1	"Word count: 9325"
2	Revision 2
3 4	Thermal metamorphic history of Antarctic CV3 and CO3 chondrites inferred from the first and second order Raman peaks of polyaromatic organic carbon.
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24	Suggested Running Title: Thermal metamorphism of Antarctic CV3 and CO3 chondrites.
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ABSTRACT

Parent body thermal metamorphism is an important process that alters the structure of organic 34 matter in the parent asteroid of meteorites. Increasing and progressing thermal metamorphism 35 results in carbonization and graphitization of carbonaceous matter in the parent body. Such 36 modifications in the carbon structures can be studied by Raman microspectroscopy, thanks to its 37 38 high sensitivity to structure and bonding within carbonaceous molecules. We have characterized polyaromatic carbonaceous matter in a total of 24 Antarctic CV3 and CO3 chondrites using 39 micro-Raman imaging spectroscopy in an effort to better understand parent body thermal 40 41 metamorphism and assess its effects on the carbon structures. Raman spectral parameters of the first order carbon peaks (D and G) were extracted from at least 200 spectra for each meteorite 42 and were compared to deduce relationships that yield information regarding the thermal 43 metamorphism conditions. We also show, for the first time, spectral trends and relations of the 44 second order carbon peaks (2D and D+G) within the 2500-3200 cm⁻¹ with thermal metamorphic 45 history. The second order peaks appear to contain information that is lacking in the first order 46 peaks. Based on the second order carbon peak parameters, we tentatively classify four CV3 47 chondrites into subtypes, and reclassify another. Peak metamorphic temperatures of the 48 investigated meteorites have been estimated based on the width of the D band as well as the 49 calculated Raman spectral curvature. Estimated temperatures appear to correlate well with the 50 assigned petrologic types. We have calculated higher peak metamorphic temperatures for the 51 52 CV3 chondrites than for the considered CO3 chondrites and further showed that the peak metamorphic temperatures of CV3_{oxA} chondrites are higher than those of CV3_{oxB}, indicating a 53 54 possibly different metamorphic conditions for the two oxidized subtypes. We observe that there is a relatively larger temperature increase going from CO3.2 to CO3.4 (150 °C increase) 55

compared to CO3.4-CO3.6 (20 °C), which may indicate that the graphitization and structural
ordering of carbon reach a critical temperature regime around petrologic type CO3.3.
Keywords: Carbonaceous chondrites, Organic matter, Raman spectroscopy, Thermal
metamorphism.

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INTRODUCTION

62 Secondary processes such as aqueous alteration and thermal metamorphism take place on the parent asteroids of chondrites, and as a result the asteroidal compositions and components are 63 subsequently modified at varying scales and intensities (Brearley and Jones, 1998; Krot et al., 64 2003; Huss et al. 2006). Thermal metamorphism is a relatively minor effect in carbonaceous 65 chondrites with petrologic type 1 and 2, although these meteorites experienced sufficient heating 66 to mobilize water, which in return initiated the aqueous alteration. Type 3 carbonaceous 67 chondrites escaped elevated temperatures in the parent body that would potentially equilibrate 68 the chemical compositions, however they still reached relatively higher temperatures than type 1 69 and 2 chondrites, which caused a wide range of compositional modifications including thermal 70 processing of the organic matter (Brearley, 2006; Huss et al. 2006). On the other hand, type 4, 5, 71 6, and 7 carbonaceous chondrites experienced even higher temperatures such that their 72 73 composition has been equilibrated (Ashworth, 1980; Kessel et al. 2007).

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Some chondrites, especially carbonaceous chondrites, contain up to 4 wt.% organic carbon in the form of soluble and insoluble organic matter, the latter comprising about ~80% of the total organic carbon (Remusat, 2014). Secondary processes such as thermal metamorphism, aqueous alteration, brecciation, and impact shock can modify the organic content of chondrites (Botta and

Bada, 2002; Pizzarello et al. 2006). For instance, organic carbon in carbonaceous chondrites include polyaromatic macromolecular organic carbon, whose structures are sensitive to heating (i.e., thermal metamorphism) and elevated temperatures make them more graphitic (Busemann et al. 2007; Cody et al. 2008). Because carbonaceous chondrites are not differentiated, signatures of thermal metamorphism are preserved and retained in their chemical content (Scott and Krot, 2007), thus opening a path for investigating the asteroidal thermal metamorphism.

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Carbonaceous chondrites exhibit a wide range of chemical diversity, and some variations exist as 86 87 a result of asteroidal secondary processes (Zolensky et al. 1993). Ornans-type (CO) and Vigarano-type (CV) carbonaceous chondrites are petrologic type 3, referred to as CO3 and CV3 88 chondites (McSween, 1977a; Greenwood and Franchi, 2004; Weisberg et al. 2006). This means 89 that they are among the least altered/modified chondrites (Krot et al. 2005). The CO3 chondrites 90 contain abundant presolar silicates (Alexander et al. 2018). They show evidence of asteroidal 91 metasomatic events, and the presence of melilite, plagioclase, nepheline, sodalite, ilmenite, 92 ferroan olivine, and ferroan diopside have been identified (Brearley and Krot, 2013). The CV3 93 chondrites contain a wide range of secondary anhydrous minerals and some hydrous phases 94 95 (Brearley and Krot, 2013). Ferroan olivine and diopside-hedenbergite solid solution pyroxenes, nepheline, sodalite, phyllosilicates and favalite have been identified in most CV3 chondrites 96 (MacPherson et al. 2014). 97

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99 The CO3 chondrites are reported to be compositionally related to the CV3 chondrites. For 100 instance the CO3 and CV3 chondrites have similar bulk chemical compositions and mineralogies 101 (Itoh and Tomeoka, 2003) although their metal phases are quite different (McSween, 1977b,

102 1977c). The CO3 chondrites span a range of petrologic types, from 3.0 to 3.9 (McSween, 1977a; Keck and Sears, 1987), and as such, they provide an excellent set of samples to study parent 103 body metamorphic processes. On the other hand, CV3 chondrites are divided into two 104 subgroups; reduced ($CV3_{red}$) and oxidized ($CV3_{ox}$) chondrites on the bases of their secondary 105 mineralogy and opaque phases such as metal, magnetite, and Ni content (McSween, 1977c). The 106 107 oxidized subgroup (CV3_{ox} chondrites) are further divided into the Allende-like (CV3_{oxA}) and Bali-like (CV3_{0xB}) types also on the bases of their secondary minerals and magnetite abundances 108 (Weisberg et al. 1997b, Krot et al. 1998). In addition to the secondary minerals and magnetite 109 abundances, thermoluminescence properties of CV3 chondrite subtypes are different as well 110 (Guimon et al. 1995). Another difference among the CV3 subtypes is the varying abundances of 111 pure fayalite. Namely, the CV_{0xA} subtypes lack pure fayalite (Fa>95 composition) and it is rare 112 in the CV3_{red} subtypes, whereas relatively larger amounts exist in the CV3_{0xB} subtypes 113 (McSween et al. 1977c; Howard et al. 2010). While these CV3 subtypes were thought to 114 originate from a single parent body, there are mineralogical differences among the three 115 subgroups due to varying degrees of alteration (Krot et al., 1995, 2003). In fact, on the basis of 116 significantly different matrix abundances and the distribution of chondrule apparent diameters, it 117 118 was argued that the CV_{ox} and CV_{red} chondrites may originate from two different parent bodies (Gattacceca et al. 2019). If true, it would be interesting to compare their thermal metamorphic 119 histories, which can be investigated via Raman spectroscopy of the polyaromatic carbonaceous 120 121 matter within the CV3 chondrites. Indeed, due to the relatively low degree of thermal processing in the CO3 and CV3 chondrites (Itoh and Tomeoka, 2003; Alexander, 2017), the 122 123 study and comparison of their carbon structures may provide valuable information regarding the 124 parent body metamorphism mechanisms.

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To investigate the effects of parent body thermal metamorphism on polyaromatic carbonaceous 126 matter and to compare these effects across the two chondrite groups, we collected Raman 127 spectroscopic data from a set of Antarctic CO3 and CV3 chondrites, and extracted spectral 128 parameters of the first and second order carbon peaks. The first order carbon peaks have been 129 previously studied and spectral trends have been presented for various carbonaceous chondrite 130 groups (Bonal et al. 2006, 2007; 2016, 2020, Busemann et al. 2007; Cody et al. 2008; Quirico et 131 al. 2018), however, to our knowledge, the second order carbon peaks have not been investigated. 132 133 In this work, these second order carbon peaks were strong enough to consider and investigate them, so these peaks and their parameters were also taken into account, for the first time, in an 134 effort to reveal relations between the organic matter and thermal metamorphic histories. We also 135 show that spectral trends and parameters of the second order carbon peaks may able to recognize 136 the subtypes of CV3 chondrites. Using such parameters, we attempt to tentatively classify four 137 carbonaceous chondrites and reclassify another into the CV3 subtypes. 138

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SAMPLES AND ANALYTICAL METHODS

The CO3 and CV3 chondrites studied in this work were loaned in the form of polished thin sections from the Antarctic meteorite collection of NASA Astromaterials Acquisition and Curation Office located at Johnson Space Center (JSC). At JSC, each sample was first cut dry on a band saw, producing a ~cm scale thick slab, which was then glued on a glass slide using epoxy for further processing using diamond paste to make the section ~30-40 μ m thin, flat and smooth. Table 1 lists the studied samples and their types. While the subtypes of most samples are known, there are four CV3 and three CO3 chondrites whose subtypes are currently unknown. Thesesamples are indicated by "?" in the associated figures and tables.

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Meteoritic components are susceptible to chemical modifications in the field and in the 150 laboratory. For instance, terrestrial weathering may alter the organic matter in meteorites, 151 152 especially those found in hot deserts (Busemann et al. 2007, Alexander et al. 2007). Meteorites found in cold deserts such as Antarctica, on the other hand, remain relatively more pristine. The 153 samples investigated in this work all have A or B terrestrial weathering grades, indicating 154 155 minimal weathering. Additionally, organic contamination in the laboratory may occur during sample preparation, however contaminant organics present Raman peaks that are different to 156 some extent than indigenous carbon and are easily identifiable. Epoxy resin used during the 157 sample preparation can also give rise to contaminant Raman carbon peaks, however these peaks 158 are quite distinct from those of indigenous carbonaceous matter, therefore they can be easily 159 distinguished (e.g., Yesiltas, 2018a). Nevertheless, all spectra included in the data analyses were 160 checked prior to fitting procedures to ensure all investigated spectra are free of contaminant 161 carbon peaks. 162

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Our samples were prepared in the form of thin sections, which involved polishing the surface of samples. Such mechanical polishing processes might introduce structural disruption on the organic matter present on the surface (Beyssac et al., 2003; Fries and Steele, 2010); however, type 3 chondrites reportedly did not contain structural modifications due to the polishing (Bonal et al. 2016). Nevertheless, extra caution was taken during the data collection and analyses procedures of this work. In order to check whether polishing causes changes in the Raman

- spectral parameters, we measured a polished thin section, powdered grains, and bulk chip of a
- type 3 carbonaceous chondrite. Spectral results in all cases appear very similar, indicating that
- the effect of surface polishing in this work should be negligible.
- **Table 1.** Meteorite samples investigated in this study.

Number*	Meteorite	Group/Subtype
1	ALH 85006	CV3 _{oxB}
2	MET 00430	CV3 _{oxB}
3	LAR 06317	CV3o _{xA}
4	DOM 10351	CV3?
5	MCY 05219	CV3 _{oxB}
6	MIL 13328	CV3?
7	QUE 93744	CV3?
8	LAP 02228	CV3 _{oxA}
9	LAP 02206	CV3 _{oxA}
10	MIL 07681	CV3 _{red}
11	LAR 12002	CV3?
12	GRA 06101	CV3 _{oxA}
13	DOM 08006	CO3.0
14	MIL 090152	CO3.?
15	MIL 090128	CO3.0-3.2
16	MIL 11213	CO3.?
17	MIL 07193	CO3.1
18	MIL 05024	CO3.1
19	MIL 090010	CO3.1
20	DOM 10104	CO3.2
21	MIL 07346	CO3.2
22	ALH 82101	CO3.4
23	ALH 83108	CO3.5
24	ALHA 77003	CO3.6

*The numbers denote sample numbers in the legends of figures.

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Raman microspectroscopy experiments were conducted using a WiTec alpha300R confocal Raman imaging system (WiTec GmbH), which was equipped with a 532 nm Nd:YAG laser, 600 g/mm grating, and a 50× (NA = 0.8) objective. The laser power on the focal plane (sample surface).was ~1-1.5 mW (corresponding to a power density of ~0.57-0.85 mW/ μ m²), which appears to cause no laser-induced thermal damage on the sample. Prior to each measurement

180 session, the spectrograph was calibrated using a silicon wafer substrate to ensure the Rayleigh laser signal was at 0 cm⁻¹ and the signal of silicon was at ~521 cm⁻¹. Following the calibration, 181 we collected two-dimensional Raman images from a carbon-bearing region of each sample with 182 0.5 µm spatial step size. The data collection procedure was automatic, as the confocal 183 microscope raster scanned the predefined area pixel by pixel and acquired a Raman spectrum 184 between the whole spectral range (0-4000 cm⁻¹) from all pixels, covering the first and second 185 order carbon peaks. The resulting hyperspectral images consist of thousands of pixels each with 186 its lateral information and a full Raman spectrum. Integration time was between 0.03-0.09 s. 187 These parameters proved to generate reproducible spectral data with no laser-induced damage to 188 the studied samples (e.g., Yesiltas et al. 2018a, 2018b; Yesiltas et al. 2019). 189

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The collected data were first corrected for cosmic rays and artificial baseline (by subtracting a 191 polynomial with shape size of 200 and noise factor of 2). Next, carbon distribution maps were 192 generated for each sample to identify the carbon-rich pixels. Figure 1 presents these distribution 193 maps for the 24 meteorites investigated in this study. We fitted the first order carbon peaks with 194 a pair of Lorentzian functions and extracted width (Γ), intensity (I), and position (ω) of each 195 carbon peak. Such a fitting procedure was repeated for at least 200 carbon-rich pixels in each 196 sample, which ensures that the spectral data are representative of the whole sample and any 197 sampling bias is minimized. The same spectral parameters were also extracted from the second 198 order carbon peaks of average meteorite spectra. The extracted parameters were then plotted 199 against each other to obtain spectral trends and relations which could help us infer thermal 200 metamorphic history of the parent bodies of the samples and relationships across a range of 201 petrologic subtypes of the CV3 and CO3 chondrites. 202

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RESULTS

Average baseline-corrected Raman spectra of investigated meteorite samples are shown in 205 Figure 2. Carbonaceous matter generally produces first and second order carbon peaks. The first 206 order peaks occur between 1000-1800 cm⁻¹ and are present in spectra of all samples considered 207 in this work. These peaks specifically appear near ~ 1350 and ~ 1600 cm⁻¹. The former peak is 208 referred to as the "D" (disorder) band and is due to sp³ carbon bonding (Busemann et al. 2007; 209 Suzuki et al. 2010). It occurs due to the breathing motion of sp³ atoms in rings, and as a result of 210 defects in the carbon structures (Tuinstra and Koenig 1970; Ferrari and Robertson 2000, 2001, 211 Starkey et al. 2013). The latter band is referred to as the "G" (graphite) band and is due to sp^2 212 carbon bonding (Tuinstra and Koenig 1970; Busemann et al. 2007; Suzuki et al. 2010). The G 213 band occurs as a result of in-plane stretching mode of sp^2 atoms in polyaromatic rings, and 214 different types of carbonaceous materials can be distinguished using the spectral properties of 215 this band (Ferrari and Robertson 2000, 2001, Starkey et al. 2013). The second order carbon 216 peaks, which appear at higher wavenumbers between 2500-3500 cm⁻¹, are overtones and 217 combinations of the first order peaks (Sadezky et al. 2005, Brunetto et al. 2009). The 2D peak 218 appears around $\sim 2700 \text{ cm}^{-1}$ and is the overtone of the D band (Vollebregt et al. 2012; Ma et al. 219 2019), whereas the peak near \sim 2930 cm⁻¹ is called the D+G band and is the overtone of the D 220 and G bands (Vollebregt et al. 2012; Ma et al. 2019). The vertical dashed lines at 1343, 1600, 221 2690, and 2930 cm⁻¹ in Figure 2 indicate positions of the D, G, 2D and D+G bands observed in 222 this work. 223

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225 By fitting the first order carbon peaks with various mathematical functions, spectral peak parameters such as full-width-half-maxima (Γ), peak intensity (I), and peak position (ω) can be 226 extracted (e.g., Bonal et al. 2006, 2007; 2016, 2020, Busemann et al. 2007; Cody et al. 2008; 227 Quirico et al. 2018). In this study, we extracted spectral parameters of the first order carbon 228 229 peaks from at least 200 Raman spectra for each meteorite by fitting the peaks with a pair of Lorentzian functions (Figure 3). As for the second order carbon peaks, we extracted the same 230 231 spectral peak parameters from the average Raman spectra given in Figure 2. The values of 232 individual parameters (given in Table S1-supplementary file) were compared across all of the 233 considered samples in order to obtain useful information to understand the thermal metamorphism that occurred on their respective parent bodies and also to assess whether the 234 second order peak parameters provide any trend or relation that could be useful for constraining 235 the thermal metamorphic history. 236

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Figure 4a shows that the peak intensity ratio (I_D/I_G) of first order carbon peaks increases with 238 increased thermal metamorphism. Namely, DOM 08006 (CO3.0, characterized by the most 239 disordered organic matter) has a I_D/I_G ratio of 0.77, whereas relatively more ordered DOM 10104 240 (CO3.2) and ALHA 77003 (CO3.6) are characterized by I_D/I_G ratios of 1.0 and 1.34, 241 242 respectively. This is due to the fact that there are two phases of thermal metamorphism; a carbonization phase that contributes disordered aromatic carbon to the D peak, and a higher 243 temperature graphitization phase that reduces the D peak. In addition, the observed trend 244 (increasing ratio as a result of increased thermal metamorphism) has been attributed to the 245 transformation of amorphous carbon to relatively crystalline carbon (i.e., nanocrystalline 246 247 graphitic domains) and then to inorganic graphite (Tuinstra and Koenig 1970; Ferrari and

Robertson, 2000, 2001; Busemann et al. 2007). The comparison in Figure 4a also shows that the 248 $\Gamma_{\rm D}$ value decreases with increasing petrologic type as expected. These trends are consistent with 249 higher petrologic types being the result of increased temperatures in the parent body (Huss et al. 250 251 2006). Moreover, these trends indicate that the considered CO3 chondrites are more primitive 252 with more amorphous and disordered carbon, whereas the CV3 chondrites appear to have experienced relatively higher levels of thermal metamorphism. While some samples show signs 253 254 of presence of relatively crystalline carbon, the complete transformation to inorganic graphite is 255 not observed in the studied samples because there is no Raman spectrum that shows prominently 256 strong G band and relatively weak or almost absent D band, which is the indication of inorganic 257 graphite (e.g., Busemann et al. 2007). On the other hand, the I_D/I_G ratio does not present any relation with Γ_{G} (Figure 4b), indicating that transformation of carbon from amorphous to 258 nanocrystalline structure may have no visible effect on the width of the G band based on the 259 samples studied here. 260

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262 Figure 5a shows that the position of the D-band (ω_D) spans a similar range for both groups of meteorites, however the D-band width ($\Gamma_{\rm D}$) is generally greater for CO3 chondrites than for CV3 263 chondrites. The greater D-band widths for CO3 chondrites suggest the presence of relatively 264 disordered carbon and less metamorphism than CV3 chondrites. In addition, the three CV3_{0xA} 265 chondrites (samples 8, 9, 12) plot at lower Γ_D values compared to the three CV3_{0xB} chondrites 266 (samples 1, 2, 5), suggesting that the former subtypes may have undergone relatively higher 267 degree of thermal metamorphism. Figure 5b presents the same parameters (peak position vs. 268 peak width) for the G-band. These two parameters, ω_G as a function of mean crystallite size and 269 $\Gamma_{\rm G}$ as a function of the distribution of crystallite size, were previously used to describe the 270

271 thermal metamorphism of carbonaceous chondrites (e.g., Busemann et al. 2007; Jenniskens et al. 2012; Bonal et al. 2016). In this work, we see that CV3 chondrites fall toward lower right in this 272 graph, indicating the presence of polycrystalline and metamorphosed organic matter in CV3 273 chondrites. The reduced and oxidized CV3 chondrites plot randomly with no apparent grouping, 274 indicating that these band parameters are unable to differentiate different CV3 subgroups. CO 275 chondrites fall below CM chondrites in this figure, showing an agreement with the previous 276 work (e.g., Busemann et al. 2007; Jenniskens et al. 2012; Bonal et al. 2016), but they span a 277 large range such that some CO3 chondrites extend into to the CV region, which is indicative of 278 279 material in those CO3s that has been metamorphosed as much as the considered CV chondrites.

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281 The width of the D band (Γ_D) is positively correlated with the width ratio of D and G bands (Γ_D/Γ_G) , as shown in Figure 6a. Increasing the degree of thermal metamorphism appears to 282 decrease the $\Gamma_{\rm D}$ value, but does not seem to affect $\Gamma_{\rm G}$ at all. Relatively more metamorphosed 283 members of the CO chondrites (types 3.4-3.6) fall in the middle of CV chondrites in this graph. 284 Unlike Γ_D , the Γ_G parameter does not seem to have any correlation to the width ratio Γ_D/Γ_G 285 (Figure 6b), except that the two groups of meteorites cluster slightly apart from each other. 286 Moreover, we show that some of the spectral properties of the first order carbon peaks do not 287 present any trend. For instance, the position of the D band does not seem to be an indicator of 288 metamorphism as the position values for all meteorites are scattered randomly (Figure S1). 289 Comparisons of peak widths (Γ_D vs. Γ_G) as well as positions (ω_D vs. ω_G) do not reveal any trend 290 that can be related to the parent body thermal metamorphism (Figure S2). Figure 7 presents the 291 I_D/I_G ratios for the investigated meteorites. CV3 chondrites appear to follow a linear trend, the 292

293 comparison indicates that $CV3_{oxB}$ chondrites have smaller I_D/I_G ratios than $CV3_{oxA}$ chondrites. 294 The I_D/I_G ratios of CO3 chondrites also appear to increase with increasing petrologic types.

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Spectral parameters of the second order carbon peaks could be valuable for understanding the 296 maturity grade (Bonal et al. 2007). Yet, to our knowledge, these peaks have not been previously 297 studied quantitatively for the purpose of understanding parent body thermal metamorphism such 298 as the parent bodies of CV and CO chondrites. Average Raman spectra in this work have high 299 enough signal-to-noise ratio within the 2500-3500 cm⁻¹ region such that we are able to perform 300 301 fitting procedures to extract spectral parameters from the second order carbon peaks. We investigated these second order peaks to explore their potential for this purpose and to check 302 whether they are able to distinguish different petrologic subtypes. Figure 8a shows a linear 303 relationship between Γ_{2D} and Γ_{2D}/Γ_{D+G} , which is very similar to the trend seen in Figure 6a for 304 the same parameters of first order peaks (Γ_D vs. Γ_D/Γ_G), although both meteorite groups span 305 similar ranges with no obvious distinction between the CO3 and CV3 chondrites in Figure 8a. 306 307 What is additionally observed in Figure 8a is that the width of the 2D band for CV3_{0xA} chondrites (samples 8, 9, 12) appears to be similar and is located near 75-100 cm⁻¹, however the value of 308 this parameter is much larger (200-275 cm⁻¹) for the $CV3_{oxB}$ chondrites (samples 1, 2, 5), 309 therefore they are spectrally separated based on the second order carbon peak parameters. A 310 similar trend is also seen in the right panel of this figure. The $CV3_{0XA}$ chondrites generally have 311 higher peak intensity ratios than the $CV3_{oxB}$ chondrites, with the exception of LAR 06317 (see 312 text below). Figure 8b shows that Γ_{2D} decreases and I_{2D} increases as thermal metamorphism 313 progresses. In this case, one must expect a linear relation between Γ_{2D} and I_D as well, which is 314 315 indeed what's seen in our data (Figure 9a). Thanks to the second order peak parameters, we

observe that while the I_D/I_G parameter does not present any trend or relationship with Γ_G , it does 316 317 have a linear relation with a second order peak parameter Γ_{D+G} (Figure 9b). Moreover, we observe that the position of the D+G band (ω_{D+G}) is linearly correlated with the Γ_D value (Figure 318 10a), shifting to higher wavenumbers as metamorphism increases. This is in contrast to the first 319 order peaks, where increased metamorphism does not seem to vary the peak position $\omega_{\rm D}$. We 320 321 also observe that the three CV3 subtypes appear to plot separately when the I_{2D}/I_{D+G} values of the considered CV3 chondrites are compared (Figure 10b), revealing that the I_{2D}/I_{D+G} values could 322 potentially be useful for distinguishing the three CV3 subtypes (see Discussion). 323

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It has been proposed in the literature that Raman spectral parameters of the first order carbon 325 bands can be used to roughly estimate the peak metamorphic temperature (PMT) of parent 326 327 asteroids. For instance, Busemann et al. (2007) investigated insoluble organic matter (IOM) that was chemically extracted from the matrices of primitive chondrites, and reported that the D band 328 parameters and peak metamorphic temperatures are strongly correlated, allowing for an 329 estimation of metamorphic temperatures using equation (1). However, this metamorphic 330 geothermometer is limited to samples with Γ_D values smaller than 280 cm⁻¹ because the 331 minimum in the second order polynomial fit occurs at this value (Busemann et al. 2007). Cody 332 et al. (2008) reported an alternative geothermometer expression for the estimation of 333 metamorphic temperatures based on Γ_D (equation 2), realizing that there exists a relationship 334 between Γ_D and Raman exciton intensity. Cody et al. (2008) also reported a geothermometer 335 thermometer expression based on $\Gamma_{\rm G}$ (equation 3). However, the metamorphic temperatures 336 calculated using eq. 2 and 3 differ significantly, indicating that estimating the parent body 337 338 metamorphic temperature using Raman spectroscopy of polyaromatic carbon may be more

complicated than previously thought. Bonal et al. (2016) concluded that the peak metamorphic 339 temperature calculations in the absence of a valid and consistent calibration procedure would not 340 vield accurate results. In other words, the obtained temperatures could simply be underestimated 341 without a proper calibration procedure. In addition, the thermometer expressions by Busemann et 342 al. (2007) and Cody et al. (2008), used to estimate the structural order and maturity level of 343 carbon in chondrites, are based only on one spectral parameter, the width of a first order carbon 344 peak (either D or G band). Recently, Young et al. (2020) reported an alternative geothermometer 345 model that is based on the calculated spectral curvature (K_T) of a given full Raman spectrum 346 347 with D and G carbon bands (equation 4). This model, therefore, takes into account all parameters of both of the first order Raman peaks at the same time. 348

349 PMT (°C) =
$$931 - 5.10 \times \Gamma_{\rm D} + 0.0091 \times {\Gamma_{\rm D}}^2$$
 (1)

350 PMT (°C) = 899.9 -
$$3 \times \Gamma_{\rm D} + 0.0014 \times {\Gamma_{\rm D}}^2$$
 (2)

351 PMT (°C) =
$$1594.4 - 20.4 \times \Gamma_{\rm G} + 0.058 \times {\Gamma_{\rm G}}^2$$
 (3)

(4)

352 PMT (°C) =
$$0.409 \times (-K_T^{-0.840})$$

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Even though the peak metamorphic temperatures obtained through these geothermometer expressions are somewhat underestimated due to their respective limitations, the Raman spectral parameters of first order carbon peaks and obtained temperatures nevertheless proved to be helpful for gaining insights on the thermal metamorphic history of parent asteroids (e.g., Bonal et al. 2016, 2020; Busemann et al. 2007; Cody et al. 2008; Yesiltas et al. 2014; Young et al. 2020).

We calculated the PMT values of the investigated meteorites using the expressions provided by Busemann et al. (2007), Cody et al. (2008), and Young et al. (2020), and compared the results of

these models. The estimated PMT values obtained by different models yield similar trends with

respect to petrologic types of the samples, although each model estimates slightly different PMT 363 (Figure 11). Among the three models, the model by Cody et al. (2008) yields the highest 364 temperatures for the same samples. There is an average difference of ~93 °C between the Cody 365 et al. (2008) and Busemann et al. (2007) models. On the other hand, Young et al. (2020) model 366 367 estimates slightly higher temperatures for the type 3.0-3.2 CO chondrites, when compared with the model of Busemann et al. (2007). Regardless of the thermometry models, the CO3 chondrites 368 369 present a lower range of temperatures than the CV3 chondrites. We note that for the PMT 370 calculations presented here, the equations based on Γ_D were used because the petrologic types of 371 the samples present better correlations with D band parameters (e.g., Busemann et al. 2007; Bonal et al. 2007, Yesiltas et al. 2014; Bonal et al. 2020) and the spectral parameters of the D 372 373 band are reported to be more sensitive to annealing in the parent body (Busemann et al. 2007; 374 Bonal et al. 2007). We additionally compared the K_T values of our CV3 subtypes in an effort to check whether the calculated spectral curvature values for the CV3 subtypes plot differently. 375 Figure 12 shows that the K_T values may potentially distinguish the CV3 subtypes as samples of 376 each subtype plot at different locations. In particular, investigated CV3_{0xA} and CV3_{0xB} chondrites 377 are separated as far as their K_T values are concerned. While the distinctions are not very 378 prominent in our case due to the limited number of samples, it would potentially be more 379 prominent when the spectral curvature values of a larger number of meteorites from each subtype 380 are compared. 381

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DISCUSSION

Polyaromatic organic carbon structures in meteorites are sensitive to heating as the thermal metamorphism induces irreversible structural/compositional transformations in the organic matter (Bonal et al. 2006). As a response to thermal metamorphism, the Raman spectral

387 parameters of carbon peaks change accordingly (Busemann et al., 2007, Cody et al., 2008; Quirico et al., 2003; Bonal et al., 2006, 2007, 2016). Several groups focused on the first order 388 carbon peaks and spectroscopically investigated the relations between carbon peak parameters 389 and thermal metamorphism for various groups of meteorites (e.g., Busemann et al., 2007, Cody 390 et al., 2008; Quirico et al., 2003; Bonal et al., 2006, 2007, 2016). First order carbon peak 391 parameters of some of the samples investigated in this work were also studied by other groups in 392 the past. Bonal et al. (2016) especially studied the first order carbon peaks of a large number of 393 samples. Our investigation shows that increased thermal metamorphism results in a more intense 394 395 and narrower D band with no change in its spectral position. On the other hand, the G band parameters are observed to be scattered randomly regardless of their petrologic types, and they 396 do not vary in any systematic manner with thermal metamorphism. This is why the D band is 397 favored for the calculation of peak metamorphic temperate of chondrites as the G band does not 398 correlate significantly with thermal metamorphism (e.g., Busemann et al. 2007; Bonal et al. 399 2007, 2016). In short, our first order spectral peak parameters and their trends with thermal 400 metamorphism are in good agreement with the literature (e.g., Quirico et al., 2003; Bonal et al., 401 2006, 2007, 2016; Busemann et al. 2007, Cody et al. 2008). 402

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To our knowledge, the second order carbon peaks have not been quantitatively explored for the purpose of inferring thermal metamorphic history of carbonaceous chondrites. This may be due to low S/N ratio within the 2500-3500 cm⁻¹ spectral region where the second order carbon peaks normally appear (e.g., Bonal et al. 2007). Sample type, sample form (powder vs. thin section), surface topography of the measured region (presence of voids or gaps), and experimental details can contribute to the obtained S/N level. We performed Raman imaging experiments on polished 410 thin sections, and considered hundreds of spectra from void-less regions to maximize the spectral quality. In our work, the second order carbon peaks are pronounced with high-enough S/N ratio 411 that allows quantitative spectral investigations. Thanks to the high S/N ratio of our Raman 412 spectra, we present spectral evidence, for the first time, that the second order carbon peak 413 parameters may be used to infer parent body thermal metamorphism of carbonaceous chondrites, 414 415 and also to potentially classify CV3 chondrites into its subtypes. These evidences are as follows: (i) The spectral parameters extracted from the second order carbon peaks show that increased 416 thermal metamorphism results in more intense and narrower 2D bands. We also show that the 417 second order D+G peak near 2930 cm⁻¹ does in fact present a correlation with thermal 418

419 metamorphism, in contrast to the G band. Therefore, we conclude that it might be better to 420 include the second order carbon peaks in the thermometric expressions/calculations to determine 421 more accurate and better constrained peak metamorphic temperatures.

(ii) The second order peak parameters may also play a role in classifying subtypes of CV3 422 chondrites. For instance, the subtypes of CV3 chondrites ($CV3_{oxA}$, $CV3_{oxB}$, and $CV3_{red}$) present a 423 unique challenge for understanding the parent body processes. The three subtypes may have 424 gone through different extents of thermal metamorphism (Huss et al. 2006; Bonal et al. 2020). 425 426 The $CV3_{oxA}$ chondrites present evidence of metasomatism, whereas the $CV3_{oxB}$ chondrites experienced substantial aqueous alteration (Huss et al. 2006). Bonal et al. (2020) reported that 427 the CV3_{oxA} chondrites contain higher abundance of metal and lower Ni in sulfides, while they 428 429 have similar abundance of matrix. The CV3_{red} chondrites present signatures of either aqueous alteration or metasomatism (Krot et al., 1995, Huss et al. 2006), they contain less matrix, more 430 431 metal and Ni-poor sulfides relative to the oxidized CV3 chondrites (Bonal et al. 2020). 432 Moreover, although it is thought that all CV3 chondrites originate from the same parent body,

Gattacceca et al. (2019) argued that CV3_{ox} and CV3_{red} chondrites may have originated from two 433 different parent bodies. Bonal et al. (2020) also concluded that CV3_{red} and CV3_{ox} may be 434 originating from the a heterogeneous parent body or multiple parent bodies on the bases that the 435 two subtypes present different matrix abundances, alteration products, and opaque mineralogy. 436 Despite the limited number of samples, we spectrally compared the three subtypes of CV3 437 438 chondrites based on their Raman spectra and peak parameters. Our data suggest that the samples of individual subtypes cluster together, and appear distant from other subtypes. The color-coded 439 groups in Figure 10b correspond to the three CV3 subtypes in this work. The cyan group has 440 average I_{2D}/I_{D+G} value of ~1.1 and contains three $CV3_{oxB}$ chondrites (samples 1, 2, and 5), three 441 currently unclassified CV3 chondrites (samples 4, 6, and 7), and a CV3_{0xA} (LAR 06317, see 442 discussion below). The green group is composed of CV3_{oxA} chondrites and presents a higher 443 ratio (an average I_{2D}/I_{D+G} value of ~2.6). The only CV3_{red} chondrite (sample 10) falls in close 444 proximity to the green (CV3_{oxA}) group, while currently unclassified sample 11 presents the 445 highest I_{2D}/I_{D+G} ratio. In this context, we can also attempt to anticipate the subtypes of samples 4, 446 6, 7, and 11. Based on Figures 8, 10, and 12, the CV3 samples 4, 6, and 7 can be tentatively 447 classified into CV3_{oxB}, while sample 11 can be tentatively classified into CV3_{red}. On the other 448 hand, the only reduced CV3 chondrite (sample 10) falls near the CV3_{oxA} group in Figure 10, and 449 should be further checked to verify its subtype. 450

(iii) Even though LAR 06317 was classified as $CV3_{oxA}$ (Lunning et al. 2016), it always plots together with the more primitive, less metamorphosed $CV3_{oxB}$ chondrites in our work when the second order carbon peak parameters are compared. While it is currently unknown why this is the case, one possibility might be the impact history of this particular meteorite in the parent body. In general, short term thermal metamorphism due to impacts and shock heating can affect 456 the structures of polyaromatic organic matter (i.e., ordering of carbon) (Quirico et al. 2018; Nemeth and Garvie, 2020). Shock effects of impacts can also convert carbonaceous matter to 457 diamond (Nemeth and Garvie, 2020). As a result, impacts can complicate the effects of thermal 458 metamorphism in meteorites. The parent body of LAR 06317 may have experienced impacts and 459 collisions that caused shock heating of LAR 06317, as evidenced by the presence of multiple a 460 461 few mm-long impact melt clasts in the LAR 06317 (Lunning et al. 2016). In addition, while LAR 06317 has a shock grade of S3, Lunning et al. (2016) reported that LAR 06317 may have been 462 derived from precursors that had experienced only low-temperature thermal metamorphism. 463 Despite the impact history of LAR 06317, the polyaromatic organic matter appears to remain 464 more primitive than other CV_{oxA} chondrites. Another possibility could be the misclassification of 465 its subtype. Lunning et al. (2016) reported that LAR 06317 is a brecciated, oxidized Allende-466 type CV3.5-3.9 (CV_{oxA}) chondrite, however Bonal et al. (2020) classified it as a CV_{oxB} based on 467 the modal abundance of metal and the average Ni content of sulfides. In our work, LAR 06317 468 469 always plots with $CV3_{oxB}$ chondrites in the second order peak parameter domains. Especially in Figure 10b, LAR 06317 plots together with other $CV3_{oxB}$ chondrites, whereas the $CV3_{oxA}$ 470 subtypes plot separately and further up in the I_{2D}/I_{D+G} parameter domain. Therefore, we 471 conclude, based on our Raman investigation, that LAR 06317 is more compatible with CV3_{oxB} 472 chondrites. We emphasize that the identification of LAR 06317 as CV3_{oxB} is not clear when the 473 first order peak parameters are considered. This can suggest either LAR 06317 is in fact a 474 shocked CV3_{0xA} but its polyaromatic organic matter structures remain primitive such that its 475 second order peak parameters still plot with CV3_{oxB} while the first order parameters are unable to 476 distinguish it from CV3_{oxA}, or alternatively LAR 06317 is actually CV3_{oxB} in which case the 477 second order peak parameters again recognize this misclassification. 478

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The peak metamorphic temperatures of the considered CV3_{oxB} are calculated to be between 220 -480 510 °C, however PMTs for CV3_{oxA} vary from 450 °C to ~636 °C, indicating that studied CV3_{oxB} 481 chondrites are less metamorphosed (thus more primitive) than CV3_{oxA} chondrites. This is in 482 483 agreement with the literature (e.g., Bonal et al. 2020). Furthermore, our data show a large temperature increase (150 °C) between the CO3.2 and CO3.4 petrologic types, but much less 484 difference between CO3.4 and CO3.6 (20 °C), as shown in Figure 11. This may indicate that 485 during the thermal metamorphism, the graphitization and/or aromatization rate of carbon 486 structures in the CO3 chondrites initially proceeds at a higher rate but then the rate slows down 487 perhaps at a critical temperature regime/threshold where the carbonaceous matter reaches a 488 certain level of maturity and structural ordering of carbon. 489

490

Other processes such as ion irradiation in space can cause amorphization of carbon as well, and 491 as a result the G band's position moves towards lower wavenumbers (Busemann et al. 2007). 492 This may complicate the study of parent body thermal metamorphism based on Raman peak 493 parameters of carbon, because the irradiated carbonaceous matter in such meteorites would 494 appear closer to that of more primitive samples, implying relatively less thermal metamorphism. 495 However our Raman data show that there is no meteorite whose G band position is at such low 496 wavenumbers (i.e., no G band is present below 1595 cm⁻¹), therefore our results and implications 497 for the thermal history of investigated meteorites are free of complications introduced by the 498 external processes such as irradiation. 499

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501 Understanding effects of asteroidal processes on organics may be more complex than previously thought. For instance, origin and starting materials of carbon may be different, and thermal 502 metamorphism may cause different levels of ordering for carbon (Sears 2016). Two of the 503 possible sources for the parent body thermal metamorphism are (i) long term heating (heating 504 over a few million years) due to the decay of radionuclides such as ²⁶Al, and (ii) short term 505 heating (a few days) due to impacts (Rubin et al. 1995; Nakato et al. 2008). The peak 506 metamorphic temperature calculations assume the former, long term, heating in the parent body 507 (Busemann et al. 2007). Possible effects of short term heating (such as impact heating) on the 508 509 carbon structures are yet to be fully understood, and require additional work.

510

It is appropriate to note that while our results show trends and correlations between the carbon 511 peak parameters and thermal metamorphism, they are not representative for the entire CV and 512 CO group members. The small number of samples from each of the petrographic subtypes could 513 reflect sampling biases. For instance, the three carbon thermometry equations yield roughly 514 similar PMT ranges even though the models of Busemann et al. (2007) and Cody et al. (2008) 515 are based only on Γ_D while the model of Young et al. (2020) is based on both Γ_D and Γ_G . In this 516 case the Γ_{G} may seem to be a poor thermal metamorphism tracer; however, this may not 517 necessarily be true because our results in this work may be affected by the sampling bias. More 518 meteorites from various types should be studied to see the differences of the carbon thermometry 519 520 models and how the parameters of the G band effects the PMT values.

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IMPLICATIONS

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523 Constraining the parent body processes is essential for understanding the early solar system and its evolution. Detailed Raman spectral trends and relationships of polyaromatic carbonaceous 524 matter in a number of CV3 and CO3 chondrites were investigated in this work in an effort to (i) 525 infer the effects of parent body thermal metamorphism on the organic matter, (ii) check whether 526 the second order peak parameters can unravel any spectral relations with thermal metamorphism, 527 (iii) assess the capability and potential of the second order carbon peak parameters for classifying 528 the CV3 chondrites into one of its subtypes. We studied at least 200 spectra from each type 3 529 chondrite, and extracted Raman spectral parameters from both the first and second order carbon 530 531 peaks. Comparison of spectral parameters provide information about the structure and maturity degree of the carbon (primitive and disordered carbon vs. ordered and graphitized carbon). The 532 CO3 chondrites appear to be more primitive and less thermally altered than CV3 chondrites, 533 although some CO3 chondrites are as thermal metamorphosed as the CV3 chondrites. For 534 instance, the comparison of I_D/I_G with Γ_D show that the CV3 and CO3 chondrites plot at two 535 distinct locations, apart from each other (Figure 4). The I_D/I_G ratio shows a strong positive 536 correlation with the petrologic types of meteorites (Figure 7), indicating that the intensity of the 537 D band is a good indicator of thermal metamorphism, at least for the investigated CV3 and CO3 538 chondrites. 539

540

Estimated peak metamorphic temperatures show that the studied CO3 chondrites in general experienced lower temperatures than CV3 chondrites. The considered CO3 chondrites span a range of 220-510 °C, whereas the CV chondrites fall between 460-636 °C. However, this conclusion applies to the considered samples and not to the entire CV3 and CO3 chondrites as some CO3 chondrites present higher peak metamorphic temperatures than some CV3 chondrite

(Figure 11). Indeed, there exists a CV3 chondrite (Kaba, non-Antarctic fall) whose petrologic 546 type is lower than a CO3 chondrite (Isna, non-Antarctic find) (Bonal et al. 2016). We also 547 observed that there is a large temperature increase between CO3.2 and CO3.4 (150 °C increase), 548 however not much difference between CO3.4-CO3.6 (20 °C). It may be worth investigating the 549 presence of a possible critical metamorphic temperature regime where the carbonaceous matter 550 reaches a certain level of maturity and structural ordering of carbon, beyond which the 551 graphitization and/or aromatization rate of carbon structures in the CO3 chondrites proceeds at a 552 slower rate. 553

554

The oxidized CV3 chondrites ($CV3_{oxA}$ and $CV3_{oxB}$) plot apart from each other when the second order peak parameters are considered, indicating their organic matter are different to some degree. This suggests a different level of thermal metamorphism for the two subtypes in the parent body in the case of a single parent asteroid. $CV3_{oxA}$ seems to be more heated than $CV3_{oxB}$ based on the samples studied here, their average peak metamorphic temperatures were estimated as ~598-653 °C for $CV3_{oxA}$ and ~490-526 °C for $CV3_{oxB}$. A larger dataset with more samples from each subtype should be considered for more conclusive interpretations.

562

The three carbon thermometers available in the literature are based on the first order carbon peak parameters (e.g., Cody et al. 2008, Busemann et al. 2007; Young et al. 2020). Among the first order carbon peaks, the D band was reported to be a better tracer for thermal metamorphism. We show that the second order peak parameters present correlations with thermal metamorphism as well. Namely, the comparison of Γ_{2D} and $\Gamma_{2D} / \Gamma_{D+G}$ presents a linear trend, and Γ_{2D} decreases while I_{2D} increases as thermal metamorphism increases (Figure 8). Because the second order

569 carbon peaks are observable, it would be interesting, for a future work, to create a 570 geothermometer expression that takes into account the second order peaks as well. With a proper 571 calibration, such a geothermometer can potentially yield more accurate peak metamorphic 572 temperatures for the parent asteroids.

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ACKNOWLEDGEMENTS

Meteorites studied in this work are recovered by the United States - Antarctic Search for 575 Meteorites (ANSMET) program. We are very grateful to NASA Johnson Space Center and the 576 577 Meteorite Working Group for generously providing the meteorite samples. We thank the associate editor Dr. Bradley De Gregorioand and the two reviewers for their helpful and 578 constructive comments, which significantly improved this manuscript. This work is funded in 579 part by the RISE2 node of NASA's Solar System Exploration Research Virtual Institute 580 (SSERVI; PI: T.D. Glotch). MY acknowledges the support by the Ministry of Industry and 581 Technology of Turkey as well as TUBITAK MAM Polar Research Institute. The data presented 582 here will be made publicly available at Turkish Spectral Database upon publication 583 (http://tsd.klu.edu.tr). 584

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REFERENCES CITED

Alexander, C.M.O.D., Fogel, M., Yabuta, H., and Cody, G. D. (2007). The origin and
 evolution of chondrites recorded in the elemental and isotopic compositions of their
 macromolecular organic matter. Geochimica et Cosmochimica Acta, 71(17), 4380-4403.

591	2.	Alexander, C.M.O.D., Greenwood, R.C., Bowden, R., Gibson, J.M., Howard, K.T.,
592		Franchi, I.A. (2018). A mutli-technique search for the most primitive CO chondrites.
593		Geochimica et Cosmochimica Acta, 221,406-420.
594	3.	Ashworth, J.R. (1980). Chondrite thermal histories: Clues from electron microscopy of
595		orthopyroxene. Earth and Planetary Science Letters, 46(2), pp.167-177.
596	4.	Bonal, L., Bourot-Denise, M., Quirico, E., Montagnac, G., and Lewin, E. (2007). Organic
597		matter and metamorphic history of CO chondrites. Geochimica et Cosmochimica
598		Acta, 71(6), 1605-1623.
599	5.	Bonal, L., Quirico, E., Flandinet, L., and Montagnac, G. (2016). Thermal history of type
600		3 chondrites from the Antarctic meteorite collection determined by Raman spectroscopy
601		of their polyaromatic carbonaceous matter. Geochimica et Cosmochimica Acta, 189, 312-
602		337.
603	6.	Bonal, L., Gattacceca, J., Garenne, A., Eschrig, J., Rochette, P. and Ruggiu, L.K. (2020).
604		Water and heat: New constraints on the evolution of the CV chondrite parent body.
605		Geochimica et Cosmochimica Acta, 276: 363-383.
606	7.	Botta, O., and Bada, J.L. (2002). Extraterrestrial organic compounds in meteorites.
607		Surveys in Geophysics, 23(5), 411-467.
608	8.	Brearley, A.J. and Jones, R.H (1998). Chondritic meteorites. In: J.J. Papike (Ed.):
609		Planetary materials. Reviews in Mineralogy, 36, pp.4-90.
610	9.	Brearley A. J. (2006) The action of water. In Meteorites and the Early Solar System II
611		D.S. Lauretta and H.Y. McSween Jr., Tucson. pp. 584-624.

- 612 10. Brearley, A.J. and Krot, A.N. (2013). Metasomatism in the early solar system: The record
- from chondritic meteorites. In Metasomatism and the chemical transformation of rock
- 614 (pp. 659-789), Springer, Berlin, Heidelberg.
- 615 11. Brunetto, R., Pino, T., Dartois, E., Cao, A.T., d'Hendecourt, L., Strazzulla, G. and
- Bréchignac, P. (2009). Comparison of the Raman spectra of ion irradiated soot and
- 617 collected extraterrestrial carbon. Icarus, 200(1), pp.323-337.
- 618 12. Busemann, H., Alexander, C.M.O.D., and Nittler, L.R. (2007). Characterization of
- 619 insoluble organic matter in primitive meteorites by microRaman
- 620 spectroscopy. Meteoritics & Planetary Science, 42(7-8), 1387-1416.
- 621 13. Cody, G.D., Alexander, C.M.O.D., Yabuta, H., Kilcoyne, A.L.D., Araki, T., Ade, H.,
- Dera, R., Fogel, M., Militzer, B. and Mysen, B.O. (2008) Organic thermometry for
 chondritic parent bodies. Earth and Planetary Science Letters 272, 446-455.
- 624 14. Ferrari, A.C., and Robertson, J. (2000). Interpretation of Raman spectra of disordered and
 625 amorphous carbon. Physical review B, 61(20), 14095.
- 15. Ferrari, A.C., and Robertson, J. (2001). Resonant Raman spectroscopy of disordered,
- amorphous, and diamondlike carbon. Physical review B, 64(7), 075414.
- 628 16. Gattacceca, J., Bonal, L., Sonzogni, C., and Longerey, J. (2019). CV Chondrites: More
- than One Parent Body, 2157, In 82nd Annual Meeting of The Meteoritical Society.
- 630 17. Greenwood, R.C., and Franchi, I.A. (2004). Alteration and metamorphism of CO3
- 631 chondrites: Evidence from oxygen and carbon isotopes. Meteoritics & Planetary Science,
- **632 39**(11), 1823-1838.

633	18. Howard, K.T., Benedix, G.K., Bland, P.A., and Cressey, G. (2010). Modal mineralogy of
634	CV3 chondrites by X-ray diffraction (PSD-XRD). Geochimica et Cosmochimica Acta,
635	74(17), 5084-5097.
636	19. Huss, G.R., Rubin, A.E., and Grossman, J.N. (2006). Thermal metamorphism in
637	chondrites. Meteorites and the early solar system II, 943, pp. 567-586.
638	20. Itoh, D., and Tomeoka, K. (2003). Dark inclusions in CO3 chondrites: New indicators of
639	parent-body processes. Geochimica et Cosmochimica Acta, 67(1), 153-169.
640	21. Jenniskens P., Fries M.D., Yin QZ., Zolensky M., Krot A.N., Sandford S.A., Sears D.,
641	Beauford R., Ebel D.S., Friedrich J.M., and others. (2012). Radar-Enabled Recovery of
642	the Sutter's Mill Meteorite, a Carbonaceous Chondrite Regolith Breccia. Science
643	338:1583–1587.
644	22. Keck B. D. and Sears D. W. G. (1987). Chemical and physical studies of type 3
645	chondrites VIII: The CO chondrites. Geochimica et Cosmochimica Acta 51:3013-3022.
646	23. Kessel, R., Beckett, J.R. and Stolper, E.M. (2007). The thermal history of equilibrated
647	ordinary chondrites and the relationship between textural maturity and temperature.
648	Geochimica et Cosmochimica Acta, 71(7), pp.1855-1881.
649	24. Kitajima, F., Nakamura, T., Takaoka, N., and Murae, T. (2002). Evaluating the thermal
650	metamorphism of CM chondrites by using the pyrolytic behavior of carbonaceous
651	macromolecular matter. Geochimica et Cosmochimica Acta, 66(1), 163-172.
652	25. Krot, A.N., Scott, E.R.D., and Zolensky, M.E. (1995). Mineralogic and chemical
653	variations among CV3 chondrites and their components: Nebular and asteroidal
654	processing. Meteoritics, 30, 748-775.

- 655 26. Krot, A.N., Petaev, M.I., Scott, E.R., Choi, B.G., Zolensky, M.E., and Keil, K. (1998).
- 656 Progressive alteration in CV3 chondrites: More evidence for asteroidal alteration.
- 657 Meteoritics & Planetary Science, 33(5), 1065-1085.
- 658 27. Krot, A.N., Petaev, M.I., and Bland, P.A. (2003). Growth of ferrous olivine in the
- oxidized CV chondrites during a fluid-assisted thermal metamorphism.
- 660 Meteoritics & Planetary Science, 38, A73.
- 28. Krot, A.N., Keil, K., Scott, E.R.D., Goodrich, C.A. and Weisberg, M.K. (2014).
- 662 Classification of meteorites and their genetic relationships. Meteorites and
- 663 Cosmochemical Processes, Volume 1 of Treatise on Geochemistry (Second Edition).
- Elsevier, 2014. Edited by Andrew M. Davis, p.1-63.
- 29. Lunning, N.G., Corrigan, C.M., McSween Jr, H.Y., Tenner, T.J., Kita, N.T., and Bodnar,
- R.J. (2016). CV and CM chondrite impact melts. Geochimica et Cosmochimica Acta,
 189, 338-358.
- 668 30. Ma, B., Rodriguez, R.D., Ruban, A., Pavlov, S., and Sheremet, E. (2019). The correlation
- between electrical conductivity and second-order Raman modes of laser-reduced
- graphene oxide. Physical Chemistry Chemical Physics, 21(19), 10125-10134.
- 31. MacPherson, G.J. and Krot, A.N. (2014). The formation of Ca-, Fe-rich silicates in
- reduced and oxidized CV chondrites: the roles of impact-modified porosity and
- 673 permeability, and heterogeneous distribution of water ices. Meteoritics & Planetary
- 674 Science, 49(7), pp.1250-1270.
- 32. McSween Jr, H.Y. (1977a). Carbonaceous chondrites of the Ornans type: A metamorphic
 sequence. Geochimica et Cosmochimica Acta, 41(4), pp.477-491.

677	33.	McSween Jr, H.Y. (1977b). Chemical and petrographic constraints on the origin of
678		chondrules and inclusions in carbonaceous chondrites. Geochimica et Cosmochimica
679		Acta, 41(12), 1843-1860.
680	34.	McSween Jr, H.Y. (1977c). Petrographic variations among carbonaceous chondrites of
681		the Vigarano type. Geochimica et Cosmochimica Acta, 41(12), 1777-1790.
682	35.	Nakato, A., Nakamura, T., Kitajima, F., and Noguchi, T. (2008). Evaluation of
683		dehydration mechanism during heating of hydrous asteroids based on mineralogical and
684		chemical analysis of naturally and experimentally heated CM chondrites. Earth, Planets
685		and Space, 60(8), 855-864.
686	36.	Németh, P., and Garvie, L.A. (2020). Extraterrestrial, shock-formed, cage-like
687		nanostructured carbonaceous materials. American Mineralogist, 105(2), 276-281.
688	37.	Pizzarello, S., Cooper, G.W., and Flynn, G. J. (2006). The nature and distribution of the
689		organic material in carbonaceous chondrites and interplanetary dust particles. Meteorites
690		and the early solar system II, 1, 625-651.
691	38.	Quirico E., Raynal P. I. and Bourot-Denise M. (2003) Metamorphic grade of organic
692		matter in six unequilibrated ordinary chondrites. Meteoritics & Planetary Science, 38,
693		795–811.
694	39.	Quirico, E., Bonal, L., Beck, P., Yabuta, H., Nakamura, T., Nakato, A., Flandinet, L.,
695		Montagnac, G., Schmitt-Kopplin, P. and Herd, C.D.K. (2018). Prevalence and nature of
696		heating processes in CM and C2-ungrouped chondrites as revealed by insoluble organic
697		matter. Geochimica et Cosmochimica Acta, 241, pp.17-37.
698	40.	Remusat, L. (2014). Organic material in meteorites and the link to the origin of life.
699		In BIO web of conferences (Vol. 2, p. 03001). EDP Sciences.

41. Rubin, A.E. (1995). Petrologic evidence for collisional heating of chondritic


701 asteroids. Icarus, 113(1), 156-167.

- 42. Sadezky, A., Muckenhuber, H., Grothe, H., Niessner, R. and Pöschl, U. (2005). Raman
- 703 microspectroscopy of soot and related carbonaceous materials: spectral analysis and
- structural information. Carbon, 43(8), pp.1731-1742.
- 43. Scott, E.R.D., Krot, A. N. (2007). In Treatise on Geochemistry, eds H. D. Holland, K. K.
 Turekian, Eds. (Elsevier Pergamon, Oxford), vol. 1, pp. 1–72.
- 44. Sears, D.W. (2016). The CO chondrites: Major recent Antarctic finds, their thermal and
- radiation history, and describing the metamorphic history of members of the
- class. Geochimica et Cosmochimica Acta, 188, 106-124.
- 45. Starkey, N.A., Franchi, I.A., and Alexander, C.O.D. (2013). A Raman spectroscopic
- study of organic matter in interplanetary dust particles and meteorites using multiple
- wavelength laser excitation. Meteoritics & Planetary Science, 48(10), 1800-1822.
- 46. Suzuki, A., Yamanoi, Y., Nakamura, T., and Nakashima, S. (2010). Micro-spectroscopic
- characterization of organic and hydrous components in weathered Antarctic
- micrometeorites. Earth, planets and space, 62(1), 33-46.
- 716 47. Tuinstra, F., and Koenig, J.L. (1970). Raman spectrum of graphite. The Journal of
 717 chemical physics, 53(3), 1126-1130.
- 48. Vollebregt, S., Ishihara, R., Tichelaar, F.D., Hou, Y., and Beenakker, C.I.M. (2012).
- 719 Influence of the growth temperature on the first and second-order Raman band ratios and
 720 widths of carbon nanotubes and fibers. Carbon, 50(10), 3542-3554.
- 49. Weisberg, M.K., Prinz, M., Clayton, R.N., and Mayeda, T.K. (1997). CV3 chondrites:
- Three subgroups, not two. Meteoritics and Planetary Science Supplement, 32, 138–139.

723	50. Weisberg, M.K., McCoy, T.J., and Krot, A.N. (2006). Systematics and evaluation of
724	meteorite classification. Meteorites and the early solar system II.
725	51. Yesiltas, M., Kebukawa, Y., Peale, R.E., Mattson, E., Hirschmugl, C.J., and Jenniskens,
726	P. (2014). Infrared imaging spectroscopy with micron resolution of Sutter's Mill
727	meteorite grains. Meteoritics & Planetary Science, 49(11), 2027-2037.
728	52. Yesiltas, M. (2018a). Investigation of carbon in the Allan Hills A77278 meteorite via 2D
729	and 3D Raman microspectroscopy. Journal of Raman Spectroscopy, 49(11), 1812-1821.
730	53. Yesiltas, M. (2018b). Investigation of carbonates in the Sutter's Mill meteorite grains
731	with hyperspectral infrared imaging micro-spectroscopy. Spectrochimica Acta Part A:
732	Molecular and Biomolecular Spectroscopy, 194, 92-101.
733	54. Yesiltas, M., Glotch, T.D., Jaret, S., Verchovsky, A.B. and Greenwood, R.C. (2019).
734	Carbonaceous matter in the Sariçiçek meteorite. Meteoritics & Planetary Science, 54(7),
735	pp.1495-1511.
736	55. Young, J., Yesiltas, M., Glotch, T.D. (2020). Reconstructing parent body metamorphism
737	via raman spectroscopy of organic materials in ordinary chondrites. Meteoritics &
738	Planetary Science, in review.
739	56. Zolensky, M., Barrett, R. and Browning, L., 1993. Mineralogy and composition of matrix
740	and chondrule rims in carbonaceous chondrites. Geochimica et Cosmochimica Acta,
741	57(13), pp.3123-3148.
742	Figure captions
743 744 745	Figure 1. Two dimensional carbon distribution maps of studied CV3 (top, black panel) and CO3 (bottom, red panel) chondrites. The numbers on each image denotes the meteorite sample listen in Table 1.

Figure 2. Raman spectra extracted from carbon-rich locations within the measured area of eachmeteorite.

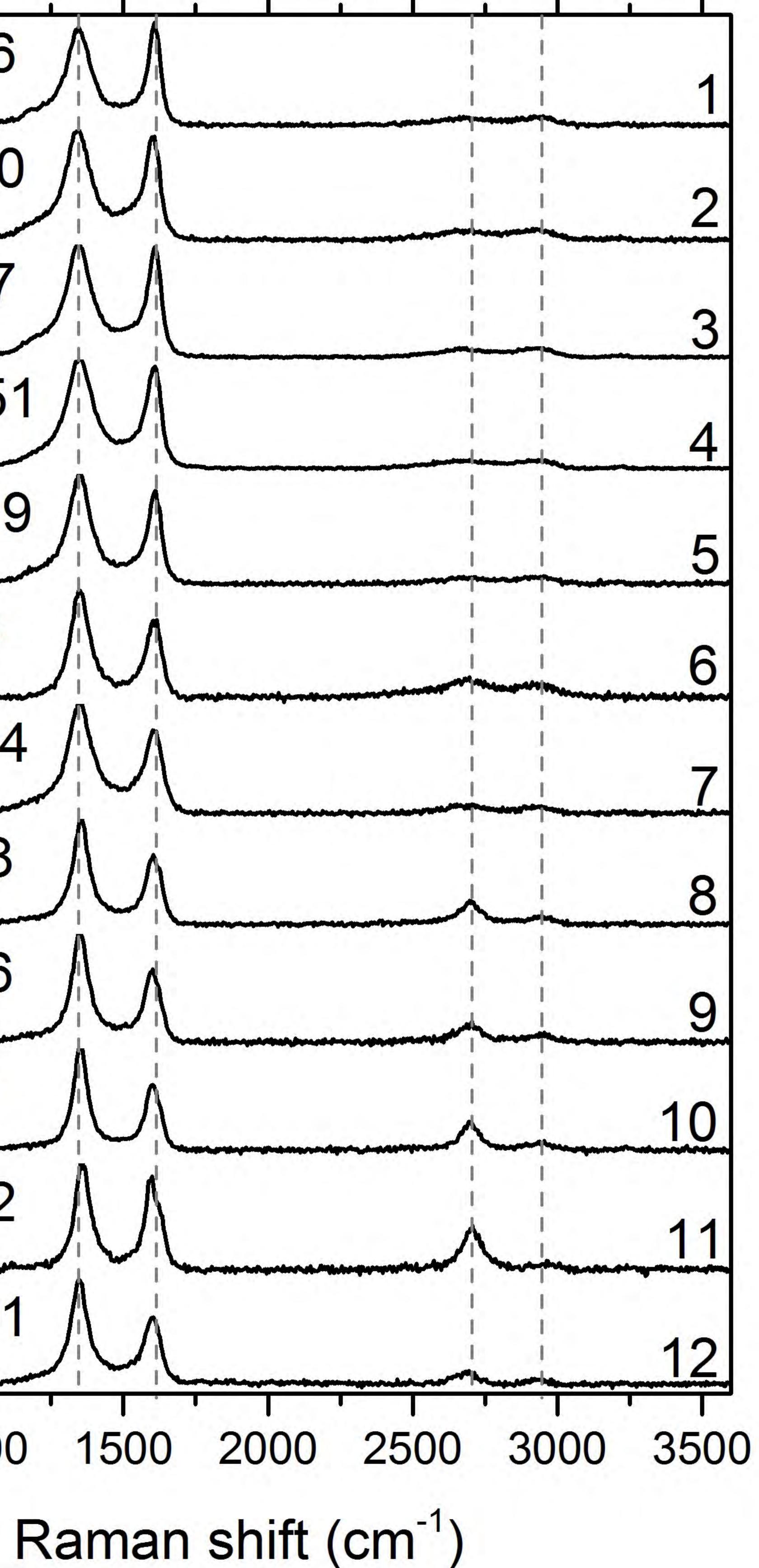
- **Figure 3.** Lorentzian fit procedure example for a single-pixel Raman spectrum. The spectrum
- contains first order (D and G) bands as well as second order (2D and D+G) carbon peaks. Gray
- solid lines are individual fits while the black solid line is the actual collected spectrum. Vertical
- 751 gray dashed lines indicate the positions of peaks.
- **Figure 4.** Peak intensity ratios of the studied meteorites vs. width of the D (a) and G (b) bands.
- **Figure 5.** Comparison of width and position for the first order D (a) and G (b) bands.
- **Figure 6.** First order width ratios Γ_D/Γ_G vs. width of D (a) and G (b) bands.
- Figure 7. Petrologic types of the studied meteorites vs. their first order peak intensity ratios (a)and width of the D band (b).
- **Figure 8.** Comparison of Γ_{2D} (width of 2D band) with Γ_{2D}/Γ_{D+G} (ratio of second order peak
- widths, a) and I_{2D}/I_{D+G} (peak intensity ratios of second order peaks, b).
- Figure 9. Comparison of first order peak intensity ratios with widths of second order peaks 2Dband (a) and D+G band (b).
- **Figure 10.** a: Comparison of Γ_{D} (width of the D band) with ω_{D+G} (position of the D+G band). b: Comparison of second order peak intensity values (I_{2D}/I_{D+G}).
- Figure 11. Peak metamorphic temperatures of CV3 and CO3 chondrites estimated using
 thermometric equations of Busemann et al. (2007), Cody et al. (2008), and Young et al. (2020).
 The top left portion of the data is shown in the inset in the lower left.
- **Figure 12.** Calculated K_T values of the investigated CV3 chondrites, following the method
- 767 described in Young et al. (2020).



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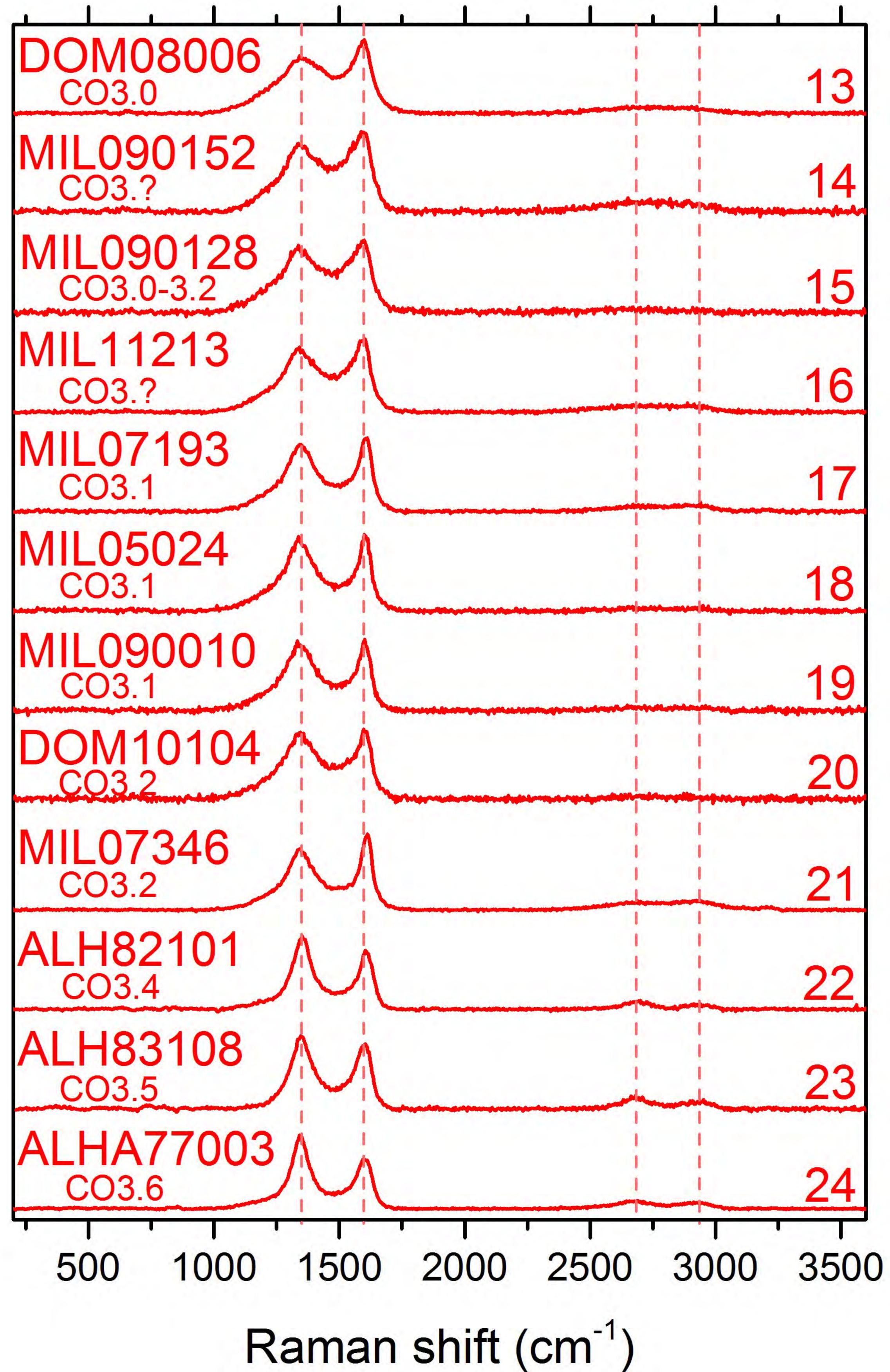
ALH85006 CV3oxB MET00430 CV3oxB LAR0631 CV3oxA DOM10351 CV3-? MCY05219 CV3oxB MIL13328 CV3-? QUE93744 CV3-? LAP02228 CV3oxA LAP02206 CV3oxA MIL07681 CV3oxRed LAR12002 CV3-? **GRA06101** CV3-? 1000 500

(in <u>a</u> Intensity

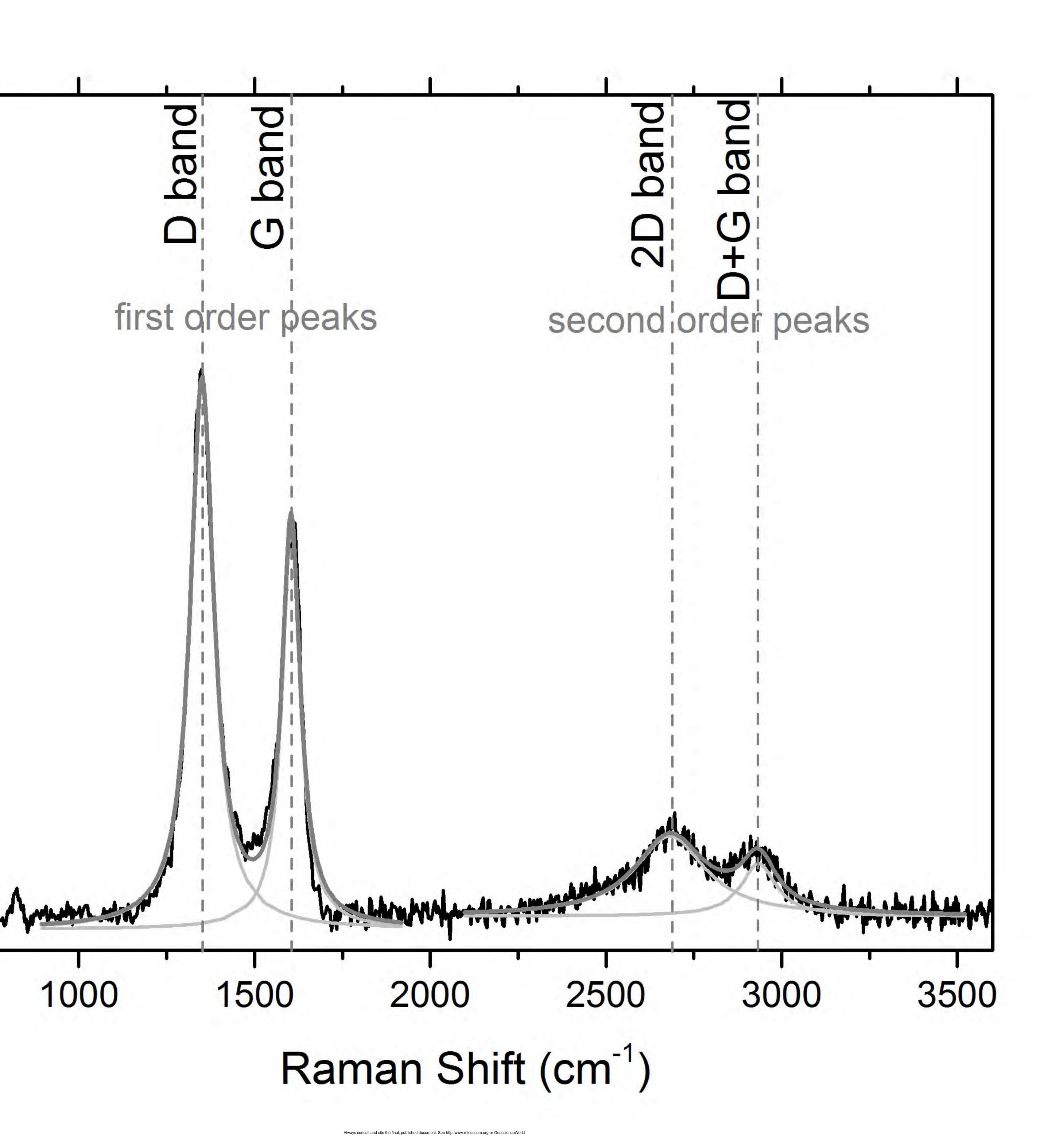


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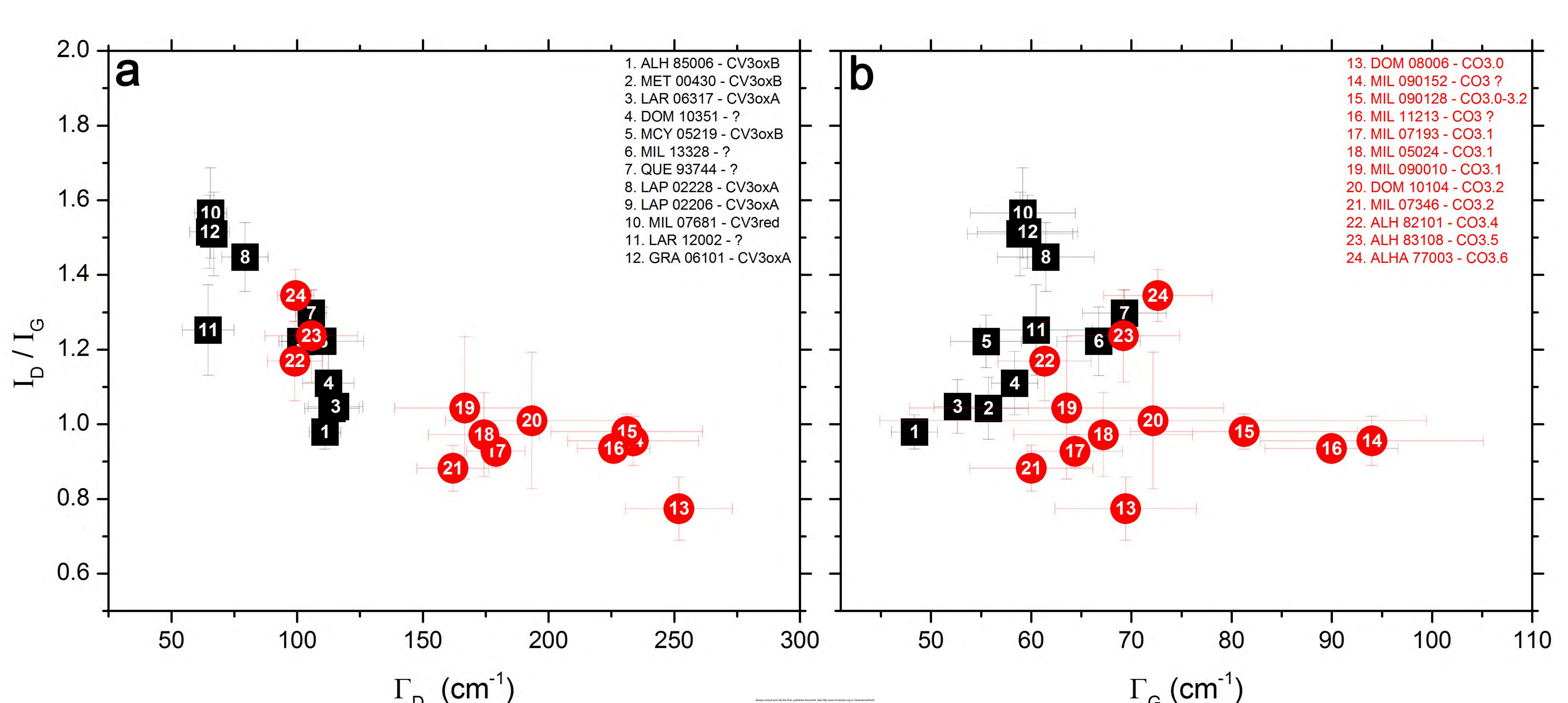
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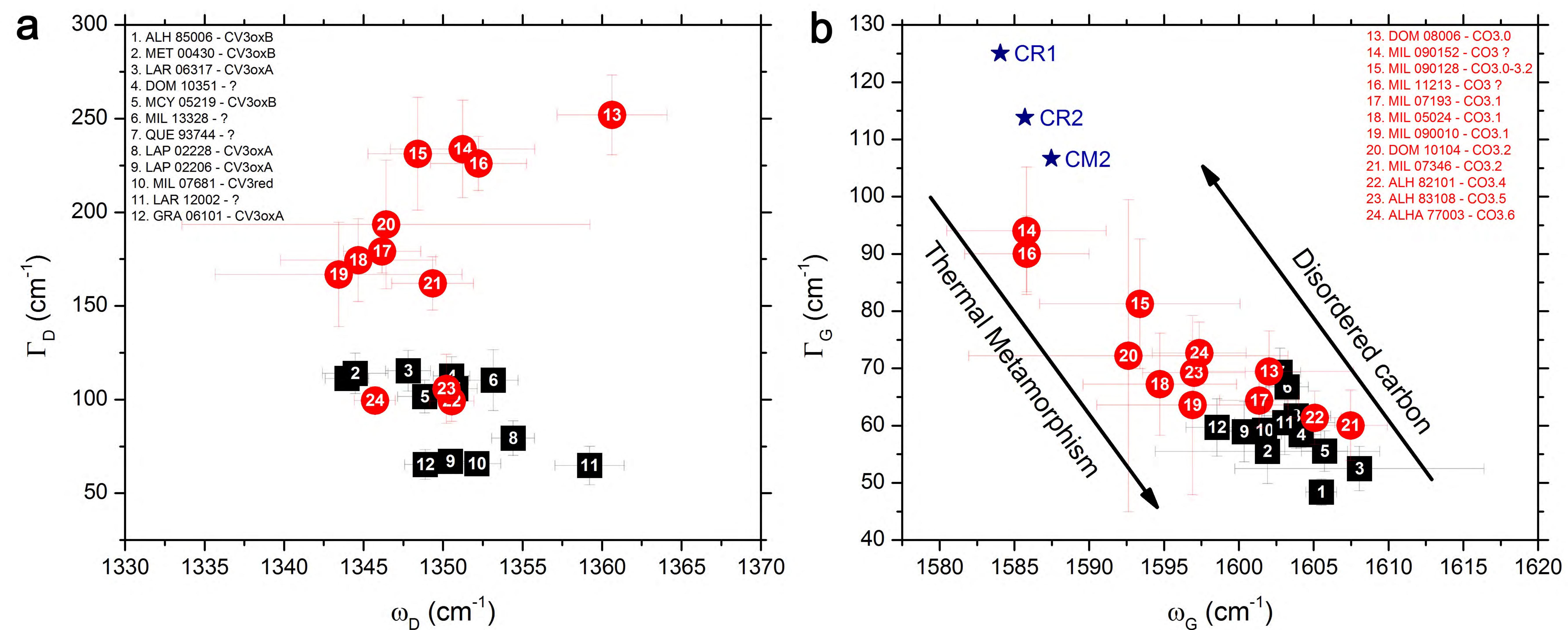
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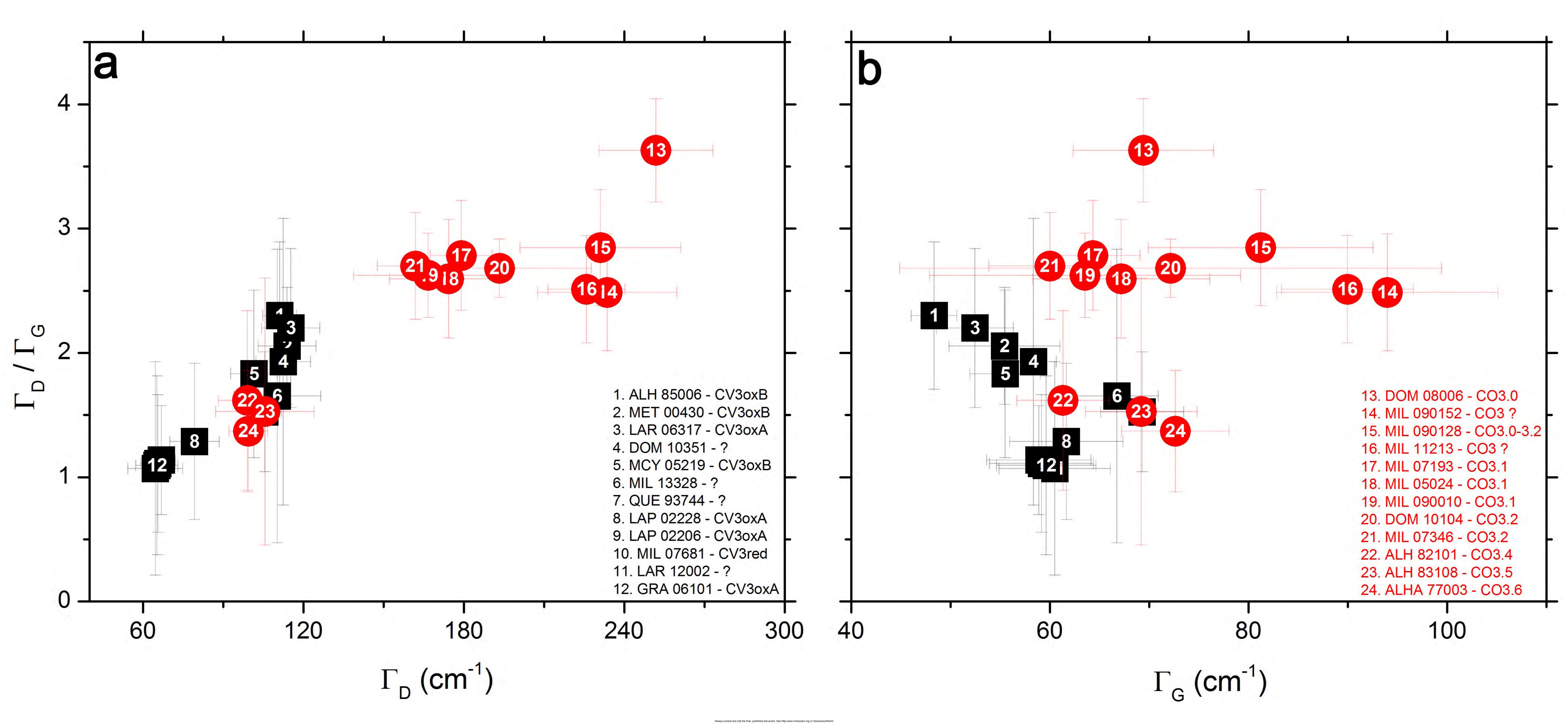
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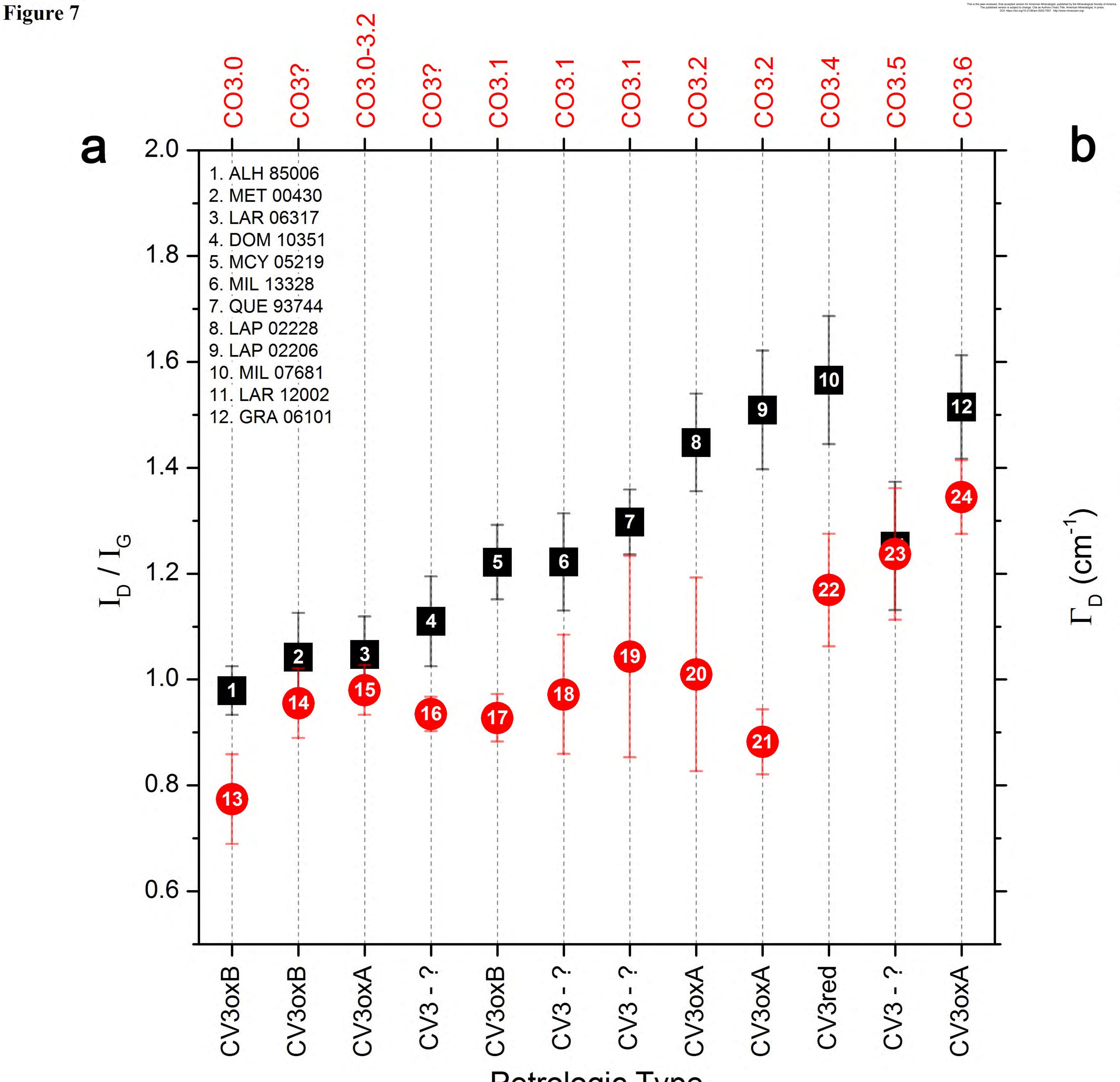


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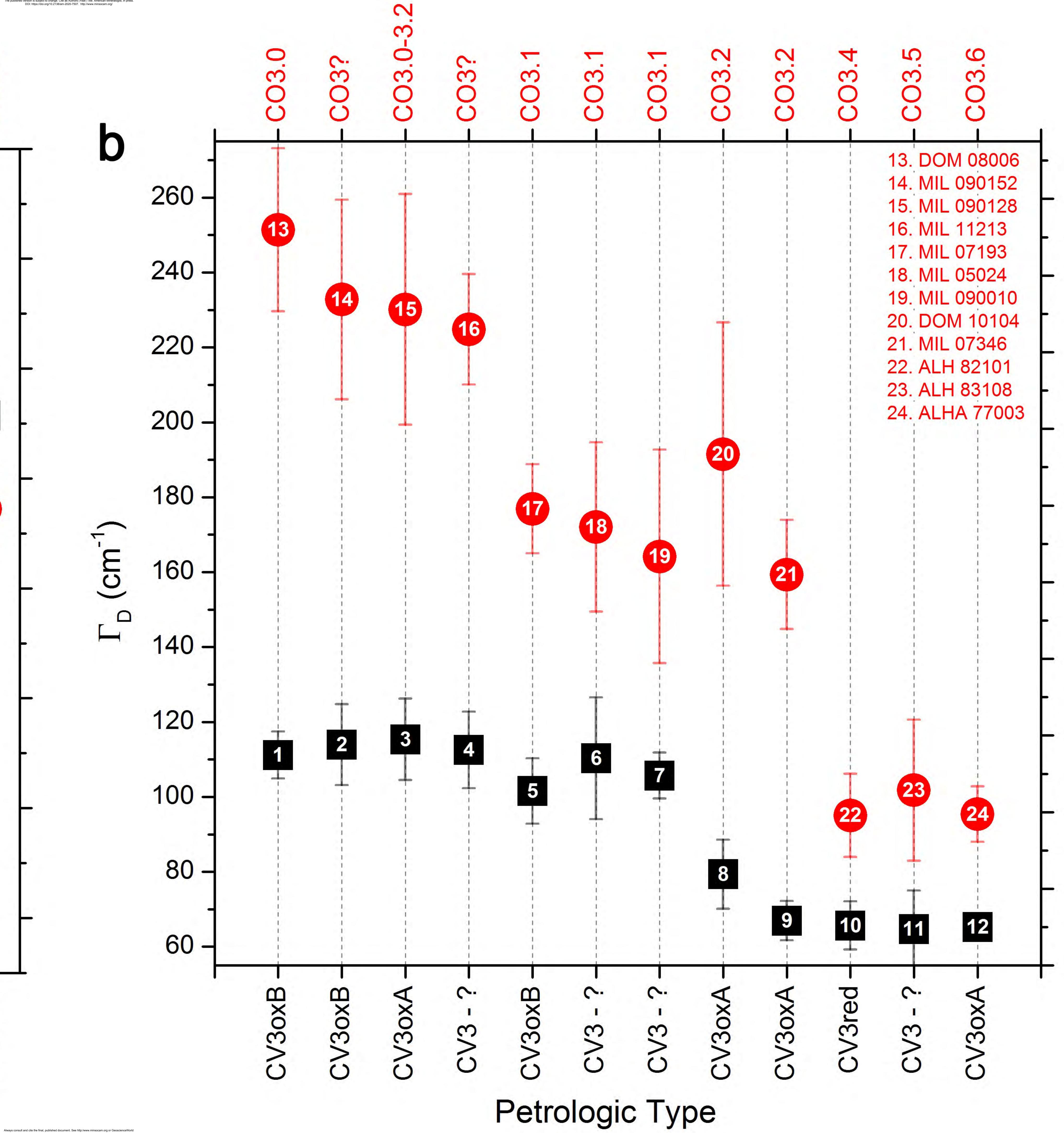
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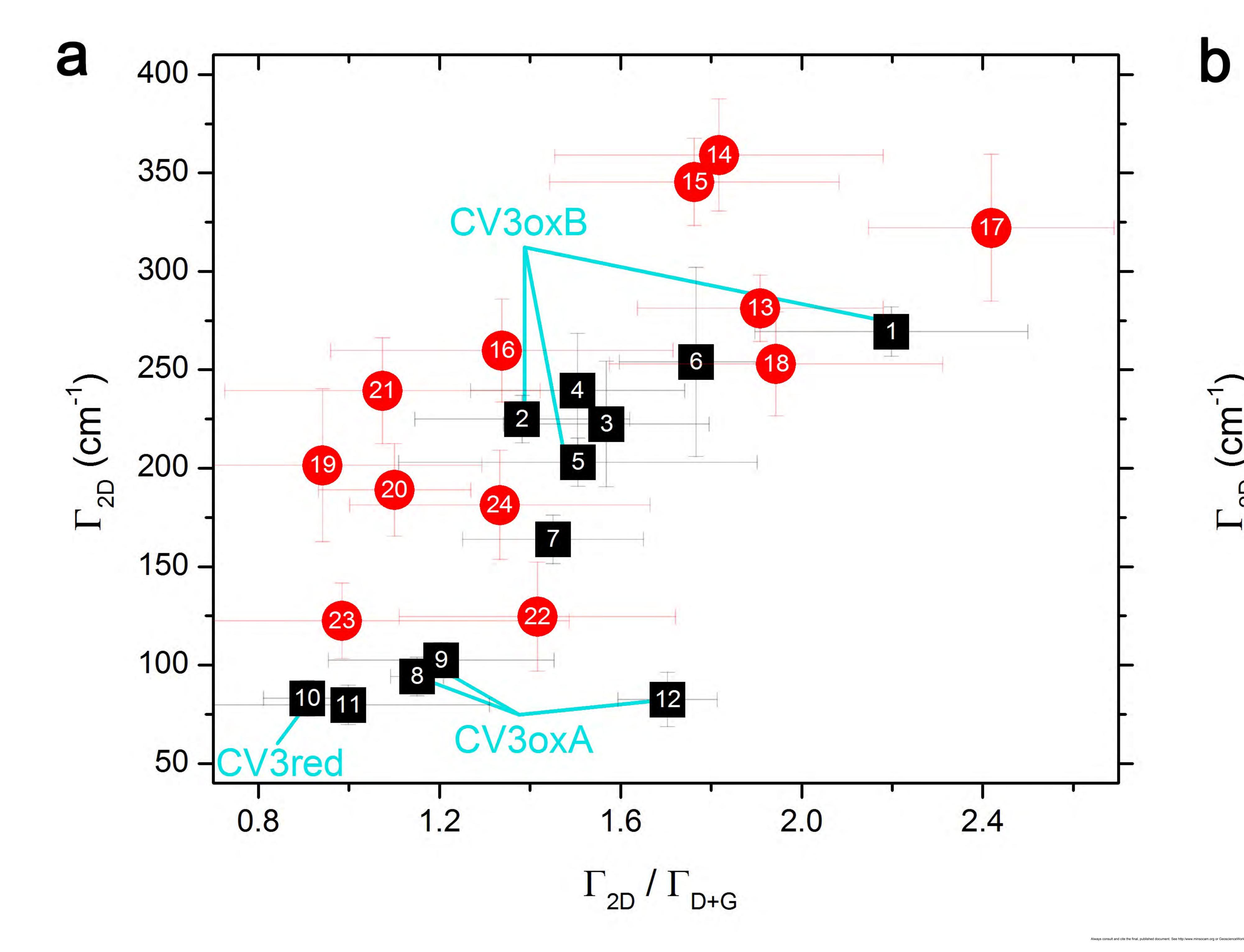


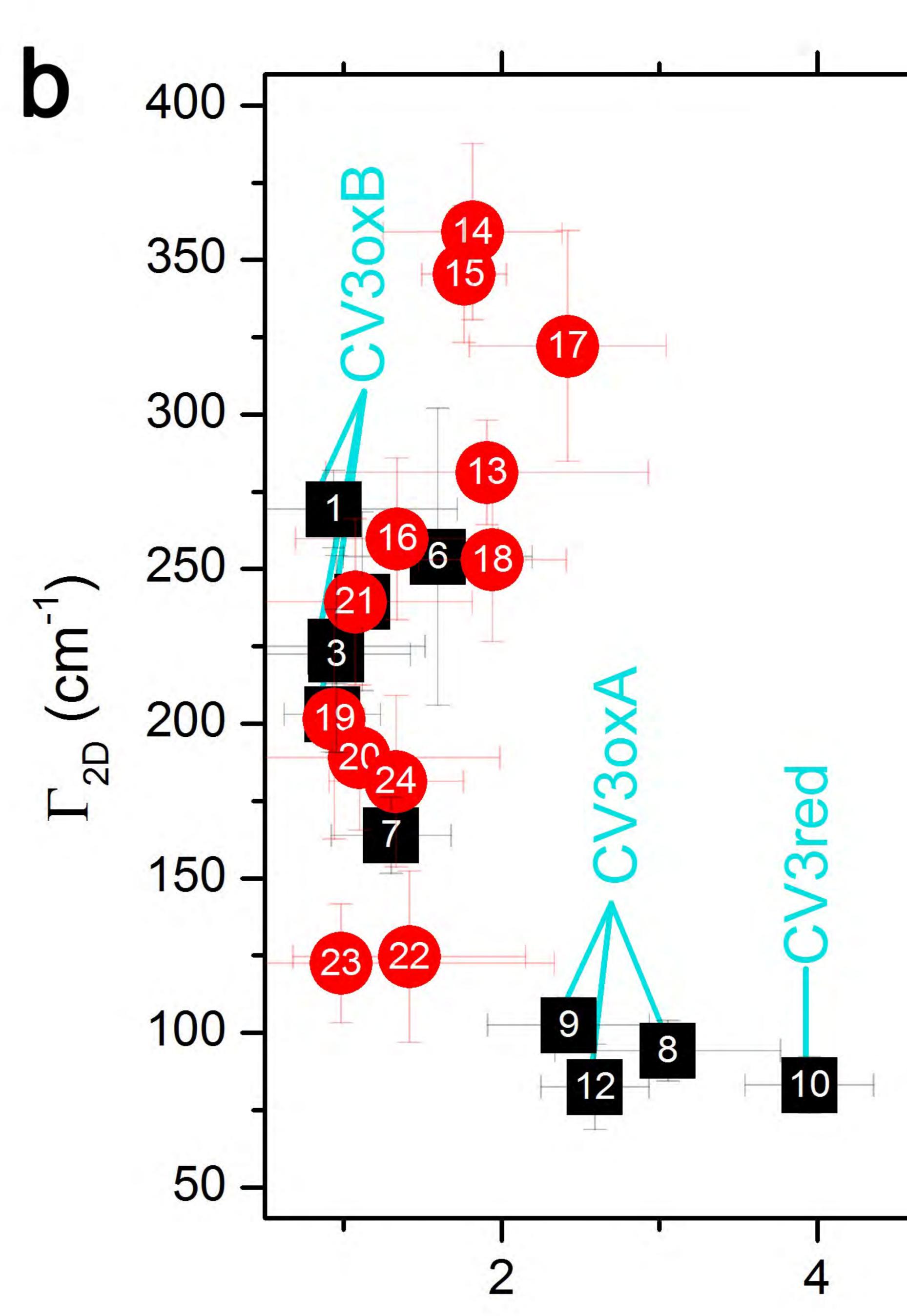
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Petrologic Type



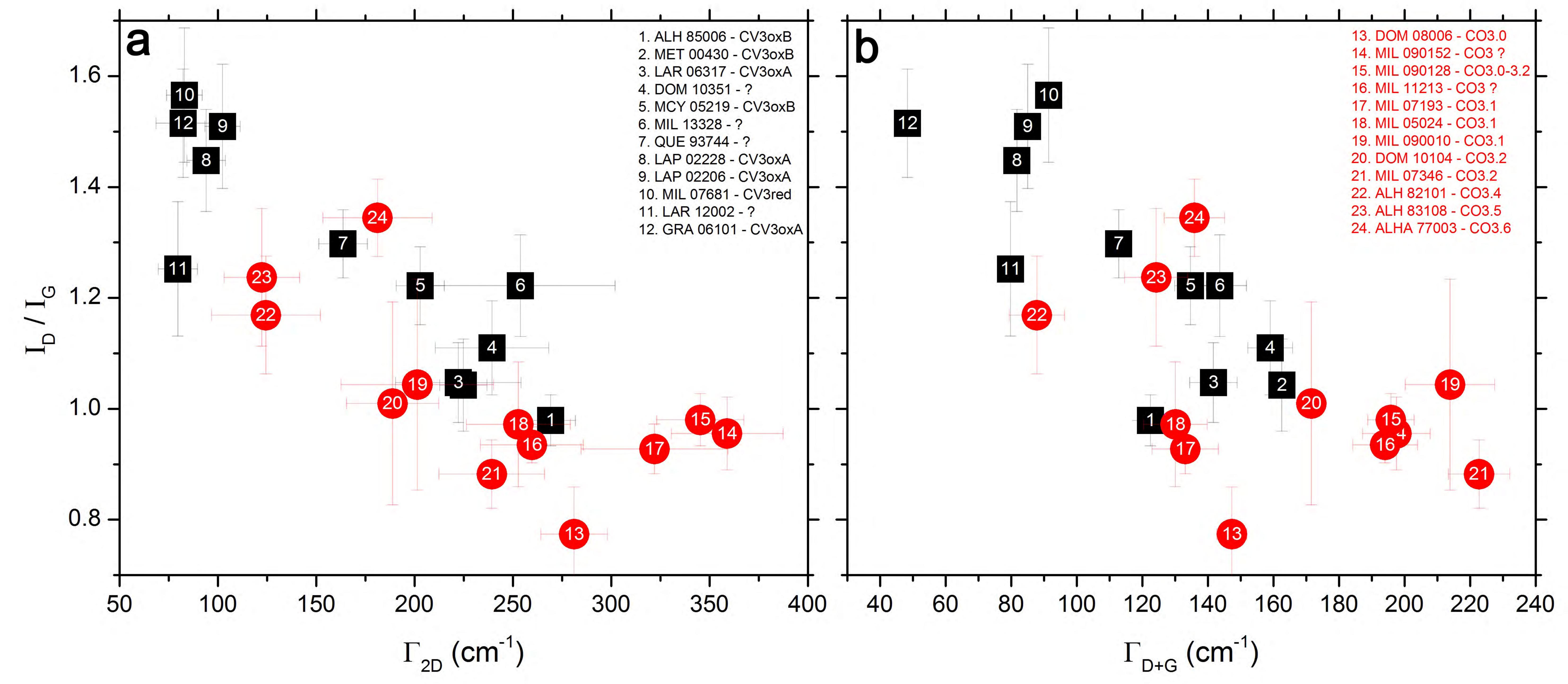




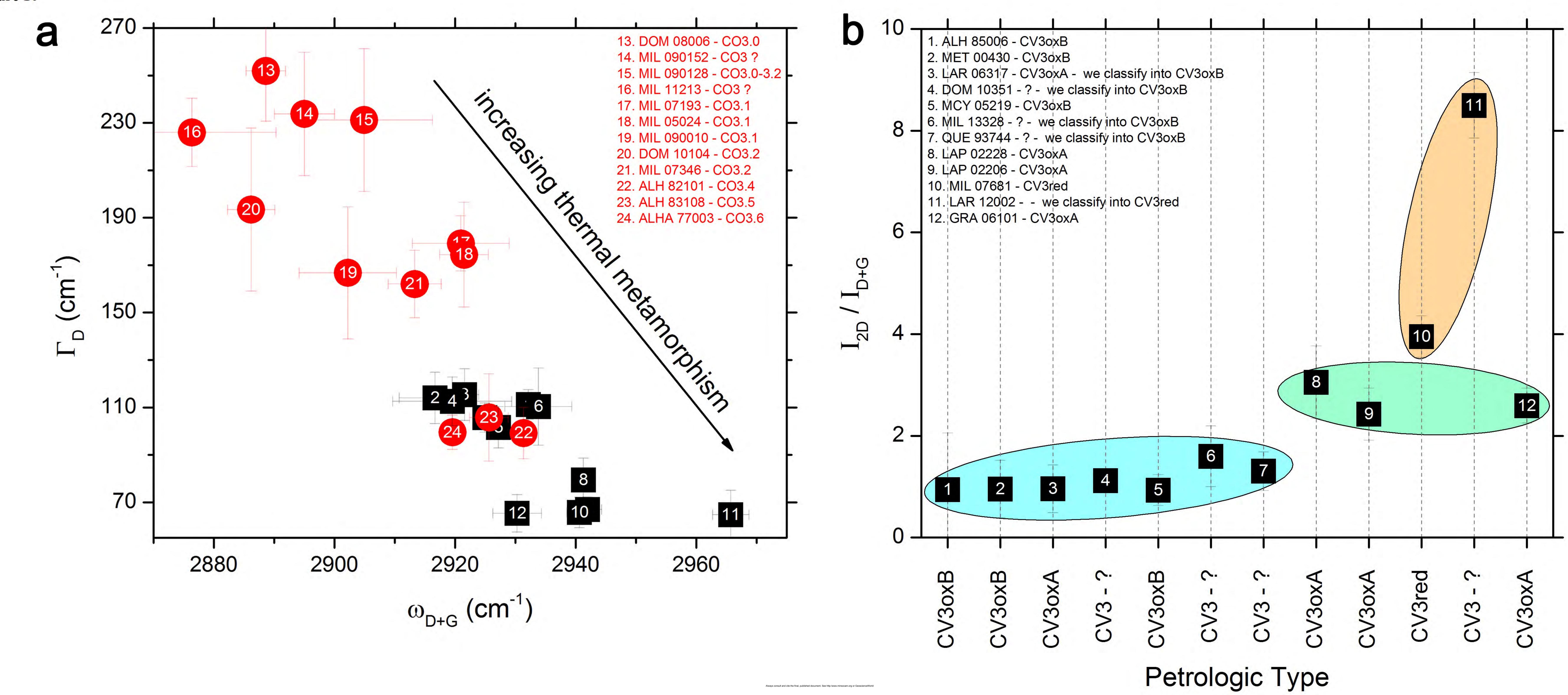
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 I_{2D} / I_{D+G}

1. ALH 85006 - CV3oxB	13. DOM 08006 - CO3.0	-
2. MET 00430 - CV3oxB	14. MIL 090152 - CO3 ?	
3. LAR 06317 - CV3oxA	15. MIL 090128 - CO3.0-3.2	-
4. DOM 10351 - ? 5. MCY 05219 - CV3oxB	16. MIL 11213 - CO3 ?	
6. MIL 13328 - ?	17. MIL 07193 - CO3.1 18. MIL 05024 - CO3.1	
7. QUE 93744 - ?	19. MIL 090010 - CO3.1	
8. LAP 02228 - CV3oxA	20. DOM 10104 - CO3.2	÷>=
9. LAP 02206 - CV3oxA	21. MIL 07346 - CO3.2	
10. MIL 07681 - CV3red	22. ALH 82101 - CO3.4	_
11. LAR 12002 - ?	23. ALH 83108 - CO3.5	
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


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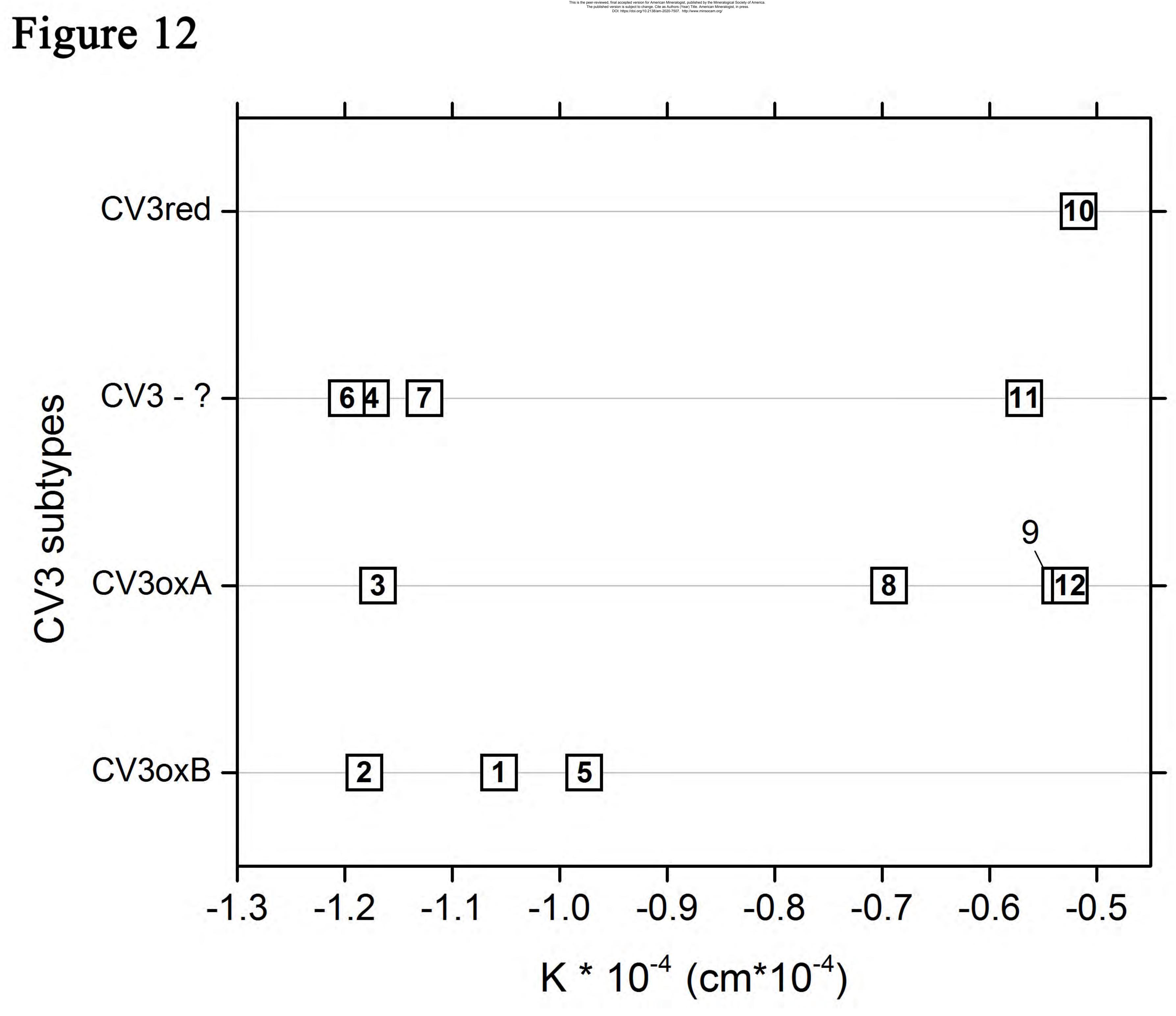


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