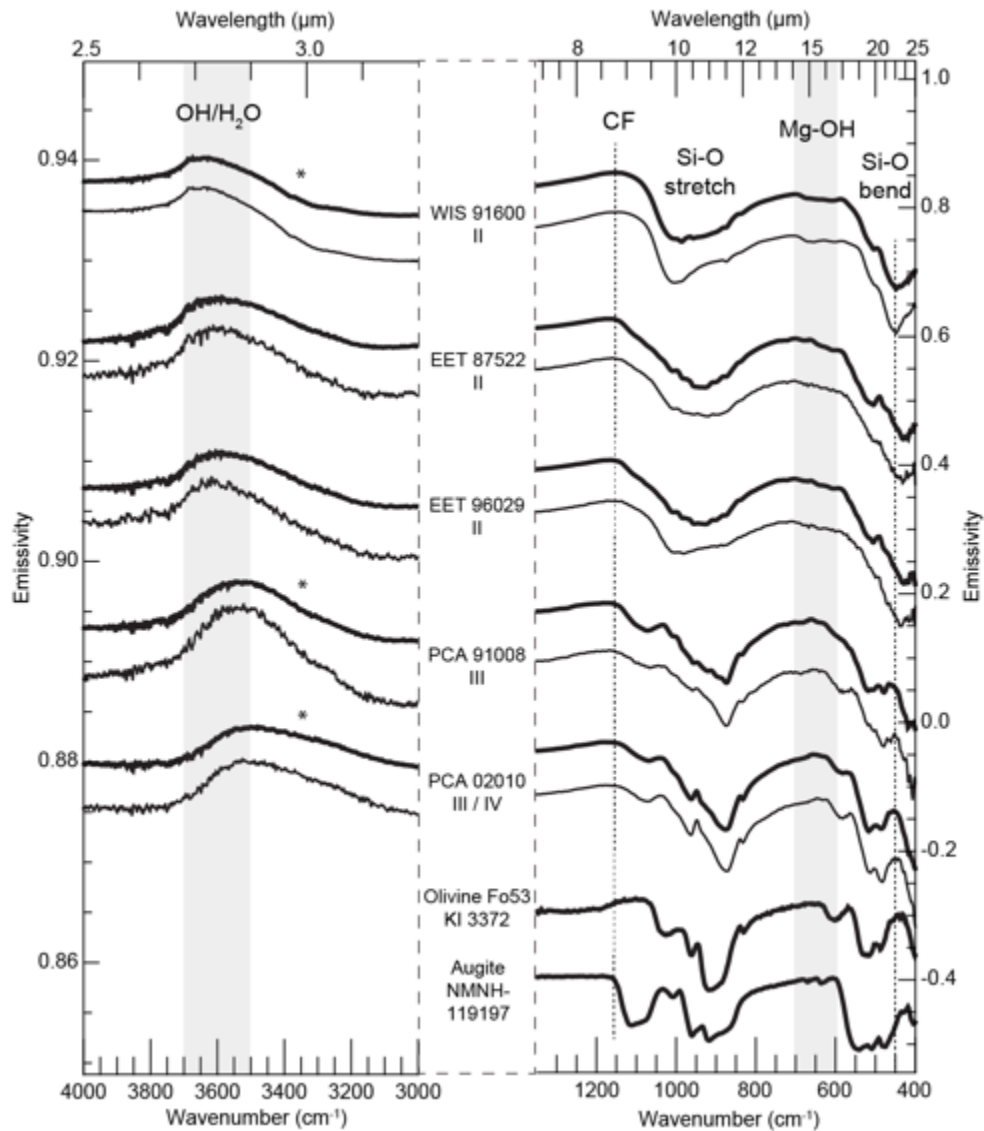


Figure 7. Average bulk sample (thick line) and matrix (thin line) spectra of five thermally metamorphosed CMs from least (top spectrum) to most (bottom spectrum) heated according to the heating stage of Nakamura (2005). The olivine Fo53 spectrum is from Koeppen and Hamilton (2008) and Hamilton (2010), and the augite spectrum is from Hamilton (2000) and Christensen et al. (2000). Asterisks denote evidence that the 3- μ m band has been contaminated by terrestrial weathering. Spectra are offset (differently for each graph—note the different emissivity scales) and normalized for clarity. Grey boxes and dashed lines highlight spectral features discussed in the text.

554

555 these shoulder bands vary with the Mg content (Fo#) of the olivine and here are most consistent

556 with an olivine of intermediate (Fo₅₀₋₇₀) composition (Koeppen and Hamilton, 2008; Hamilton,

557 2010) (Fig. 7). All heated samples except WIS 91600 show numerous minor bands

558 superimposed throughout the Si-O stretching region that are characteristic of Mg-rich, high-Ca

559 pyroxene (Hamilton, 2000) and olivine (Duke and Stephens, 1964; Burns and Huggins, 1972;
560 Hamilton, 2010) consistent with the PSD-XRD results (Fig. 7, Table 2). A band at $\sim 1085\text{ cm}^{-1}$,
561 also indicative of pyroxene (Hamilton, 2000), is present in the samples heated to Stage III and
562 above (Fig. 7). While EET 96029 also has a relatively high pyroxene abundance (15.7%; Table
563 2), this band is masked by the Si-O stretching band of the amorphous silicate (64.7%; Table 2).

564 At lower wavenumbers ($<600\text{ cm}^{-1}$), the bulk sample spectra for all heated CMs show
565 features generally attributable to the presence of olivine and pyroxene (Fig. 7) in differing
566 proportions. All Stage II samples have a broad Si-O bending band with a local emissivity
567 maximum near 490 cm^{-1} that is present in the least aqueously altered CMs (Fig. 2). Because
568 these samples have not yet formed secondary olivine (Table 2) due to their low heating stage
569 (Nakamura, 2005), this spectral feature represents primary olivine in the samples. The more
570 highly heated samples PCA 91008 and PCA 02010 both show spectral features associated with
571 Fe-bearing olivine and pyroxene in this region, with absorptions near 588 , 518 , and 479 cm^{-1}
572 (Duke and Stephens, 1964; Hamilton, 2000; Hamilton, 2010). These bands are more pronounced
573 in the more extensively heated PCA 02010 despite the similar olivine and pyroxene abundances
574 in these two samples (Table 2), likely indicating that these phases are more crystalline than in
575 PCA 91008, which is consistent with its higher heating stage (Nakamura, 2005). Additionally,
576 although difficult to verify because it is at the edge of our spectral range, it appears that the band
577 minimum of the Si-O bending band moves to lower wavenumbers with increasing thermal
578 metamorphism and is less than 400 cm^{-1} for PCA 91008 and PCA 02010—also consistent with
579 an Fe-bearing olivine (Hamilton, 2010).

580 The $3700\text{--}3300\text{ cm}^{-1}$ ($2.7\text{--}3.0\text{ }\mu\text{m}$) OH/H₂O band emission maximum consistently moves
581 to lower wavenumbers with increased degree of heating, from 3643 cm^{-1} ($2.75\text{ }\mu\text{m}$) to 3495 cm^{-1}

582 (2.86 μm) (Table 4 and Fig. 7). In all samples, this band is broad, with a band center that
583 overlaps its band maximum within their uncertainties (Table 4), and a broad shoulder is present
584 with increased emissivity on the low wavenumber side ($< 3450 \text{ cm}^{-1}$; $\geq 2.9 \mu\text{m}$), suggesting that
585 molecular H_2O is present (Aines and Rossman, 1984; Salisbury et al., 1987). Like for the
586 unheated CM sections, we checked for an increased emissivity at 3450 cm^{-1} near sample
587 surfaces, and only PCA 91008 showed a slight increase near the fusion crust. No fusion crust is
588 visible in the sections of EET 87522, EET 96029, and PCA 02010, and for WIS 91600 there is
589 no increase in 3450 cm^{-1} emissivity with proximity to its fusion crust. Previous studies have
590 noted that the OH/ H_2O bands of PCA 91008 and PCA 02010 are deeper than expected and
591 therefore have been affected by terrestrial weathering (Tonui et al., 2014; King et al., 2016). Our
592 data supports this interpretation as both samples show mineralogical evidence of terrestrial
593 weathering (Section 3.2.1) and display prominent OH/ H_2O bands despite their IR spectra at
594 lower wavenumbers ($< 1200 \text{ cm}^{-1}$) being dominated by olivine and pyroxene spectral features
595 (Fig. 7). There is also no PSD-XRD evidence for hydrous phases within these samples (Table
596 2). Because WIS 91600 displays a band near 1600 cm^{-1} that could be attributed to molecular
597 water (Aines and Rossman, 1984; Salisbury et al., 1987) (Supplemental Materials; Fig. SM2),
598 and there is considerable terrestrial weathering in this section (Section 3.2.1), its OH/ H_2O band
599 likely has also been affected by terrestrial weathering.

600

601 3.2.3 *Matrix spectra of heated CM chondrites*

602 At wavenumbers lower than 1200 cm^{-1} , the matrix-only spectra differ from the bulk
603 sample spectra of the heated samples (Fig. 7). The matrix-only spectra of WIS 91600 and EET
604 96029 both exhibit a more asymmetric shape and higher wavenumber minimum for the Si-O

605 stretching band relative to their bulk sample spectra (Fig. 7 and Table 4). The matrix spectrum
606 of PCA 91008 shows a narrower Si-O stretching band with a weaker pyroxene band near 1085
607 cm^{-1} compared to its bulk spectrum. The Si-O stretching band of PCA 02010 is similar in the
608 matrix and bulk sample spectra, although the olivine and pyroxene bands may be slightly deeper
609 in the matrix spectrum. All three Stage II CMs have a noticeably weaker or absent emissivity
610 maximum near 490 cm^{-1} (attributable to olivine) in their matrix-only spectra. For the more
611 highly heated CMs PCA 91008 and PCA 02010, the largest differences between the matrix and
612 bulk sample spectra are in the strength of the olivine bands near 588 and 479 cm^{-1} , which are
613 both stronger in the matrix-only spectra. For PCA 91008, the 588 cm^{-1} olivine band is not
614 discernable in the bulk sample spectrum.

615 The $3700\text{--}3330 \text{ cm}^{-1}$ ($2.7\text{--}3.0 \mu\text{m}$) OH/H₂O band emission maximum of the matrix-only
616 spectral shape is very similar to that of the bulk sample spectrum of the heated CMs, although
617 the band maximum of the matrix is at a slightly higher wavenumber (by $6\text{--}26 \text{ cm}^{-1}$) for all
618 samples except EET 87522 (Table 4). Another difference between matrix and bulk sample
619 spectra in this wavelength region is that the OH/H₂O band depth of the matrix-only spectrum is
620 consistently greater than for the bulk sample spectrum (Table 4), as was found for the unheated
621 CMs, and probably represents the exclusion of some fraction of anhydrous phases.

622

623 4. Discussion

624 4.1 Low-wavenumber ($<1200 \text{ cm}^{-1}$) spectral indicators of secondary processes in CMs

625 4.1.1 Aqueous alteration indicators

626 There are several spectral trends in the IR at wavenumbers $<1200 \text{ cm}^{-1}$ that can be correlated
627 with the relative degree of aqueous alteration among the CMs. At this wavenumber range,
628 spectral features are dominated by both hydrated and anhydrous silicates. With increasing

629 degree of aqueous alteration (i.e., lower petrographic subtype), the CF moves to lower
630 wavenumbers, the Si-O stretching ($\sim 950\text{ cm}^{-1}$) and Si-O bending ($\sim 440\text{ cm}^{-1}$) band minima
631 move to higher wavenumbers, the separation of the CF and Si-O stretching band minimum
632 decreases, and the depth of the Mg-OH band ($\sim 625\text{ cm}^{-1}$) increases (Figs. 2-3). The strongest
633 correlation with petrographic subtype ($R^2 = 0.90$) is the separation of the CF and Si-O stretching
634 band minimum, and using the equation defined by the linear fit of that relationship:

$$635 \quad \text{petrologic subtype} = \frac{y+105.2}{122.2} \quad (3)$$

636 the petrologic subtype of the sample is predicted to within 0.1 accuracy based on the
637 measurement of the separation y in wavenumbers for the sample suite presented here.

638 Because all CMs are volumetrically dominated by phyllosilicates, and their proportion
639 increases with aqueous alteration (Table 1; see also Howard et al., 2015), the CF and spectral
640 bands are dominated by hydrous silicates, with contributions from the anhydrous silicates olivine
641 and pyroxene in the least altered CMs (Fig. 4), as noted by previous workers (Sandford, 1984;
642 Beck et al., 2014; Beck et al., 2018). Therefore, the shifting of these bands (and change in depth
643 for the Mg-OH band) could reflect the relative abundance, structure, and composition of the
644 phyllosilicate that shifts from an Fe-bearing serpentine (i.e., cronstedtite) to a more Mg-
645 dominated serpentine as alteration proceeds (Tomeoka et al., 1989; Zolensky et al., 1993;
646 Browning et al., 1996). The depth of the Mg-OH band, which is attributable to Mg-bearing
647 serpentine, is consistent with this interpretation, as it systematically increases with decreasing
648 petrologic subtype ($R^2 = 0.87$) (Figs. 2 and 3E). Olivine, which has higher abundances within the
649 least altered CMs (Table 1), also has an absorption in this region (narrower and centered at a
650 slightly lower wavenumber) but has a relatively weaker spectral signature compared to Mg-
651 bearing serpentine (Fig. 4). However, the other spectral parameters (CF, Si-O stretching

652 minimum, Si-O stretching symmetry, and Si-O bending minimum) are significantly influenced
653 by the presence of olivine, as well as pyroxene, which have strong absorptions in these regions
654 (Figs. 4 and 7). In the Si-O stretching region, the presence of these anhydrous silicates in the
655 least altered CMs causes a strong absorption at a lower wavenumber than serpentine, which
656 results in a movement of the Si-O stretching minimum to a lower wavenumber, as well as a more
657 symmetrical band shape (Fig. 2). The CF likewise shifts to higher wavenumbers with increasing
658 anhydrous abundance due to the higher wavenumber CF of olivine and pyroxene compared to
659 serpentine. In the Si-O bending region, as the proportion of serpentine increases with alteration,
660 this band is less influenced by the strongest olivine absorption near 420 cm^{-1} , and the band
661 minimum shifts to higher wavenumbers (Fig. 2). In summary, the spectral trends at
662 wavenumbers $<1200\text{ cm}^{-1}$ among the unheated, aqueously altered CMs are a result of the
663 mineralogical and compositional changes as ferromagnesian silicates are altered to increasingly
664 Mg-rich phyllosilicates (Zolensky et al., 1997; Rubin et al., 2007; Howard et al., 2015).
665 Specifically, as olivine and pyroxene are replaced by phyllosilicate with increasing degree of
666 alteration among the CMs (Rubin et al., 2007; Howard et al., 2015), all bands become relatively
667 more influenced by the phyllosilicate (serpentine) compared to the anhydrous silicates (primarily
668 olivine but also pyroxene).

669

670 4.1.2 *Thermal metamorphism indicators*

671

672 With subsequent heating of the CMs, several spectral features at low wavenumber (< 1200
673 cm^{-1}) are associated with the different heating stages. First, the Si-O stretching band broadens
674 (Stage II) and then, with higher heating stages (Stage III+), becomes sharp with noticeable
675 olivine bands with positions consistent with Fe-bearing olivine (Fig. 7) that can be attributed to

676 secondary olivine formation (Nakamura, 2005). The Si-O bending minimum also shifts to lower
677 wavenumbers with heating, forming strong olivine bands in the 500 cm^{-1} region. We attribute
678 the initial broadening of the Si-O stretching band in the mildly heated (Stage II) samples to the
679 thermal decomposition of phyllosilicates, which several studies have shown forms a highly
680 disordered, amorphous phase that is intermediate to the secondary olivine formed at higher
681 temperatures (Akai, 1988; Nakamura, 2005; Tonui et al., 2014). Amorphous and poorly
682 crystalline phases typically result in broader Reststrahlen bands relative to their well-crystalline
683 counterparts due to the wide range of site sizes and symmetries and variable orientations of
684 molecules within those sites (Farmer, 1958; Gaffey et al., 1993b). Although the spectral changes
685 for CMs heated at \geq Stage III are readily visible as strong bands from the secondary olivine
686 appear, the changes associated with only mild heating (Stage II) are subtle. Further, because the
687 original petrologic subtype (i.e., 2.0 to 2.7) of the Stage II samples is not known, some of these
688 spectral modifications may not be attributable to mild heating and thus are ambiguous.

689 Some of this ambiguity may be resolved with other observations, however. First, if we
690 assume that the amorphous component for the Stage II samples was originally phyllosilicate, we
691 can calculate the PSF prior to thermal metamorphism to derive an alteration index. For EET
692 96029, this results in an alteration index of 1.6 [petrologic subtype 2.5 (Howard et al., 2015)]; for
693 EET 87522, 1.5 (petrologic subtype 2.4); and for WIS 91600, 1.3 (2.2). For the mildly heated
694 EET 96029, Lee et al. (2016) assigned a pre-heating petrologic subtype of 2.7 based on detailed
695 observations of components least likely to be affected by mild heating, including chondrule
696 mesostasis and Fe,Ni metal. Because the low stage of heating (II) for EET 96029 precludes the
697 formation of secondary olivine, the emissivity maximum near 490 cm^{-1} , attributable to olivine,
698 must represent primary olivine, similar to the least aqueously altered CMs (≥ 2.5 ; Fig. 2). This

699 olivine signature is very weak in the matrix-only spectrum of EET 96029 (Fig. 7), suggesting
700 that, as for the unheated CMs, the olivine is primarily located within the chondrules and other
701 large inclusions (i.e., not the fine-grained matrix). The isolation of the olivine spectral signature
702 to the chondrules [as opposed to the matrix, where heating effects and secondary products are
703 concentrated (Nakamura, 2005)], further supports that EET 96029, despite mild heating, can be
704 classified as a very mildly aqueously altered CM, as suggested by Lee et al. (2016). The 490
705 cm^{-1} olivine feature is also present in the spectra of WIS 91600 and EET 87522, suggesting that
706 they were also only mildly aqueously altered prior to heating, although the relatively smaller 490
707 cm^{-1} emissivity minimum, the lower wavenumber position of its CF, and absence of the minor
708 pyroxene bands in its Si-O stretching region suggests that WIS 91600 has experienced more
709 aqueous alteration than EET 87522 and EET 96029. This is supported by the estimation of its
710 alteration index prior to heating (1.3), which is lower than for EET 87522 (1.5) and EET 96029
711 (1.6).

712 Because we have established, both from the prior petrographic work of Lee et al. (2016)
713 and the spectral data presented here, that EET 96029 is a relatively unaltered CM (2.7), we can
714 now further confirm the specific spectral changes that occur solely from mild heating by
715 comparing the spectrum of EET 96029 to that of another CM 2.7 (LAP 04514) that has not been
716 heated (Fig. 8). Between these samples, the spectral band with the largest amount of

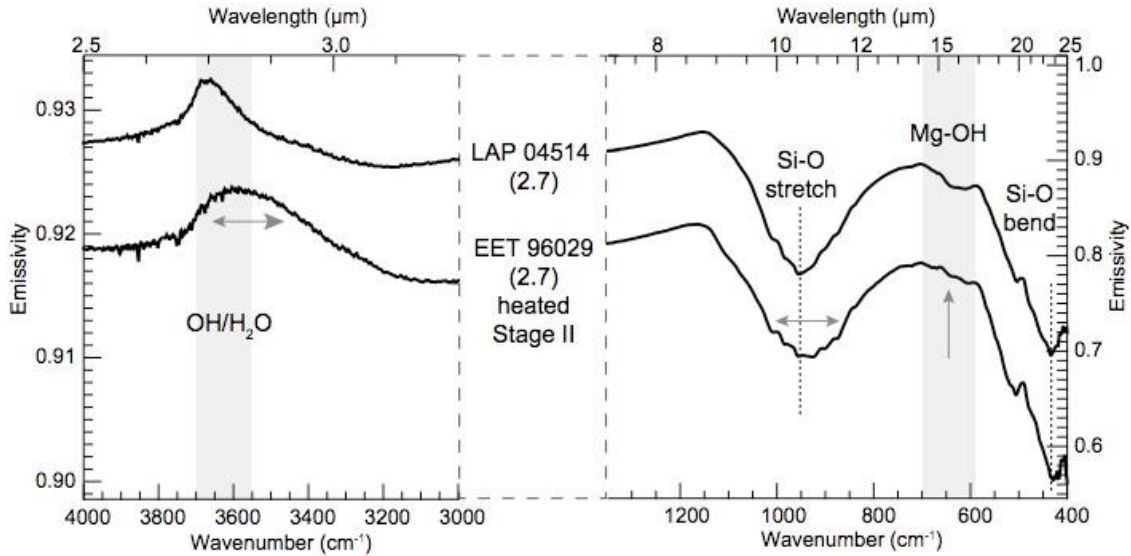


Figure 8. Unheated LAP 04514 (2.7) compared to mildly heated Stage II EET 96029 (2.7). Grey arrows and boxes highlight the spectral changes associated with mild heating. With mild heating, the Si-O stretching band broadens (right horizontal arrow) and its minimum shifts to smaller wavenumber (left dashed line), the Mg-OH band disappears (vertical arrow and grey box) and the OH/H₂O band broadens and moves to longer wavelengths (left horizontal arrow and grey box), although this may also be due to rehydration from terrestrial weathering (see Section 4.2). There is no significant change in the location of the Si-O bending minimum (right dashed line). Spectra are offset (differently for each graph—note the different emissivity scales) and normalized for clarity.

717

718 modification with heating is the Si-O stretching region. First, the CF location is different
 719 between them (1165 cm^{-1} for EET 96029 and 1155 cm^{-1} for LAP 04514). This difference could
 720 be the result of heating; however, the position of the CF is highly sensitive (i.e., highly
 721 correlated; $R^2 = 0.82$) to the degree of aqueous alteration due to the varying proportions of
 722 phyllosilicate and anhydrous silicates as discussed above. In addition, when examining samples
 723 of the same petrologic subtype (ALH 85013 and LEW 90500; both 2.2), the CF location differs
 724 by 13 cm^{-1} (greater than the 10 cm^{-1} here). Therefore, although mild heating could cause the CF
 725 to shift to a higher wavenumber, as it does for strongly heated samples (Table 4; Fig. 7), it is
 726 more difficult to attribute this solely to heating rather than to a minor difference in degree of
 727 aqueous alteration, even within the same petrologic subtype. The other major change within the

728 Si-O stretching region is that for the mildly heated EET 96029, the band is wider and less sharp
729 at the minimum than that of LAP 04514, and its band minimum is at lower wavenumber (935 ± 4
730 cm^{-1}) than for LAP 04514 ($946 \pm 2 \text{ cm}^{-1}$). The other band that is modified by mild heating is the
731 Mg-OH band, which is present, although weak, in the LAP 04514 spectrum, but absent from the
732 EET 96029 spectrum. Finally, the Si-O bending minima for LAP 04514 and EET 96029 are
733 within the 2σ uncertainty of one another (432 and 428 cm^{-1}), indicating that no significant shift
734 of this band occurs with mild heating.

735 In summary, within the low-wavenumber region ($<1200 \text{ cm}^{-1}$), where spectral features
736 are dominated by both hydrated and anhydrous silicates, the largest effect of mild heating is a
737 broadening of the Si-O stretching band, a low-wavenumber shift of its band minimum, and the
738 disappearance of the Mg-OH band (Fig. 8). The broadening and shifting of the Si-O stretching
739 band are also seen in experimental space weathering studies of simulated solar wind irradiation
740 in CMs (Lantz et al., 2015; Lantz et al., 2017; Brunetto et al., 2018), which is unsurprising as ion
741 irradiation results in the amorphization of silicates (Brucato et al., 2004; Demyk et al., 2004).
742 However, it appears that simulated space weathering of this type does not noticeably affect the
743 depth of the Mg-OH band (Lantz et al., 2017), which could help distinguish the effects of mild
744 heating from space weathering on an asteroidal surface. More work is needed in this area.

745

746 *4.2 Modification of the OH/H₂O band with aqueous alteration and heating*

747 The OH/H₂O band is also modified as the degree of aqueous alteration or heating changes
748 among our CM suite. However, the correlation of band center or band maximum with petrologic
749 subtype is weak (Fig. 3G-H), and some of the heated CMs may be affected by terrestrial
750 weathering (Section 3.2.2; Fig. 7). Among the unheated CMs, the OH/H₂O band maximum for

751 subtypes 2.0–2.3 are all located at 2.71 μm (Table 3). This 2.71- μm maximum of the highly
752 altered CMs coincides with the band maximum of Mg-rich serpentines lizardite and chrysotile
753 (Calvin and King, 1997; Post and Borer, 2000; Takir et al., 2013). The three higher petrologic
754 subtypes (≥ 2.5) have maxima at longer wavelengths, although the maximum for LAP 04514
755 (2.7) is only at 2.72 μm , whereas Murchison (2.5) and LAP 02333 (2.6) are both located at 2.76
756 μm . This shift of the OH/H₂O band maximum to longer wavelengths is consistent with a
757 contribution from Fe-bearing serpentines that display an OH⁻ peak longward of $\sim 2.74 \mu\text{m}$
758 (Calvin and King, 1997; Cloutis et al., 2008; Takir et al., 2013; Bates et al., 2020). Similar to the
759 findings of previous studies, the spectral shape of this band in our CMs does not exactly match
760 any terrestrial Fe-bearing serpentine collected to date (Calvin and King, 1997; Takir et al., 2013).
761 We hypothesize that the presence of Fe-bearing serpentine in the least altered CMs is causing a
762 wider, more complex OH/H₂O band that is a combination of both Mg- and Fe-serpentine (Figs. 2
763 and 5); a similar conclusion was reached by Beck et al. (2010). In LAP 031214 (2.3), the Mg-
764 serpentine is more dominant, causing a peak at 2.71 μm , but in Murchison (2.5), the Fe-
765 serpentine peak at 2.76 μm is higher, suggesting more Fe-bearing serpentine relative to Mg-rich
766 serpentine (Fig. 5). This interpretation is consistent with their relative petrologic subtypes,
767 where the dominant phyllosilicate phase becomes Mg-rich serpentine with increasing aqueous
768 alteration (decreasing petrologic subtype) (Tomeoka et al., 1989; Zolensky et al., 1993;
769 Browning et al., 1996; Rubin et al., 2007), and with their ratios of measured Mg-rich serpentine
770 to Fe-rich serpentine (1.3 for LAP 031214 and 0.44 for Murchison; Table 1). This is also
771 consistent with Calvin and King (1997), who found that the shape of OH/H₂O band in Murchison
772 was best approximated with a linear combination of both Mg- and Fe-bearing phyllosilicates.

773 Another hydrated phase that may be contributing to the shape and location of the
774 OH/H₂O band is tochilinite, which has an absorption band in this region (Moroz et al., 2006) and
775 is commonly intergrown within Fe-serpentine (cronstedtite) in the less altered CMs (Mackinnon
776 and Zolensky, 1984; Tomeoka and Buseck, 1985; Zolensky et al., 1993; Lauretta et al., 2000).
777 Unfortunately, there is no pure tochilinite standard that allows reliable determination of its
778 volume abundance in CMs using PSD-XRD (Howard et al., 2011), but estimates based on mass
779 balance calculations and modal analysis from point counting are up to 8 vol.% and likely higher
780 for the least altered CMs (Zolensky et al., 1993; Howard et al., 2011). Moroz et al. (2006)
781 measured the reflectance minimum (emissivity maximum) of synthetic tochilinite at 2.78 μm,
782 which is a shorter wavelength minimum than for cronstedtite (~2.85 μm), although the latter
783 could be influenced by adsorbed water (e.g., Takir et al., 2013). We identified a large (~200 μm)
784 clump of tochilinite in the section of LAP 02333 (2.6) with significant Fe, S, Cr, Ni, and P,
785 moderate O, and negligible Mg and Si (determined via EDS K α peak mapping); we collected an
786 isolated μ -FTIR spectrum (Fig. 9). Our tochilinite spectrum shows an emission peak near 2.79

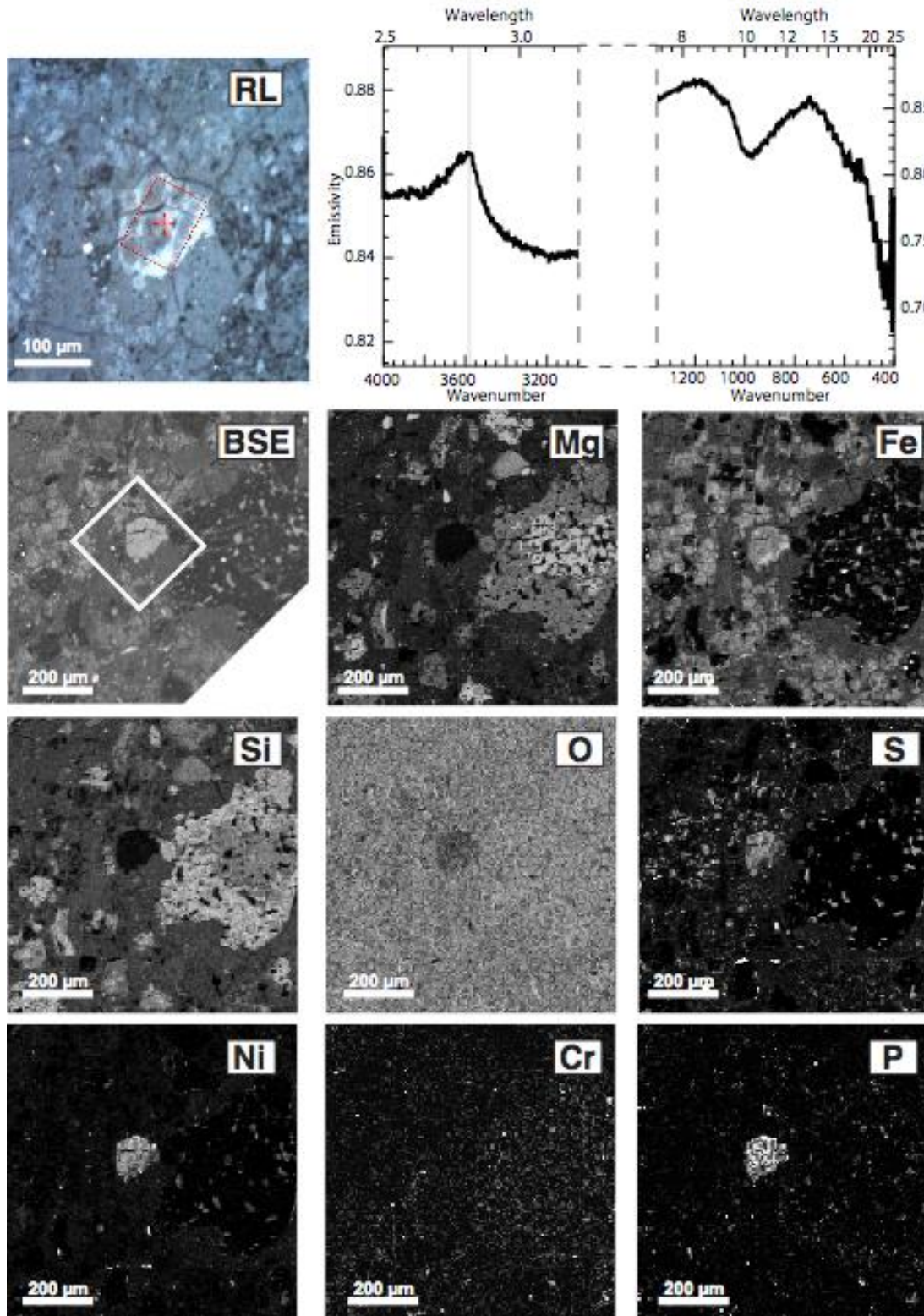


Figure 9. Tochilinite inclusion in CM 2.6 LAP 02333. RL: Reflected light image showing location (box) of IR spectrum to right (note different emissivity scales for the two sides of the plot to the right). Grey line marks the emissivity maximum of the OH band at 3585 cm^{-1} ($2.79\text{ }\mu\text{m}$). BSE: BSE image

highlighting tochilinite inclusion (white box). The other images are EDS maps of the [Fig. 9 caption continued from previous page] designated element. Negligible Mg and Si with high Fe, S, and Ni, and the absence of a 2.71 μm Mg-OH spectral band, confirms that the inclusion is nearly pure Fe-rich tochilinite.

787
788 μm but—unlike the synthetic tochilinite measured by Moroz et al. (2006)—tochilinite in LAP
789 02333 does not show the sharp Mg-OH peak at 2.71 μm . The absence of this peak confirms that
790 significant Mg is not present in this meteoritical tochilinite. Our tochilinite spectrum has two
791 other spectral features in the IR—a weak band centered near 980 cm^{-1} and a stronger, broader
792 band with a minimum near 425 cm^{-1} (Fig. 9). The position and relative strength of these two
793 bands are somewhat consistent with synthetic $\text{Fe}(\text{OH})_2$ (a brucite-type Fe oxyhydroxide) (Lutz et
794 al., 1994) although their exact band positions differ, perhaps due to the presence of Ni and P in
795 this natural specimen. The OH emission peak of this tochilinite is also at a slightly longer
796 wavelength (2.79 μm) compared to synthetic $\text{Fe}(\text{OH})_2$ (2.76 μm) (Lutz et al., 1994). In
797 summary, the longer OH/H₂O band emissivity maximum ($> 2.71 \mu\text{m}$) among our least altered
798 CM chondrites may be influenced not only by the presence of Fe-bearing phyllosilicate, but also
799 tochilinite, where these phases are commonly intergrown (forming TCIs) in these meteorites.
800 Such intergrowths likely contribute to the lack of a strong correlation of the OH/H₂O band
801 maximum with degree of aqueous alteration (Fig. 3G-H) because tochilinite abundance has not
802 been reported to vary in a predictable way with alteration. A similar conclusion was reached by
803 Nakamura et al. (2017), who observed an imperfect correlation between the OH/H₂O band
804 position and CM petrologic subtype. This study also reported a peak position of 2.79 μm for a
805 TCI (i.e., not pure tochilinite) grain in CM 2.4 DNG 06004 (spectrum not shown in that work).

806 While previous studies have also found that the maximum (or minimum in reflectance;
807 hereafter referred to as ‘peak’ for simplicity) of the OH/H₂O band shifts to longer wavelength
808 (smaller wavenumbers) with decreasing degree of alteration or hydration among the CMs (Beck

809 et al., 2010; Takir et al., 2013; Garenne et al., 2016; Nakamura et al., 2017; Bates et al., 2020),
810 the position of the measured peak varies, even for the same meteorite. For example, the OH/H₂O
811 band peak of CM Murchison has been estimated at 2.76 μm (this study), ~2.78 (Miyamoto,
812 1992), ~2.8 μm (Calvin and King, 1997; Garenne et al., 2016), and 2.82 μm (Bates et al., 2020) .
813 And, in general, the peak positions measured among CMs in this study are at slightly shorter
814 wavelengths than in previous studies (Fig. 10). Takir et al. (2013) found peak positions between
815 2.72 and 2.78 μm for petrologic subtype 2.0–2.2 (cf. this study 2.71 μm), and for subtypes ≥ 2.3,
816 the peaks were from 2.77 to 2.80 μm (cf. this study 2.71–2.76 μm). Other reflectance studies [IR
817 transmission data cannot be compared directly as the spectral band positions and shapes will
818 likely be different (Salisbury, 1993; Post and Borer, 2000)] have also found generally longer
819 wavelength positions for CM OH/H₂O band peaks: ~2.8 μm for CM 2.4/5 Murray and CM 2.5
820 Murchison (Calvin and King, 1997); >~2.80 μm for CMs as low as subtype 2.3 (Beck et al.,
821 2018); and > ~2.75 μm for all CMs (2.0 to 2.6) (Garenne et al., 2016).

822 All of these studies collected reflectance spectra on powdered samples rather than in thin
823 section, and therefore the longer wavelength positions of the band could be caused by particle
824 size differences (e.g., volume vs. surface scattering) or adsorbed water effects. An early study by
825 Miyamoto (1987) examined particle size effects on the OH/H₂O band of Murchison and found
826 that the band depth increased and the peak shifted to longer wavelengths with decreasing particle
827 size, but hypothesized that atmospheric water contamination, rather than particle size effects
828 [i.e., increase in volume scattering due to decreased grain size (e.g., Salisbury, 1993)] could be
829 the cause. Spectral heating studies by Beck et al. (2010) and Takir et al. (2013) confirmed that
830 the OH/H₂O band depth decreases and the peak location can move to shorter wavelengths with
831 heating (i.e., removal of adsorbed water), and so these and later spectral studies heated the

832 powders (typically to $\sim 150\text{-}300^\circ\text{C}$) to minimize this effect (Garenne et al., 2016; Bates et al.,
833 2020). Because our spectra still have a shorter wavelength peak compared to these heated
834 powders (Fig 10), it is unclear whether there is still a residual adsorbed water effect or a real
835 difference in wavelength position due to scattering effects. There are only two other studies that
836 have collected FTIR spectra of phyllosilicate-bearing materials in thin section. Unfortunately,
837 the Murchison section measured by King et al. (2018) was contaminated by terrestrial water, as
838 evidenced by a molecular water band near 1630 cm^{-1} (compared to our sections which apart from
839 CI Alais and WIS 91600 show no evidence of such a band; Fig. SM2), so its OH/H₂O band peak
840 position cannot be directly compared to those measured in this study. Moroz et al. (2006)
841 measured a minimum of $\sim 2.71\text{ }\mu\text{m}$ for CM 2.2 Cold Bokkeveld in thin section, which is
842 consistent with our measured peak for CM 2.2 LEW 90500. They also measured broad bands for
843 CM 2.3 Mighei and CM 2.4/5 Murray with minima located between ~ 2.71 and ~ 2.77 (precise
844 location not determined).

845 Therefore, the (albeit limited) data collected on CMs in thin section by this study and
846 Moroz et al. (2006) suggest that spectra of powdered CM meteorites have OH/H₂O band
847 positions at longer wavelength positions compared to solid surfaces. A direct comparison of
848 powdered and thin section spectra for two samples, LAP 02277 and Murchison, also suggests
849 that the shape of the OH/H₂O band, in addition to its position, varies from that of powdered
850 samples (Fig. 10). We could find only one study, Potin et al. (2019), that measured the OH/H₂O
851 band of both a chip and powder (while controlling for adsorbed terrestrial water on the latter) for
852 the same phyllosilicate-bearing sample (CM2 Mukundpura), finding that the OH/H₂O band
853 position and shape are the same. This suggests that the OH/H₂O band shape change and position
854 shift in thin section versus a powder (or chip) is caused by the unique observational geometry of

855 a polished thin section. It seems probable that there is a contribution from specular reflection on
856 the smooth surface of the section, but our OH/H₂O band spectra do not have an obvious
857 derivative shape typical of strong specular reflection (Moroz et al., 2006; Prinsloo et al., 2014)
858 (see also Supplemental Materials; Fig. SM1). Regardless, although our analysis and conclusions
859 regarding the OH/H₂O band remain the same, this discrepancy between thin section and
860 powdered/chip meteorite spectra suggest that the OH/H₂O band measurements in this study
861 cannot be directly compared to spectra of asteroids (e.g., Takir et al., 2015). Note that this does
862 not apply to spectra presented herein collected at longer wavelengths (> ~8 μm), as this region is
863 dominated by surface scattering (whether in thin section, chip, or coarse particulates down to ~
864 75 μm), making our reflectance spectra at these wavelengths equivalent to emissivity
865 measurements of planetary surfaces through Kirchhoff's Law (Section 2.4; Salisbury et al., 1991;
866 Salisbury, 1993; Hamilton, 2018).

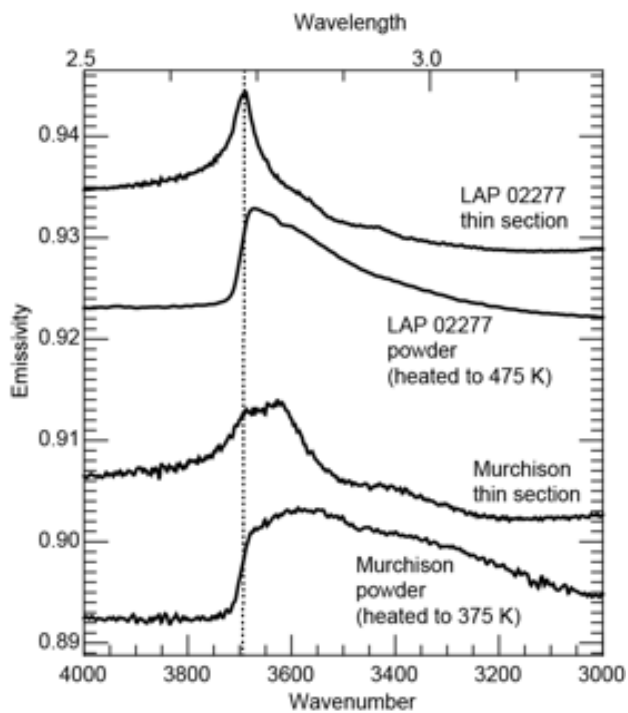


Figure 10. Comparison of powdered and thin section OH/H₂O band for two CMs. The OH/H₂O band of the thin section spectra is sharper and positioned at a slightly shorter wavelengths compared to that of the powdered samples. Dashed line marks the minimum of the LAP 02277 thin section (2.71 μm). Powdered spectra are from Takir et al. (2013; 2019) and were heated to remove adsorbed terrestrial water that contaminated the powders during sample preparation.

867

868 Among the heated CMs in our study, the OH/H₂O band maxima is at wavelengths ≥ 2.75
869 μm for all samples, and this maximum generally moves to longer wavelengths with increased
870 degree of heating (Fig. 7 and Table 4). This is consistent with previous studies that also found
871 OH/H₂O band peaks at longer wavelengths in thermally metamorphosed CMs than in unheated
872 CMs (Miyamoto, 1992; Hiroi et al., 1997; Beck et al., 2018). Qualitatively, the OH/H₂O band
873 shape of the heated CMs displays a more rounded shape than that of the unheated CMs (Fig. 8),
874 which has also been observed by previous workers (Hiroi et al., 1996; Tonui et al., 2014;
875 Matsuoka et al., 2017). For the weakly heated (Stage II) CMs, this shift and broadening of the
876 OH/H₂O band could be related to the decomposition of phyllosilicate, which creates an
877 amorphous, intermediate phase that has been well documented (Akai, 1988; Nakamura, 2005;
878 Tonui et al., 2014). Therefore, this band could behave similarly to the Si-O stretching band for
879 these weakly heated CMs (Section 4.1). The interpretation of the OH/H₂O band for the more
880 highly heated CMs PCA 91008 and PCA 02010 is more complicated owing to the contamination
881 from terrestrial weathering that has resulted in deeper than expected bands for dehydrated
882 samples (Section 3.2.2) (Tonui et al., 2014; King et al., 2016). However, the result on the band is
883 the same: a broadening and movement to the longer wavelengths. This suggests that the mildly
884 heated CMs are also affected by terrestrial weathering, although we could only find
885 mineralogical and spectral evidence of such alteration within WIS 91600 (Fig. SM2). By
886 comparing the OH/H₂O band of heated CMs to terrestrially weathered Antarctic ordinary
887 chondrites, Miyamoto (1992) proposed that all heated CMs are contaminated by terrestrial
888 weathering, but their unheated, powdered samples were likely also influenced by adsorbed
889 terrestrial water.

890 Nakamura et al. (2017) documented movement of the OH/H₂O band center to longer
891 wavelengths with increased heating in experimentally heated Murchison but concluded that these
892 samples were rehydrated by atmospheric water after heating. Subsequent heating experiments
893 that limited exposure to atmospheric water before spectral measurement showed that the band
894 actually becomes sharper, smaller, and moves to shorter wavelength (2.72 μm when heated to
895 400°C) (Mogi et al., 2017). In addition, experiments investigating terrestrial chrysotile
896 dehydration showed that the OH/H₂O band got smaller and shifted to a shorter wavelength (by
897 19 nm) with heating (Freund, 1974). Another experiment involving gradual heating of terrestrial
898 lizardite confirmed that the band becomes smaller with heating (no shift noted) (McKelvy et al.,
899 2004). Therefore, heating experiments that control for adsorbed terrestrial water demonstrate
900 that with heating, the OH/H₂O band of serpentine (and serpentine-dominated CM Murchison)
901 does not shift to longer wavelengths as suggested by the naturally heated CMs in our study. This
902 could indicate that all heated CMs have been compromised by rehydration from terrestrial water,
903 despite being bulk (non-powdered) samples. However, the bulk spectra of our unheated CM suite
904 do not show strong evidence of such a rehydration within their OH/H₂O bands, despite similar
905 weathering grades to the heated CMs (Tables 1–2). We can think of two possibilities for this
906 discrepancy. First, it is possible that the heating experiments described above are not
907 comparable to the heating conditions (e.g., duration, temperature, oxygen fugacity) experienced
908 by naturally heated CMs. The second possibility is that dehydrated phyllosilicates are more
909 susceptible to terrestrial rehydration. This is supported by the surface rehydration (increased
910 emissivity at 3450 cm⁻¹) near fusion crust where phyllosilicates would have been preferentially
911 initially dehydrated (LAP 031166, LAP 02277, PCA 91008). However, the lack of a 1630 cm⁻¹
912 band (expect for WIS 91600; Fig. SM2) diagnostic of molecular water that would normally

913 indicate terrestrial hydration challenges this interpretation. Regardless, if dehydrated
914 phyllosilicates are indeed more susceptible to rehydration from terrestrial water, particular care
915 should be taken with samples returned from the surfaces of carbonaceous asteroids that have
916 experienced heating and therefore may contain dehydrated phyllosilicates, such as Ryugu and
917 Bennu (Hanna et al., 2019; Kitazato et al., 2019; Molaro et al., in revision).

918

919 *4.3 Location and nature of alteration and heating within the CMs highlighted by spatially*
920 *resolved FTIR*

921 A unique aspect of our study is that we collected spectral data in thin section, in contrast
922 to previous studies that have used powdered bulk and matrix materials; this provides spatial
923 context for the spectral trends that we have observed among aqueously altered and heated CMs.
924 The spectral trends at wavenumbers $<1200\text{ cm}^{-1}$ in the unheated, aqueously altered CMs
925 attributed to the alteration of anhydrous silicates to phyllosilicates (Section 4.1) apply primarily
926 to the bulk samples and are not reflected in the matrix-only spectra of the samples (Fig. 2 and
927 Tables 3–4). The strong spectral similarity of the matrix-only spectra at these wavenumbers
928 suggests that the mineralogy of their matrices is similar, regardless of the petrologic subtype.
929 Thus, it may be the chondrules and other inclusions (refractory inclusions, larger disaggregated
930 anhydrous minerals) that experience the progressive alteration (of anhydrous silicates to
931 phyllosilicates) with decreasing petrologic subtype. Garenne et al. (2014) also proposed that the
932 relative alteration among the CMs was largely defined by the alteration of chondrules, based on
933 thermogravimetric analysis data and the typical volume proportion of matrix within the CMs.
934 Indeed, the Rubin et al. (2007) scales uses the relative alteration of the mafic silicates within the
935 chondrules to distinguish among the petrologic subtypes 2.0 to 2.4.

936 The Rubin et al. (2007) scale also distinguishes among the petrologic subtypes via the
937 volume abundance and composition (“FeO”/SiO₂) of “poorly characterized phases” (now
938 referred to as TCI), which is confined to the matrix. This variation in TCI abundance and
939 composition should result in some spectral modification of the matrix-only spectra among the
940 CMs, and it does, in the shape and position of the OH/H₂O band (Fig. 2). This band probes only
941 the hydrated components [phyllosilicates and hydrated sulfides (i.e., tochilinite)], and the band
942 center of this feature in the matrix-only spectra, similar to the bulk sample spectra, moves to
943 longer wavelengths with decreasing petrologic subtype. Because this band center shift results
944 from the relative Fe/Mg composition of the phyllosilicate and tochilinite (Section 4.2), the
945 OH/H₂O band is highlighting the compositional change of the TCIs within the matrix, as
946 indicated by the Rubin et al. (2007) scale. In contrast, anhydrous silicates have bands at
947 wavenumbers <1200 cm⁻¹ that overlap with those of the phyllosilicates and tochilinite (Figs. 4
948 and 9) and therefore the bulk CM spectra in this region are a combination of the matrix and
949 chondrules. Because mixing is linear in this wavenumber region (Ramsey and Christensen,
950 1998), we readily see modification of spectral features attributable to their changing proportions.
951 As the chondrules progressively alter to Fe-Mg phyllosilicates, the spectral contribution of the
952 anhydrous silicates decreases, and the bulk CM spectrum [especially for LAP 02277 (2.0) and
953 LAP 03116 (2.1)] strongly resembles that of the matrix-only spectrum that is dominated by the
954 hydrous silicates and sulfides. Thus, FTIR reveals the subtle progressive alteration of the CMs in
955 two ways: the OH/H₂O band probes the variation in abundance and composition of Mg-Fe
956 serpentine and tochilinite (the bulk of which is in the matrix, especially for higher subtypes), and
957 the wavenumber region <1200 cm⁻¹ reflects the changing proportions of anhydrous silicates
958 (mainly in chondrules and larger inclusions) to Mg-Fe phyllosilicates.

959 The fact that the different FTIR wavenumber regions (OH/H₂O band at 3700-3330 cm⁻¹
960 vs. the low-wavenumber region <1200 cm⁻¹) reveal different aspects of CM aqueous alteration
961 provides some context for the differences that we noted when comparing the Rubin et al. (2007)
962 and Howard et al. (2015) scales (Section 3.1.1). By converting the Howard et al. (2015)
963 alteration scale to the Rubin et al. (2007) petrologic subtype, it appeared that our CM suite
964 showed a smaller degree of relative alteration between samples than suggested by using the latter
965 scale directly (Fig. 1). However, the Howard et al. (2015) scale uses only the proportion of
966 phyllosilicates to anhydrous silicates to classify the CMs, and therefore mainly reflects the
967 relative degree of aqueous alteration among the chondrules that is revealed via FTIR in the
968 wavenumber region <1200 cm⁻¹. However, the solid solution composition of the phyllosilicate
969 and tochilinite (TCIs) also evolves with degree of relative alteration (Tomeoka and Buseck,
970 1985) as evidenced by the variation of the OH/H₂O band among our CMs. The Rubin et al.
971 (2007) scale captures this subtle compositional variation. Therefore, because the Howard et al.
972 (2015) classification scheme does not take into account the compositional changes that occur
973 with increasing alteration, it appears less sensitive to the degree of relative aqueous alteration
974 within the CM class.

975 The spectral differences between the bulk and matrix-only spectra of the heated CMs also
976 provide information regarding the location of heating within the samples. Similar to the
977 aqueously altered CMs, spectral features <1200 cm⁻¹ differ substantively between bulk and
978 matrix-only spectra for all but the most highly heated CM (PCA 02010). But for the heated
979 CMs, the matrix-only spectra display differences between the different heating stages, suggesting
980 that the matrix is being considerably modified by the thermal metamorphism. Between Stage II
981 and III matrix-only spectra, several spectral changes occur that arise from the formation of

982 secondary Fe-bearing olivine and pyroxene within the matrices of CMs with heating (Nakamura
983 et al., 2000; Nakamura, 2005; Tonui et al., 2014). In particular, for Stage III PCA 91008, the
984 588 cm^{-1} band indicative of Fe-bearing olivine is present only in the matrix spectrum. This
985 indicates that the Fe-bearing olivine that formed with heating is located primarily within the
986 matrix. This concentration of thermal effects within CM matrices is consistent with petrographic
987 observations both in this study (Section 3.2.1; Fig. 6) and previous studies (e.g., Nakamura,
988 2005; Tonui et al., 2014).

989

990 *4.4 WIS 91600: CM or CI(-like)?*

991 Finally, our spatially resolved spectral analysis of heated WIS 91600 highlights the
992 uniqueness of this heated ‘CM’ chondrite. The matrix-only spectrum of WIS 91600 is more
993 similar to CI Alais in Si-O stretching band shape and location than to any bulk or matrix-only
994 CM spectrum (Figs. 2 and 7). In particular, its Si-O stretching band minima is at a high
995 wavenumber (1001 cm^{-1}) and has a low band symmetry (0.42), similar to that of CI Alais (1008
996 cm^{-1} and 0.40, respectively; Tables 3–4). The wavenumber location of their Si-O bending band
997 minima also matches within uncertainty. Because the presence of chondrules precludes its
998 classification as a CI, it is intriguing that when isolating the matrix of WIS 91600, it spectrally
999 (and thus chemically and mineralogically) resembles one. Tonui et al. (2014) described the
1000 matrix of WIS 91600 as CI-like and found that its bulk oxygen isotopes placed it in the field of
1001 non-heated CIs [see also Choe et al. (2010)]. Hiroi et al. (2005) noted spectral similarities in the
1002 $3 \mu\text{m}$ (OH/H₂O) band region between WIS 91600 and CI Orgueil. Other workers have noted
1003 similarities between WIS 91600 and Tagish Lake based on spectroscopic, mineralogic, isotopic,
1004 and organic evidence (Hiroi et al., 2005; Yabuta et al., 2010; Yamanobe et al., 2018).

1005 Apart from a low abundance of olivine (10.1%) and pyroxene (1.5%), the modal mineralogy
1006 of WIS 91600 matches that of CI Alais, with high phyllosilicate (76.3%; X-ray amorphous)
1007 followed by significant magnetite (7.8%) and Fe sulfide (3.7%) (Table 2). Because the matrix-
1008 only FTIR spectrum of WIS 91600 at $<1200\text{ cm}^{-1}$ is similar to that of CI Alais, we can interpret
1009 that its matrix is likewise dominated by phyllosilicate with lesser magnetite and Fe sulfide, with
1010 no detectable spectral contributions from anhydrous silicates. Therefore, the Si-O stretching and
1011 bending regions of the matrix-only spectrum are the spectral signature of the amorphous
1012 phyllosilicate, which, because its spectral signature is broadly similar, appears to be structurally
1013 and chemically similar to the CI Alais phyllosilicate. However, there are subtle, but important,
1014 spectral differences between them. First, the Si-O stretching region of WIS 91600 matrix is
1015 broader than that of CI Alais, with a slightly lower wavenumber minimum. Second, the OH/H₂O
1016 band of WIS 91600 is broader and at a lower wavenumber than that of CI Alais. These
1017 differences are consistent with spectral modifications due to phyllosilicate dehydration and
1018 dehydroxylation, but unlike for the mildly heated CMs EET 96029 and EET 87522, the pre-
1019 heated phyllosilicate in WIS 91600 appears to be similar to that of a CI (e.g., intergrown saponite
1020 and serpentine) rather than the pure serpentine that dominates the CMs (e.g., Zolensky et al.,
1021 1993). Tonui et al. (2014) observed flakes of dehydrated saponite with transmission electron
1022 microscopy, and the matrix phyllosilicate compositions plotted between smectite (e.g., saponite)
1023 and serpentine on an Fe-Si-Mg ternary diagram. Therefore, we hypothesize that the pre-heated
1024 matrix mineralogy (especially the structure and composition of its phyllosilicate) of WIS 91600
1025 was very similar to that of a CI, and that mildly heated CIs may have a spectral signature similar
1026 to the matrix-only spectrum of WIS 91600. An alternative explanation for the CI-like
1027 mineralogy of WIS 91600 matrix is that post-heating aqueous alteration of initially CM-type

1028 mineralogy (i.e., dominated by serpentine) took place and resulted in a CI-like matrix
1029 mineralogy. More work is needed to distinguish between these two scenarios.

1030

1031 5. Conclusions

1032 We have characterized the IR spectra of a suite of CM chondrites that record a variety of
1033 degrees of both aqueous alteration and heating. We find spectral variations that are directly
1034 correlated to these processes.

- 1035 1. The spectral variations among unheated CMs are controlled by the mineralogical and
1036 compositional changes as ferromagnesian silicates are progressively altered to Mg-rich
1037 serpentine. The strongest, most highly correlated spectral trend with degree of aqueous
1038 alteration (i.e., petrographic subtype) is the separation of the CF and Si-O stretching band
1039 minimum ($R^2=0.90$), although the position of the CF and the Si-O bending minimum are
1040 also significantly correlated ($R^2=0.82$ for both). The depth of the Mg-OH band also
1041 systematically increases ($R^2=0.87$) with alteration.
- 1042 2. Weakly heated CMs (Stage II) exhibit spectral features due to dehydration and
1043 dehydroxylation of phyllosilicates that have formed an intermediate phase identified by
1044 previous workers (e.g., Akai, 1988). These features are broadening of the Si-O stretching
1045 band, a short wavenumber movement of its band minimum, and the disappearance of the
1046 Mg-OH band.
- 1047 3. The spectra of extensively heated CMs (\geq Stage III) are distinct from that of unheated
1048 and mildly heated CMs and are dominated by secondary, Fe-bearing olivine and
1049 pyroxene.

- 1050 4. The OH/H₂O band emissivity peak associated with OH⁻ moves to longer wavelengths
1051 with decreasing alteration, but the correlation is not strong. All moderately to highly
1052 altered CMs (≤ 2.3) have a 2.71 μm maximum. Mildly aqueously altered CMs (≥ 2.5)
1053 have wider OH/H₂O bands with a complex shape that results from contributions of Fe-
1054 bearing serpentine and tochilinite.
- 1055 5. The OH/H₂O of heated CMs is broad and rounded with a peak at longer wavelengths (\geq
1056 2.75) compared to that of unheated CMs. However, this band may be contaminated by
1057 terrestrial alteration, or heating experiments to date are not replicating natural heating
1058 within the CMs, especially for very mild heating.
- 1059 6. Our study confirms that thermal metamorphism effects, especially for mild degrees of
1060 heating, are concentrated within the matrix. The matrix of WIS 91600 had a CI-like
1061 mineralogy prior to heating and may be spectrally similar to a heated CI chondrite.

1062

1063 These documented spectral trends can be used to characterize the relative degree of aqueous
1064 alteration and heating of CM material using IR spectroscopy (2–25 μm) and will be helpful in
1065 the interpretation of laboratory, telescopic, and spacecraft observations of carbonaceous material
1066 and asteroids.

1067

1068 **Acknowledgements**

1069 R.D.H. was supported by the OSIRIS-REx Participating Scientist Program – Grant
1070 80NSSC18K0229. V.E.H. was partially supported by the OSIRIS-REx mission (NASA) under
1071 Contract NNM10AA11C issued through the New Frontiers Program. A.J.K. was funded by the
1072 UK Science and Technology Facilities Council (STFC) through grant ST/R000727/1. We thank

1073 Pierre Beck and an anonymous reviewer for insightful comments that improved our manuscript.
1074 We thank James Maner, Phil Orlandini, and Tom Etzel for their assistance during acquisition of
1075 electron beam data collection. U.S. Antarctic meteorite samples are recovered by the Antarctic
1076 Search for Meteorites (ANSMET) program which has been funded by NSF and NASA, and
1077 characterized and curated by the Department of Mineral Sciences of the Smithsonian Institution
1078 and Astromaterials Curation Office at NASA Johnson Space Center. Many thanks to the
1079 Meteorite Working Group and the Astromaterials Acquisition and Curation Office for their time
1080 and effort in getting ANSMET sample requests processed efficiently. We thank Phil Bland for
1081 the loan of CI Alais and Driss Takir for providing spectra for Figure 10. Thanks also to the
1082 Smithsonian National Museum of Natural History, curator Tim McCoy, and collection manager
1083 Julie Hoskin for the extended loan of Murchison USNM 5487, which we continually find new
1084 ways to study. Thanks to Alice Praet for sharing MATLAB code for calculating band
1085 parameters, to Deanne Rogers for useful discussions regarding band indices, and to Hannah
1086 Kaplan and Tim Glotch for insights into the behavior of the OH/H₂O and organics spectral bands
1087 in thin section. We thank the OSIRIS-REx mission editor Catherine Wolner for help in
1088 preparing this manuscript for publication and Harold Connolly Jr. for edits and suggestions
1089 which improved the quality of the manuscript.

1090

1091 **Data Availability**

1092 Laboratory spectral data are deposited in the spectral library hosted by the Arizona State
1093 University (<http://speclib.mars.asu.edu/>).

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