

1 **Raman characterization of carbonaceous material in the Macraes orogenic**  
2 **gold deposit and metasedimentary host rocks, New Zealand**

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13  
14 **Abstract**

15 Raman spectroscopic and petrographic analyses were performed on samples collected from  
16 zones distal and proximal to the Macraes gold deposit in the Otago Schist of New Zealand to  
17 characterize the features and possible origins of Carbonaceous Material (CM) and to assess  
18 the potential role of CM in the formation of gold deposits. CM is a common component in  
19 meta-sedimentary orogenic gold deposits, and it has been proposed that CM contributes to  
20 gold mineralization processes, but the details of the mechanisms responsible are not fully  
21 understood. Documentation of the origins of the Otago schist CM will improve our  
22 understanding of the role of CM in gold deposits.

23 This work has identified four types of CM of varying thermal maturity and origins from  
24 prehnite-pumpellyite grade to lower greenschist grade samples. In prehnite-pumpellyite and  
25 pumpellyite-actinolite grade rocks, low-maturity CM 1 coexists with framboidal pyrite,  
26 indicating an *in-situ*, sedimentary origin, with a potential association with the source of gold.  
27 Low crystallinity CM 2 is also found in low grade samples and is likely to have been  
28 deposited from fluids unrelated to gold mobilization. CM 3 is the highest maturity CM  
29 recognized. CM 3 is found in samples from the highest metamorphic grades studied (lower  
30 greenschist facies), where bands of CM 3 cross cut the foliation, CM 3 is therefore thought to  
31 have been transported by fluids, though possibly only at short length scales. CM 4 is less  
32 mature than CM 3 and is found in mineralized rocks in association with sulfide minerals and

33 gold. CM 4 is likely to have a depositional origin but its precise role with respect to gold  
34 mineralization has not been identified.

35

36 **Key words: Carbonaceous Material; Macraes gold deposit; Raman Spectra;**  
37 **Petrographic Analysis; Maturity; Ore Genesis**

38

### 39 **Highlights**

40 \* Four types of carbonaceous materials have been identified in the distal and proximal zones  
41 of Macraes gold deposit, New Zealand;

42 \* Raman spectroscopic and petrographic analyses were applied to samples to identify the  
43 thermal maturity and possible origins of carbonaceous materials;

44 \* Some carbonaceous materials may contribute to the source and deposition of gold.

45

### 46 **1. Introduction**

47 Carbonaceous material (CM) is commonly associated with gold in metasediment-hosted  
48 orogenic and Carlin-type gold deposits (Bierlein et al., 2001; Cox et al., 1995; Large et al.,  
49 2011; Thomas et al., 2011). Detrital CM, especially in organic-matter (OM)-rich shales, can  
50 contribute to the sequestration of metals during sediment deposition, and these OM-rich  
51 sediments can then act as sources for metals during subsequent metamorphic processes  
52 (Large et al., 2011, 2012; Peters et al., 2007; Zhang et al., 1997). During ore deposition, the  
53 presence of CM in metasedimentary host rocks may facilitate precipitation of gold from  
54 hydrothermal fluids by chemical reduction (Bierlein et al., 2001; Cox et al., 1995; Craw et al.,  
55 2010; Goldfarb et al., 2007; Zoheir et al., 2008;). Alternatively, CM may be deposited from  
56 hydrothermal fluids containing volatile organic compounds during gold deposit formation  
57 (Craw, 2002; Gu et al., 2012; Huizenga, 2011; Luque et al., 1998, 2009; Vallance et al.,  
58 2003).

59

60 Because of the close associations between CM and gold in metasedimentary terranes, it is  
61 important to understand the nature of changes in CM during the transitions that occur with  
62 increasing metamorphism and associated fluid migration, and between primary source rocks  
63 and gold depositional systems. Metamorphism of detrital CM has been well studied in several  
64 metasedimentary belts (Beysac et al., 2002, 2003a; Landis, 1971; Pasteris and Wopenka,

65 [1991; Rahl et al., 2005](#)). However, links between organic maturation, CM mobility, and  
66 regional gold mineralization processes have received less attention.

67

68 The texture and structure of CM can be used to assess whether it has been remobilized, and to  
69 infer the role of CM in metal mobilization and deposition ([Luque et al., 1998](#)). The usual  
70 analytical methods employed to provide structural characterization of CM are quantitative  
71 reflectance, X-ray diffraction (XRD), high-resolution transmission electron microscopy  
72 (HRTEM) and Raman microspectroscopy ([Beysac et al., 2002, 2003a; Henne and Craw,](#)  
73 [2012; Wopenka and Pasteris, 1993](#)). With the advantages of *in-situ* analysis and high  
74 resolution data acquisition, Raman microspectroscopy has become increasingly popular (e.g.  
75 [Beysac et al., 2002, 2003a; Jehlička et al, 2003; Pasteris and Wopenka, 2003; Quirico et al.,](#)  
76 [2005, 2009; Rahl et al., 2005](#)). It has long been observed that Raman spectra are sensitive to  
77 changes in crystallinity and structure of CM, which largely depend on temperature during  
78 metamorphism. The graphitization is presumed to be an irreversible process ([Beysac et al.,](#)  
79 [2002; Wopenka and Pasteris, 1993](#)). [Beysac et al. \(2002\), Lahfid et al. \(2010\) and Rahl et al.](#)  
80 [\(2005\)](#) found a linear relationship between quantifiable features in the Raman spectra of CM  
81 and peak metamorphic temperature, and used this relationship to develop a geothermometer  
82 for metamorphic samples, which was calibrated for temperature ranges of 330 – 650 °C, 200  
83 – 320 °C and 100 – 700 °C by the respective authors. However, few studies have combined  
84 the characteristics of Raman spectra with the petrographic features of CM in metamorphic  
85 rocks as a means to trace the origins of CM. It is the aim of this paper to use a combination of  
86 Raman and petrographic analysis to document the CM transformations that occurred during  
87 prograde metamorphism in a metamorphic belt in which Au is thought to have been  
88 mobilized by the same regional metamorphic processes ([Large et al., 2012](#)). The results are  
89 used to quantify the changes that have occurred to the CM within the linked metamorphic and  
90 hydrothermal systems.

91

92 Gold-bearing rocks used for this study are taken from the vicinity of the world-class Macraes  
93 orogenic gold deposit, which is hosted by the Otago Schist in southern New Zealand ([Craw,](#)  
94 [2002](#)). The gold in this deposit was emplaced by metamorphic-hydrothermal fluids in the  
95 latter stages of metamorphism ([Craw, 2002](#)), and is thought to have been generated by  
96 metamorphism of host metasediments that contained gold accumulated during diagenesis  
97 ([Large et al., 2012; Pitcairn et al., 2006](#)). There is abundant CM throughout the host rock

98 sequence, from low grade metamorphic schists to the gold deposit itself where hydrothermal  
99 enrichment of up to 3 wt% carbon has occurred (Craw, 2002; Henne and Craw, 2012).

100

## 101 **2. Geological setting and regional gold mobility**

102 The Otago Schist is a Mesozoic metasedimentary belt with a core zone of upper greenschist  
103 facies rocks flanked on either side by zones of progressively lower grade rocks (Figure 1;  
104 Mortimer, 1993, 2000). The protoliths for the schist belt are Paleozoic to Mesozoic turbidites  
105 which were metamorphosed to prehnite-pumpellyite facies in the Jurassic (Mackinnon, 1983;  
106 Mortimer, 1993). There is a generally symmetrical regional increase in metamorphic grade of  
107 these protolith metaturbidites through pumpellyite-actinolite facies and lower greenschist  
108 facies towards the core zone of the schist belt (Figure 1; Mortimer, 1993). The rocks become  
109 progressively more recrystallized and foliated through this increase in metamorphic grade,  
110 and the schists in the core of the belt have been pervasively recrystallized with several  
111 generations of folding and foliation development (Mortimer, 1993). Amphibolite facies rocks  
112 underlie the core upper greenschist facies rocks, and these have been tectonically exposed  
113 farther to the northwest of the main belt (Mortimer, 2000; Pitcairn et al., 2006). In detail, the  
114 boundaries between metamorphic zones are commonly post-metamorphic structures,  
115 especially extensional faults that were initiated in the middle Cretaceous (Figure 1; Deckert et  
116 al., 2002; Henne and Craw, 2012).

117

118 The consistent protolith composition that persists across the whole schist belt has enabled  
119 geochemical comparison of metal and metalloid contents at different metamorphic grades, in  
120 order to quantify metamorphogenic mobilization of these elements (Pitcairn et al., 2006, 2010,  
121 2014). Gold and arsenic, in particular, have been demonstrably mobilized on a regional scale  
122 during metamorphism, with prominent decreases in contents of these elements in the  
123 transition from the lower greenschist facies to amphibolite facies (Pitcairn et al., 2006, 2014).  
124 These elements were initially weakly enriched compared to the average crustal  
125 concentrations, on a regional scale, in diagenetic pyrite in the prehnite- pumpellyite facies  
126 protoliths, and prograde metamorphic recrystallization of that pyrite facilitated mobilization  
127 of Au and As (Large et al., 2012; Pitcairn et al., 2006, 2010, 2014). Minor intercalated  
128 metabasic layers in the metamorphic pile did not contribute significantly to the amount of  
129 mobilized Au, and were local sinks for mobilized As (Pitcairn et al., 2014). The regional  
130 scale metamorphogenic mobilization of Au and As, along with other elements commonly

131 associated with orogenic hydrothermal deposits, such as Sb, W, and Hg, has been responsible  
132 for widespread formation of orogenic gold deposits across the schist belt in the late Mesozoic  
133 (Mortensen et al., 2010; Pitcairn et al., 2006). A similar regional scale system, in the same  
134 rock sequence, was reactivated in the late Cenozoic in rocks northwest of the Otago Schist  
135 (Pitcairn et al., 2006; 2014).

136

137 All of the orogenic systems depicted in Figure 1 have been mined historically at some stage,  
138 but production has been small. However, one such set of historic mines, at Macraes (Figure  
139 1), has been developed into a world-class deposit, with more than 9 million ounces gold  
140 resource. The Macraes deposit is a mineralized late metamorphic shear zone hosted in lower  
141 greenschist facies meta-turbidites. The mineralized shear zone formed during Jurassic-Early  
142 Cretaceous uplift through the brittle-ductile transition (Craw et al., 1999; Craw, 2002;  
143 Mortensen et al., 2010). The mineralized rocks include a complex array of syndeformational  
144 quartz veins and adjacent sheared and hydrothermally altered schists (Craw et al., 1999; Craw,  
145 2002). The total width of the mineralized zone locally exceeds 200 m, with a strike  
146 length >30 km, and known down-dip extension in the main mining area of >500 m (Figure 1).

147

148 Gold is closely associated with metamorphic-hydrothermal pyrite and arsenopyrite, some of  
149 which occurs as porphyroblasts in hydrothermally altered rock (Craw, 2002; Henne and Craw,  
150 2012; Large et al., 2012). Early-formed auriferous sulfides were deformed by subsequent  
151 shearing, with additional sulfidic mineralization, leading to several generations of sulfide and  
152 gold emplacement (Craw et al., 1999; Large et al., 2012). Deposition of abundant  
153 hydrothermal CM accompanied all stages of mineralization, and post-mineralization shearing  
154 has remobilized some of that CM (Craw et al., 1999; Craw, 2002; Henne and Craw, 2012).

155

### 156 **3. Sampling and analytical methods**

#### 157 **3.1 Sample selection and characterization**

158 A set of samples of metasedimentary rocks from a range of metamorphic grades was obtained  
159 from unweathered outcrops at road cuts, river gorges, lake shore, and mine excavations  
160 (Figure 1). In the Fiddlers Flat area (Figure 1), in a section described by Henne and Craw  
161 (2012) and Large et al. (2012), a traverse was made across the transition from prehnite-  
162 pumpellyite facies to lower greenschist facies schists. At Lake Hawea (Figure 1),  
163 carbonaceous metapelitic samples were collected from pumpellyite-actinolite facies and

164 lower greenschist facies schists. Graphitic lower greenschist facies host schists proximal to  
165 the Macraes gold mine, as well as mineralized graphitic sheared rocks, were collected from  
166 the Golden Bar pit, a satellite pit of the main Macraes mine described by [Large et al. \(2012\)](#).  
167 A total of 40 samples were collected, with 6 samples from the prehnite-pumpellyite (P-P)  
168 facies, 18 samples from the pumpellyite-actinolite (P-A) facies and 16 samples from the  
169 lower greenschist (GS) facies.

170

### 171 **3.2 Non-carbonate carbon and gold content analysis**

172 Samples were crushed into powder for non-carbonate carbon and gold analyses in a tungsten  
173 carbide ring mill. Analyses were conducted by Intertek Genalysis Lab (Perth, Australia). For  
174 non-carbonate carbon, samples were treated with dilute acid to remove carbonate, and the  
175 residue was analyzed for carbon using infrared spectroscopy. For gold analysis, a lead fire  
176 assay preconcentration step was used to separate the gold from the matrix as a pellet, which  
177 was then dissolved in dilute aqua regia and analyzed for Au with flame atomic absorption  
178 spectrometry.

179

### 180 **3.3 Petrographic methods**

181 Petrographic samples were prepared as thin sections for optical microscopy, scanning  
182 electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) to characterize  
183 the petrographic features. Thin sections were cut perpendicular to the foliation and parallel to  
184 the stretching lineation. Petrographic inspection of the samples was conducted with a Nikon  
185 optical transmitted and reflected light microscope. SEM and EDS observations were made  
186 using a Zeiss Neon 40EsB field-emission gun scanning electron microscope (FEGSEM) in  
187 the Curtin Materials Research Lab of Curtin University (Perth, Australia). For the BSE (back-  
188 scattered electron) signal, the energy was 20.00 kV and the working distance was 7.7 mm.

189

### 190 **3.4 Raman spectroscopy**

#### 191 **3.4.1 Raman spectra of carbonaceous material**

192 Two wavelength intervals at 1100 – 1800  $\text{cm}^{-1}$  and 2500 – 3100  $\text{cm}^{-1}$  have been documented  
193 in studies of the Raman spectra of CM, and have been referred to as the first- and the second-  
194 order regions respectively ([Beysac et al., 2002, 2003a; Pasteris and Wopenka, 2003;](#)  
195 [Wopenka and Pasteris, 1993; Yui et al., 1996](#)). In the first-order region, well-organized  
196 graphite with  $D_{6h}^4$  crystal symmetry ( $D_{6h}^4 = P6_3/mmc$ , hexagonal Brillouin zone) has a  
197 detectable  $E_{2g2}$  vibration mode at 1580  $\text{cm}^{-1}$  in Raman spectra, which is an in-plane mode

198 (Figure 2; Pasteris and Wopenka, 1991; Wopenka and Pasteris, 1993). This single peak is  
199 named the “G band,” and splits into two peaks when the CM becomes disordered (Figure 3A  
200 & B; Beyssac et al., 2002; Wopenka and Pasteris, 1993). In disordered and poorly-organized  
201 CM, the Raman spectra consist of two bands, the G band at  $1600\text{ cm}^{-1}$ , and the D band at  $1355$   
202  $\text{cm}^{-1}$  (Figure 3B). The D band is considered to be due to in-plane defects caused by  
203 heteroatoms or structural defects (Beyssac et al., 2002; Pasteris and Wopenka, 1991;  
204 Wopenka and Pasteris, 1993). The D band includes, in addition to the main D peak, an  
205 intense single peak (D1) on the left shoulder of the D peak at  $\sim 1200\text{ cm}^{-1}$  (Figure 3C, D & F).  
206 The G band includes a wide peak at  $\sim 1550\text{ cm}^{-1}$  on the left shoulder of the main G peak, and  
207 this is referred to as the D2 peak (Figure 3C, D & F). D1 has been attributed to vibration  
208 modes of polyene-like structures, and D2 is thought to be associated with amorphous carbon  
209 (Dippel et al., 1999; Jawhari et al., 1995). In well-organized CM, an additional D3 peak  
210 around  $1613\text{ cm}^{-1}$  appears on the right shoulder of the G band (Figure 3B & E).

211

212 In the second-order region, the typical peaks for CM in previous studies are located at 2400,  
213 2700, 2900 and  $3300\text{ cm}^{-1}$  (Figure 3A & B; Beyssac et al., 2002; Nemanich and Solin, 1979;  
214 Wopenka and Pasteris, 1993). Usually, the peaks in the second-order region are interpreted as  
215 overtones ( $2 \times 1335\text{ cm}^{-1} \approx 2670\text{ cm}^{-1}$ ;  $2 \times 1600\text{ cm}^{-1} \approx 3200\text{ cm}^{-1}$ , and so on) and  
216 combination scattering of energy in the low wavenumber region ( $1335\text{ cm}^{-1} + 1600\text{ cm}^{-1} \approx$   
217  $2925\text{ cm}^{-1}$ ) (Beyssac et al., 2002, 2003a; Wopenka and Pasteris, 1993). Wopenka and Pasteris  
218 (1993) stated that the intensity of peaks in the second-order region is a reflection of three-  
219 dimensional ordering. Among the second order peaks, S1 ( $2700\text{ cm}^{-1}$ ) has been used to  
220 represent the two-dimensional extent of graphitic layers and the three-dimensional ordering  
221 of the graphite lattice; this peak splits into two as the graphite lattice changes from  
222 dominantly two-dimensional to three-dimensional (Lespade et al., 1984). The S2 ( $2900\text{ cm}^{-1}$ )  
223 peak has been proposed to be a result of C-H bonding, but there is a lack of consensus on this  
224 interpretation (Beyssac et al., 2002; Tsu et al., 1978).

225

### 226 3.4.2 Raman methods

227 Quantitative Raman analysis was carried out on CM in 17 selected samples from various  
228 metamorphic grades. The instrument, which is located at the CSIRO laboratories in Bentley,  
229 Perth, Australia, is a Horiba<sup>®</sup> LabRAM HR Evolution using a  $600\text{ gr/mm}$  grating and a  
230 Synapse Visible detector. The  $532\text{ nm}$  incident radiation was produced by a  $100\text{ mW}$  Laser

231 Quantum Torus consisting of a continuous wave single frequency diode laser. During the  
232 analyses, the laser beam was focused to a width of about 0.72  $\mu\text{m}$  with a 100X objective. The  
233 numeric aperture (NA) of objective was 0.90. The beam was aimed perpendicular to the thin  
234 section. Visible damage on the surface of the sample or alteration of the Raman signal were  
235 monitored and avoided by adjusting the laser power. Filters decreased the laser power to 0.3  
236 mW on the sample surface. Data were collected in the 700 – 4000  $\text{cm}^{-1}$  range to capture the  
237 first-order and second-order Raman bands.

238

239 The measurements were collected on randomly oriented grains, with a fixed orientation of the  
240 polarized laser beam (Table 1). 5 - 10 spectra were acquired for each sample except FF-14  
241 and GB-4-B. Polishing has been reported to induce disorder of CM at the nanometre scale  
242 (Beysac et al., 2003a; Pasteris, 1998). Intensity ratio of D and G peaks is supposed to be  
243 sensitive to the polishing, but the width of G peak remains more stable, as determined in  
244 investigations by Ammar et al. (2011). Such polishing effects are thought to be of no concern  
245 for CM with low degrees of structural order, such as the bulk of those examined for this study  
246 (Bonal et al., 2010). However, a few samples may contain CM with sufficient structural order  
247 that polishing effects may be significant. To assess the extent of polishing effects, we  
248 compared the Raman spectra from polished and unpolished areas of billets that contained low  
249 maturity and the highest maturity CM. The intensity ratio of D and G peaks and width of G  
250 peak of low maturity CM remained almost unchanged. However, those in high mature CM  
251 varied to a minor extent only. Thus, the absence or presence of a polished surface did not  
252 induce any significant change in the Raman spectra. It is assumed that polishing effects are  
253 negligible in this study.

254

255 Additionally, as anisotropic materials may produce pleochroism in Raman (Yoon et al., 2008),  
256 the extent to which sample orientation affected the spectra was also investigated.

257 Measurements presented in this study were made with a linearly polarized laser, so  
258 measurements made with a circular polarized laser, which is insensitive to crystal orientation,  
259 were made to assess the extent to which pleochroism affected the spectra. CM grains from  
260 five selected samples covering all metamorphic grades investigated were analyzed in a  
261 variety of orientations. The polarization angle of the laser relative to the material was  
262 changed by rotation of the sample from 0 to 90° at 15° intervals using a petrographic stage  
263 with an analyzer plate placed in the Raman spectrometer after the edge filter. This procedure  
264 was then applied to the same grains using circular polarized light with a quarter wave plate



265 placed in the laser path before reaching the sample (de-polarization of the laser). The  
266 averages and the standard deviations of the measured parameters for the various sample  
267 orientations were calculated for each set of data (Table 2). Uncertainties presented in Table 2  
268 are the ratios of one standard deviation to the average value.

269

270 Peak positions, widths, relative intensities and areas were obtained by fitting the spectra in  
271 “MagicPlot” (Magicplot Systems LLC, Saint Petersburg, Russia). The background was  
272 removed manually by creating splines, moving anchor points on the splines to set appropriate  
273 fit intervals which contain only baseline without peaks, and fitting. Then a mixed Gaussian-  
274 Lorentzian curve-fitting procedure was applied to deconvolute the spectra. Initial  
275 Gaussian/Lorentzian curves were first fitted into spectra manually, then fit procedures were  
276 run by the software during which the parameters of fit function would vary iteratively to  
277 minimize the residual sum of squares. The output parameters are the position of peaks,  
278 intensity, full width at half maximum (FWHM) and integrated area. The positions of all the  
279 peaks were constrained into a certain range with first-order region between 900 – 2000 cm<sup>-1</sup>  
280 and second-order region between 2300 – 3500 cm<sup>-1</sup> following studies in Sadezky et al. (2005)  
281 and Sfora et al. (2014). The intensity of D3 was restricted to be less than half of the intensity  
282 of the G band (Sfora et al., 2014). In the first-order region, spectra were deconvoluted into  
283 the primary peaks, the D peak (1330 - 1350 cm<sup>-1</sup>) and G peak (1580 - 1610 cm<sup>-1</sup>), and three  
284 smaller peaks, the D1 peak (1190 - 1250 cm<sup>-1</sup>), D2 peak (1500 – 1550 cm<sup>-1</sup>) and D3 peak  
285 (1610 – 1620 cm<sup>-1</sup>). In the second-order region, the commonly-observed peaks are S1 (2630 –  
286 2700 cm<sup>-1</sup>), S2 (2900 – 2940 cm<sup>-1</sup>) and S3 (3190 – 3240 cm<sup>-1</sup>). However, in some higher  
287 metamorphic grade samples, additional S peaks are displayed at wavenumbers of 2128 cm<sup>-1</sup>  
288 (S4), 2470 cm<sup>-1</sup> (S5), 3351 cm<sup>-1</sup> (S6) and 3610 cm<sup>-1</sup> (S7). Typical results of the fits are  
289 displayed in Figures 3D to F.

290 The following ratios were used to characterize the Raman spectra:

291

$$292 \quad R1 = I_D/I_G \quad [1]$$

$$293 \quad R2 = W_D/W_G \quad [2]$$

$$294 \quad R3 = (A_D+A_{D1}) / (A_D+A_{D1}+A_G+A_{D2}+A_{D3}) \quad [3]$$

$$295 \quad R4 = A_{S1} / (A_{S1}+A_{S2}+A_{S3}) \quad [4]$$

296

297  $I_X$  is the intensity of peak X above the background-corrected baseline,  $W_X$  is the width of  
298 peak X at half maximum height, and  $A_X$  is the integrated area of peak X above the baseline.

299 These ratios are plotted against the estimated ranked metamorphic grade, from P-P to lower

300 GS facies. Samples from the Fiddlers Flat traverse are ranked by position within the sequence,  
301 increasing from northeast to southwest (Figure 1). Lake Hawea P-A samples were ranked  
302 above the Fiddlers Flat P-A samples, because these samples come from the P-A: lower GS  
303 transition. In the lower GS facies the Fiddlers Flat samples were ranked the lowest, followed  
304 by the Lake Hawea samples and the Golden Bar samples. The Golden Bar samples are from  
305 close to the upper GS: lower GS transition, so the assignment of the highest ranking to these  
306 samples is reasonable. The Lake Hawea samples and the Fiddlers Flat samples come from a  
307 similar position relative to the P-P/P-A and P-A/lower GS boundary, so the assignment of  
308 the Lake Hawea samples to the higher ranked metamorphic grade was somewhat arbitrary,  
309 but is consistent with the trends in Raman spectral parameters (see below).

310

## 311 **4. Results**

### 312 **4.1 Raman spectra**

313 The CM in these samples was divided into four types, designated CM 1– 4 herein, based on  
314 Raman spectra observations (Figure 3). CM 1 is the dominant form of CM in P-P facies  
315 samples with a mode (volume concentration) around 5%. CM 2 is present at all metamorphic  
316 grades, but is less common in P-P facies (mode  $\approx$  2%) and lower GS facies (mode  $\approx$  3%) and  
317 more abundant in P-A facies (mode  $\approx$  6 – 10%). CM 3 is found in P-A facies (mode  $\approx$  7%)  
318 and lower GS facies (mode  $\approx$  8%), including the host rocks of the Golden Bar pit, and CM 4  
319 (mode  $\approx$  5%) is only observed in mineralized rocks.

320

321 CM 1 (see Figure 3C) is characterized by a high intensity, wide (up to  $134.69 \text{ cm}^{-1}$  FWHM)  
322 D band at around  $1336.5 \pm 2.4 \text{ cm}^{-1}$  ( $n = 4$ ,  $n$  is equal to total sample number) and a relatively  
323 low intensity, narrow (up to  $52.18 \text{ cm}^{-1}$  FWHM) G band at  $1604.1 \pm 3.54 \text{ cm}^{-1}$  ( $n = 4$ ). The  
324 spectra also display a low intensity, wide (up to  $148.04 \text{ cm}^{-1}$  FWHM) D1 band and a wide (up  
325 to  $159.12 \text{ cm}^{-1}$  FWHM) D2 band. In the second-order region, the major peaks occur at  
326 wavenumbers of  $2670 \text{ cm}^{-1}$  (S1),  $2925 \text{ cm}^{-1}$  (S2), and  $3207 \text{ cm}^{-1}$  (S3) and they are typically  
327 present in spectra from low-maturity CM at  $2663 \pm 27 \text{ cm}^{-1}$ ,  $2923 \pm 17 \text{ cm}^{-1}$ , and  $3206 \pm 9$   
328  $\text{cm}^{-1}$ , respectively ( $n = 4$ ).

329

330 The Raman spectra of CM 2 (see Figure 3D) exhibit a relatively low intensity, wide (up to  
331  $113.61 \text{ cm}^{-1}$ ) D peak and high intensity, narrow (up to  $48.56 \text{ cm}^{-1}$ ) G peak. The positions of  
332 the D peak and G peak are  $1330.67 \pm 7.4 \text{ cm}^{-1}$  ( $n = 10$ ) and  $1598.2 \pm 5.1 \text{ cm}^{-1}$  ( $n = 10$ )

333 respectively. The width of D peak in CM 2, which is around  $100\text{ cm}^{-1}$ , is much wider than  
334 that in CM 1 which is around  $85\text{ cm}^{-1}$ . CM 2 has similarly-located D1 and D2 bands ( $1210$   
335  $\text{cm}^{-1}$  and  $1550\text{ cm}^{-1}$  respectively) as compared with CM 1, but the D1 band is much wider (up  
336 to  $180.4\text{ cm}^{-1}$  for CM 2, and up  $148.0\text{ cm}^{-1}$  for CM 1. The S peaks for CM 2 are qualitatively  
337 indistinguishable from those in CM 1.

338

339 The Raman spectra of CM 3 (see [Figure 3E](#)), which is found in upper P-A and lower GS  
340 facies, are considerably different from those of CM 1 and CM 2. In the first-order region,  
341 both the D and G peaks are relatively narrow, with about  $30\text{ cm}^{-1}$  FWHM. The position of the  
342 D band is  $1348.4 \pm 1.3\text{ cm}^{-1}$  ( $n = 5$ ) while that of the G band is  $1581.24 \pm 1.45\text{ cm}^{-1}$  ( $n = 5$ ).  
343 The D1 and D2 peaks are found at similar positions to the equivalent peaks in CM 1 and CM  
344 2, but an additional D3 band is observed on the shoulder of the G band at  $1615.25 \pm 4.1\text{ cm}^{-1}$   
345 ( $n = 5$ ). In the second-order region, CM 3 is distinguished by spectra with a very high  
346 intensity S1 peak and an additional S5 peak around  $2470\text{ cm}^{-1}$  that is not observed in the  
347 other samples. Some spectra also have an S4 peak ( $2128\text{ cm}^{-1}$ ), S6 peak ( $3351\text{ cm}^{-1}$ ) and S7  
348 peak ( $3610\text{ cm}^{-1}$ ).

349

350 The Raman spectra of CM 4 (see [Figure 3F](#)), which is found in the mineralized rocks, are  
351 similar to those of CM 1, but the widths of the D and G bands are significantly narrower, with  
352 maximum FWHM of  $57.14\text{ cm}^{-1}$  and  $49.69\text{ cm}^{-1}$  respectively.

353

#### 354 **4.2 The effects of crystal orientation on Raman spectra**

355 [Table 2](#) summarises the relationship between crystal orientation and Raman spectra  
356 parameters for polarized and circular polarized laser beam measurements. Results for each  
357 sample under circular polarized light are independent of orientation, but are somewhat  
358 different to measurements made under the polarized light used in the bulk of the  
359 measurements. For example, FWHM of the D peak in the P-P sample FF-16 was  $77.8 \pm 1.2$   
360  $\text{cm}^{-1}$  in polarized light, and  $65.7\text{ cm}^{-1}$  in circular polarized light. Under polarized light, the  
361 effect of orientation on measured parameters was similar to the expected analytical error for  
362 the majority of parameters in most samples. Notable exceptions, with relative uncertainties  
363 greater than 10%, are the R4 ratio in CM 1 from FF-16 (25%), R1 in CM 2 from P-A facies  
364 sample FF-13 (11%). S4 and S6 peaks, which have highly variable intensity as a function of  
365 orientation, were only observed in CM 3. These peaks, therefore, were not considered further.

366 The effect of crystal orientation is therefore considered to be negligible for most measured  
367 parameters, although interpretations based on the R4 ratio, which involves the second order  
368 peaks, are treated with caution.

369

### 370 **4.3 Variation in individual parameters**

#### 371 *R1 (Figure 4A)*

372 The ratio of the intensity of the D and G peaks ( $R1: I_D/I_G$ ) decreases from 1 to 0.62 as  
373 metamorphic grade increases through P-P facies and into P-A facies. Data for CM 1 and CM  
374 2 overlap for P-P facies samples. R1 then increases sharply from 0.99 (CM 3, P-A) to 2.15  
375 (CM 2, lower GS). The four highest grade samples, one from Lake Hawea and the three from  
376 Golden Bar, then exhibit a drop in R1 to values between 0.98 and 1.66.

377

#### 378 *R2 (Figure 4B)*

379 R2, the ratio of the width of the D peak to that of the G peak ( $W_D/W_G$ ) fluctuates without any  
380 clear trend from P-P to upper P-A facies, with an average value of  $2.5 \pm 0.3$  ( $n = 12$ ). The  
381 higher values in this population are from CM 2 grains ( $2.78 \pm 0.07$ ,  $n = 6$ ). The R2 of CM 1  
382 grains is  $2.32 \pm 0.25$  ( $n = 4$ ). R2 drops to 1.20 in the upper P-A facies (CM 3). Further  
383 increases in grade do not affect R2 significantly. R2 is  $1.25 \pm 0.11$  ( $n = 9$ ) for grains of CM 2,  
384 CM 3 and CM 4 from L-GS and GS facies.

385

#### 386 *R3 (Figure 4C)*

387 R3, the ratio of the total area of D peaks to the total D and G peak area, drops from 0.71 to  
388 0.53 from P-P to P-A facies, and then increases to 0.69 in CM 3 grains from upper P-A grade  
389 samples. R3 values for CM 1 decrease with increasing metamorphic grade from 0.70 to 0.59  
390 with some overlap with CM 2 in P-P grade samples. R3 for CM 2 also decreases with  
391 metamorphic grade. CM 2 and CM 3 in samples from the lower GS facies also exhibit a  
392 general decrease with metamorphic grade down to values of 0.51. This trend is not followed  
393 by CM 4, which shows values for R3 of  $0.66 \pm 0.02$  ( $n = 2$ ).

394

#### 395 *R4 (Figure 4D)*

396 R4, the ratio of the S1 peak to the total S peak area, is consistently low at  $0.42 \pm 0.05$  ( $n = 16$ )  
397 for CM 1, CM 2 and CM 4. CM 3 grains provide a significantly different population, in  
398 which R4 is  $0.78 \pm 0.04$  ( $n = 5$ ).

399

## 400 **4.4 Chemical and petrographic characterization**

### 401 **4.4.1 Bulk Rock Analysis**

402 The non-carbonate carbon (NCC) content in all samples collected, except for 7 quartz vein-  
403 bearing samples, ranges from 0.02% to 2.58%. NCC content is 0.06 – 0.24% ( $0.15 \pm 0.07$  %,   
404  $n = 5$ ) in P-P facies samples, 0.04 – 2.58% ( $0.34 \pm 0.61$ %,  $n = 16$ ) in P-A facies samples, 0.06  
405 – 0.66% ( $0.24 \pm 0.24$ %,  $n = 9$ ) in lower GS facies samples and 0.4 – 0.63% ( $0.48 \pm 0.13$ %,  $n$   
406 = 3) in mineralized samples.

407

408 Gold concentrations were below the detection limit of 0.01 ppm in all P-P facies samples.  
409 However, gold was detected in some samples from other metamorphic grades (excluding the  
410 samples with Au concentrations below the detection limit), with  $0.11 \pm 0.04$  ppm ( $n = 4$ ) gold  
411 in P-A facies samples,  $0.03 \pm 0.01$  ppm ( $n = 4$ ) gold in lower GS facies samples and  $7.3 \pm 2.7$   
412 ppm ( $n = 2$ ) gold in mineralized samples from the Golden Bar pit.

413

### 414 **4.4.2 Petrography**

415 CM 1, as defined by the Raman spectral characteristics has an appearance quite distinct to  
416 that of the other CM types. CM 1 is opaque in plane polarized light (ppl) and grey with low  
417 reflectivity in reflected light (Figure 5). In weakly deformed and folded P-P facies samples,  
418 grain shapes are round to sub-round with grain sizes ranging from 1 to 10  $\mu\text{m}$ . In pelitic  
419 samples, CM 1 is usually intergrown with very fine-grained pyrite and chalcopyrite (about 1  
420 – 5  $\mu\text{m}$ ) that occur as framboidal clusters (Figure 5A). The largest cluster observed is about  
421 0.1 x 0.2 mm and is surrounded by quartz, albite, muscovite and stilpnomelane (Figure 5A).  
422 Finer-grained CM 1 has a grain size of about 1  $\mu\text{m}$ , which is similar to that of fine-grained  
423 pyrite and chalcopyrite (Figure 5B). Both CM 1 and sulfide minerals are sparsely  
424 disseminated through the sediment matrix. In more sheared and deformed P-P samples, CM 1  
425 occurs as angular grains with widths of about 10 – 20  $\mu\text{m}$  (Figure 6A & B).

426

427 CM with the Raman spectral characteristics of CM 2 differs in appearance and textural  
428 position from CM 1 in a number of ways. This CM appears pale yellow, with low reflectivity,  
429 in reflected light. It occurs as short strips or slabs interstitial to other minerals (Figures 7A &  
430 B). The lengths of the strips are up to 150  $\mu\text{m}$ . CM 2 has a different association with pyrite to  
431 CM1; framboidal pyrite was observed to be sparsely disseminated through CM 2, but did not  
432 occur within the sediment matrix as observed for CM 1 samples. Large (100 – 150  $\mu\text{m}$ ) flakes  
433 of CM 2 were observed in carbonate veins (Figure 7C). In lower GS facies rocks, bands of

434 black material with high CM 2 content aligned parallel to the foliation are observed  
435 throughout the thin sections. In these bands, CM 2 has the same optical properties as above,  
436 but it is present as fragments with widths of about 20  $\mu\text{m}$  and lengths of about 40  $\mu\text{m}$ , and is  
437 associated with cubic pyrite (Figure 7D).

438

439 CM with the Raman spectral characteristic defined as CM 3 occurs in samples of P-A facies  
440 and lower GS facies from Lake Hawea and lower GS facies samples from the host rock at the  
441 Golden Bar Pit. This CM is also optically and texturally distinct from the other CM types.  
442 CM 3 has a sub-rounded grain shape with an elongate elliptical habit, is less than 4 x 10  $\mu\text{m}$   
443 in size, and is light grey with low reflectivity in reflected light (Figure 8A). In all of the CM  
444 3-bearing samples, the foliation is defined by segregation of the sample into quartz-rich and  
445 quartz-poor layers. The quartz-poor layers mainly comprise recrystallized quartz, albite,  
446 chlorite and muscovite and are cross cut by black bands (Figure 8A & B). These bands are  
447 made up of consistently aligned CM 3 grains (Figure 8C).

448

449 CM with the Raman spectral characteristics defined to present CM 4 is present in mineralized  
450 rocks from Golden Bar pit (Figure 9A). This CM is angular and grey with low reflectivity,  
451 and grain size is up to 10  $\mu\text{m}$  in the largest dimension (Figure 9B). Some CM 4 grains are as  
452 small as 1  $\mu\text{m}$  in the smallest dimension, and occur in aggregates with pyrite, arsenopyrite,  
453 galena and clay minerals. These smaller CM grains are hard to characterize petrographically,  
454 but can be analyzed without difficulty using the high spatial resolution Raman microscope.

455

## 456 **5. Discussion**

### 457 **5.1 CM Raman spectra compared with previous work**

458 Previous studies have documented decreases in R1, R2 and the widths of the D and G bands  
459 of CM with increasing temperature (Beysac et al, 2002; Wopenka and Pasteris, 1993). These  
460 studies were made on samples from GS facies metamorphic grade and higher. R3 has been  
461 observed to decrease with increasing degree of crystallinity, but this trend was not observed  
462 in very low maturity CM, where vitrinite reflectance is less than 2.5% (Beysac et al, 2002;  
463 Quirico et al., 2005; Wopenka and Pasteris, 1993). With respect to the S peaks, as crystallite  
464 size decreases, S1 is expected to become wider, S2 to become more intense and S3 to be  
465 suppressed (Wopenka and Pasteris, 1993). Thus, R4 has been used to estimate the relative  
466 crystallite size for well-organized CM (Wopenka and Pasteris, 1993).

467

468 From the above, we may infer that low maturity CM should have a high R1, R2 and R3, and a  
469 low R4, combined with relatively wide D and G peaks. High maturity CM, on the other hand,  
470 should have the opposite characteristics. Spectra from this study exhibit D and G bands with  
471 widths that decrease with metamorphic grade, consistent with previous work, and R1  
472 decreases with grade through the P-P facies. However, in contrast to most previous results,  
473 R1 shows an overall increase between P-A to lower GS facies in spectra measured from  
474 samples from this study. The observations of R1 trends from this study are, however,  
475 consistent with those [Quirico et al. \(2005\)](#) who measured the Raman spectra of coal samples  
476 with a vitrinite reflectance of 2 – 7%.

477

478 CM 1 and CM 2 have relatively low R4, and high R2 and R3 and wide D and G peaks,  
479 consistent with low maturity CM. An exception is seen for one CM 2 sample taken from the  
480 lower GS facies, but an increase in maturity in CM 2 relative to the one in other CM 2  
481 bearing samples from P-P and P-A facies is expected. An observed alignment with  
482 metamorphic foliation and association with cubic rather than framboidal pyrite suggests that  
483 this CM 2 likely experienced some degree of metamorphic recrystallization. CM 3 and CM 4  
484 have relatively high R4 and low R2 and R3 compared to CM 1 and CM 2, consistent with a  
485 higher degree of maturity for these samples. CM 3 has much higher R4, due to the very high  
486 S1 peak, than CM 4, so CM 3 is interpreted to have a higher degree of crystallinity and 3D  
487 ordering than CM 4. This relative maturity is consistent with X-ray diffraction and  
488 reflectance data from samples of similar grade ([Figure 10](#)).

489

## 490 **5.2 Temperature estimates of CM from Raman spectra**

491 A geothermometer for the Raman spectra of carbonaceous material, based on an  
492 observed linear correlation between D: G area ratios (equivalent to the R3 ratio in our study)  
493 and peak metamorphic temperature has been described ([Beysac et al., 2002](#); [Lahfid et al.,  
494 2010](#); [Rahl et al., 2005](#)). The equations of [Lahfid et al. \(2010\)](#) and [Rahl et al. \(2005\)](#) both  
495 work for low temperature metamorphic rocks, as the former is applicable from 200 – 320 °C  
496 and the latter ranges from 100 - 700°C. Both geothermometers have been applied to our rocks  
497 used for this study. Results from [Rahl et al. \(2005\)](#) geothermometer, which uses the  
498 parameters of the relative intensity and areas of the D and G peaks, were consistent with  
499 those from mineral composition-based temperature-pressure estimates ([Frey, 1991](#); [Mortimer,  
500 2000](#)). However, results from [Lahfid et al. \(2010\)](#) geothermometer, which only contains the

501 parameter of the relative areas of the D and G peaks, were up to 100 °C higher than estimated  
502 temperature. [Rahl's \(2005\)](#) thermometer is considered to be more applicable to our study area,  
503 as the evolution of Raman spectra in the samples is probably more complex than can be  
504 described simply by an area ratio. The equation is as follows:

$$505 \quad T \text{ (}^\circ\text{C)} = 737.3 + 320.9 R_1 - 1067 R_3 - 80.638 R_1^2. \quad [5]$$

506  
507  
508 The temperatures obtained from the above equation indicate that  $T_{CM2} \approx T_{CM1} \ll T_{CM4} < T_{CM3}$   
509 ([Table 3](#)), which is consistent with the relative maturity of CM inferred from the spectra,  
510 unsurprisingly, given that both methods use the same ratios. The Raman-derived  
511 temperatures ( $T_R$ ) of CM 1 are in agreement with the metamorphic grades which have been  
512 estimated from previous studies ([Mortimer, 2000](#)). Calculated  $T_R$  for most CM 2 is lower  
513 than the estimated metamorphic temperature ranges ( $T_M$ ), and is the same, within error, for  
514 CM 2 in P-P and P-A facies samples. CM 3 has higher values of  $T_R$  than CM 1, CM 2 and  
515 CM 4 in all samples investigated, and  $T_R$  for CM 3 are at the high end or slightly higher than,  
516 estimated ranges for  $T_M$ . The  $T_R$  of CM 4 is lower than, but within error of, the estimated  
517 metamorphic temperature range for the lower GS facies, and is lower than  $T_R$  for CM 3. The  
518 structure of low temperature CM may be affected by other parameters, such as carbon  
519 precursor and the duration of metamorphism ([Beysac et al., 2003b](#); [Lahfid et al., 2010](#)).  
520 However, [Beysac et al. \(2003b\)](#) demonstrated that temperature still plays the key role during  
521 the graphitization of CM. Our study was conducted on the basis of this argument.

522

### 523 **5.3 Possible origins of CM**

#### 524 **CM 1**

525 Framboidal diagenetic pyrite grows in low-energy environments where the distinctive  
526 framboidal texture can be preserved for long periods of time ([Love, 1964](#); [Rickard, 1970](#)).  
527 Early diagenetic processes have long been known to form framboidal textures through the  
528 involvement of organic matter ([Chauhan, 1974](#); [Love, 1965](#); [Rickard, 1970](#); [Taylor and](#)  
529 [Macquaker, 2000](#)). [Rickard \(1970\)](#) proposed that framboids form from by pseudomorphism  
530 of organic material; clusters of organic globules may be replaced by intermediate  
531 monosulphides such as mackinawite ((Fe,Ni)<sub>1+x</sub>S) or greigite (Fe<sub>3</sub>S<sub>4</sub>) and in turn replaced by  
532 pyrite microcrysts, creating the framboidal aggregates. The coexistence of framboidal pyrite,  
533 inferred to be diagenetic, with low maturity and low temperature CM 1 in lower P-P facies  
534 suggests an *in-situ* origin for CM 1.



535

536 Chalcopyrite with framboidal texture is also observed in the Fiddler's Flat framboids.  
537 [Oszczepalski \(1999\)](#) attributed the presence of framboidal chalcopyrite with relict pyrite  
538 cores at the Kupferschiefer to oxidative alteration of diagenetic pyrite framboids by  
539 cupriferous fluids; the chalcopyrite associated with framboidal pyrite in this study may have  
540 formed through analogous secondary processes. In upper P-P facies samples, the more  
541 angular morphology of CM 1 and decreasing association of CM 1 with pyrite may be  
542 associated with recrystallization and possible loss of pyrite due to the secondary processes.

543

## 544 **CM 2**

545 In previous work on the Mount Isa Basin, short ribbons of carbonaceous material with  
546 petrographic characteristics similar to those of CM 2 are considered to be a result from  
547 carbon migration ([Glikson et al., 2000; 2006](#)). In Otago schist samples, some CM 2 is present  
548 as flakes in carbonate veins, which is consistent with deposition from a fluid during  
549 metamorphism ([Luque et al., 1998](#)). These textures suggest that CM 2 may have been  
550 deposited during the passage of carbon-rich fluid through the host rocks.

551

552 Though fluid-deposited CM is often documented as well-organized (e.g. [Luque et al., 1998](#)),  
553 disordered CM, such as the CM 2 described here, can be also deposited from fluids, and such  
554 fluid-deposited CM has a spectral signature similar to that of *in-situ* kerogen as a metastable  
555 precursor to graphite ([Foustoukos, 2012; Luque et al., 1998; Pasters and Chou, 1998](#)). The  
556 Raman spectra of CM 2 show relatively low crystallinity with low R2 and R3 values,  
557 comparable to those of kerogen. However, CM 2 in lower GS facies rocks has higher  
558 maturity Raman parameters than CM 2 in P-P and P-A facies samples, which can be  
559 attributed to either deposition from higher temperature fluids in the lower GS rocks, or to  
560 metamorphism subsequent to deposition.

561

562 Rare framboidal pyrite grains are found sparsely disseminated through CM 2 in sample FF-04.  
563 This inclusion of pyrite in CM 2 is quite different to the more intimately intergrown CM 1 –  
564 pyrite association described above. Although more commonly attributed to a diagenetic  
565 origin, framboidal pyrite has been observed to grow from metal-enriched H<sub>2</sub>S-bearing  
566 hydrothermal fluids during low-grade regional metamorphism ([Scott et al., 2009](#)). Thus,  
567 framboidal pyrite associated with CM 2 may have deposited from C and H<sub>2</sub>S-bearing  
568 hydrothermal fluids.

569

570 The above discussion suggests that attribution of an origin to CM requires evaluation of both  
571 textural and Raman evidence. The flakes of CM 2 in veins are unambiguously associated,  
572 texturally, with fluid-related features, whereas if Raman evidence alone was considered then  
573 interpretation of the origin as *in-situ* deposition of CM 2 would be more likely. Detailed  
574 studies of CM from Fiddlers Flat by [Henne and Craw \(2012\)](#) demonstrated that CM referred  
575 to as graphite in this area was deposited from metamorphic fluids prior to gold mineralization.  
576 We propose that CM 2 is similar to the graphite studied by [Henne and Craw \(2012\)](#) ([Figure](#)  
577 [10](#)), and infer that CM 2 was deposited from fluids.

578

### 579 **CM 3**

580 According to the Raman results, CM 3 is the highest maturity carbonaceous material  
581 examined in this study, and the strikingly high R4 value and S1 peak area indicate that CM 3  
582 has high crystallinity. The orientation dependence of the S peaks for CM 3 supports this  
583 conclusion; as the grains of CM become larger and better ordered then greater anisotropy is  
584 expected ([Table 2](#)). The black bands that contain CM 3 cross cut the foliation, which suggests  
585 that CM 3 has been recrystallized and remobilized during syn- to late metamorphic processes  
586 in mainly lower GS facies rocks ([Figure 8A, B & C](#)). CM 3 is, on the basis of Raman spectra  
587 results, the most mature CM type observed in this study.

588

589 This CM 3 material is assumed to be equivalent to the CM documented by [Pitcairn et al.](#)  
590 ([2005](#)) in unmineralized samples from Lake Hawea taken from the same outcrops as those  
591 used for this study, since only one type of CM was observed in these rocks. Interestingly,  
592 Fourier Transform IR (FTIR) analyses of the CM studied by [Pitcairn et al. \(2005\)](#) reveals a  
593 sub-graphitized carbon spectra with features attributed to the presence of  $\text{CH}_2+\text{CH}_3$   
594 and  $>\text{C}=\text{O}$  groups ([Figure 11](#)). These spectral features mitigate against deposition from  
595 aqueous fluids because CH and  $>\text{C}=\text{O}$  groups are generally thought to be destroyed during  
596 fluid-transport ([Luque et al., 1998; Pitcairn et al., 2005](#)). However, it is possible that CM 3  
597 was mobilized only on short length scales (millimetres), possibly within a hydrocarbon-rich  
598 or bitumen-like,  $\text{H}_2\text{O}$ -poor fluid. In such a fluid the CH or  $>\text{C}=\text{O}$  groups could be retained.

599

### 600 **CM 4**

601 CM 4 from mineralized rocks is less-well crystallized than CM 3 that occurs in the  
602 immediate host rocks ([Figure 3E, F; Table 3](#)). On Raman spectral evidence alone, CM 4

603 could be either fluid-deposited or a remnant of primary CM. However, CM 4 is found only in  
604 the mineralized rocks from Golden Bar (GB-04-A & B) that contain abundant of  
605 hydrothermal sulfide minerals (Figure 9A, B). This CM material also occurs in hydrothermal  
606 veins and mineralized shears, and is interpreted to have been deposited from hydrothermal  
607 fluids (Craw, 2002; Henne and Craw, 2012; Pitcairn et al., 2005). The bulk Au contents of  
608 the Golden Bar samples are 5.4 and 9.3 ppm respectively, an enrichment of more than 2000  
609 times over background values near 1 ppb (Pitcairn et al., 2006). The estimated formation  
610 temperature of CM 4 from Raman spectra is around 339 °C (Table 3), which is similar,  
611 within error, to the mineralization temperature of 300 - 350 °C (Craw, 2002). Thus it is  
612 reasonable to consider a link between CM 4 and gold mineralization (see below).

613

614 CM 4 is similar to the kerogen-like CM described by Pitcairn et al. (2005). The FTIR results  
615 of Pitcairn et al. (2005) suggest the CM in mineralized rocks has less CH or >C=O groups  
616 (Figure 11) than that in adjacent unmineralized rocks, consistent with a fluid deposition  
617 origin. CM 4 is also commonest in the Golden Bar rocks, where significant deposition of  
618 fluid-borne CM is thought to have occurred (Craw, 2002). Raman spectra of CM 4 indicate  
619 that this material is relatively immature and poorly organized compared to graphite (Figure  
620 11), which could argue against the deposition of CM 4 from fluids. However, as for CM 2,  
621 there are documented cases of deposition of poorly organized CM from fluids, and in these  
622 cases the poorly organized CM is interpreted to be metastable relative to well-organized CM  
623 (Foustoukos, 2012; Luque et al., 1998; Pasters and Chou, 1998). However, the estimated  
624 temperature of CM 4 is similar to the metamorphic temperature so *in situ* origins cannot be  
625 ruled out.

626

#### 627 **5.4 Synthesis of relationships between CM and Au in the Otago Schist**

628 There is a general increase in maturity of CM towards graphite with increasing metamorphic  
629 grade in the Otago Schist, from CM 1 to CM 2 to CM 3 (Figure 3; Table 3). The crystallinity  
630 of CM 1 - 3 also increases with metamorphic grade in parallel with the Raman-documented  
631 maturation, as indicated by X-ray diffraction and reflectance data (Figure 10; Henne and  
632 Craw, 2012; Landis, 1971; McKeag and Craw, 1989). The principal CM X-ray diffraction  
633 peak becomes narrower, and the optical reflectance becomes progressively higher as  
634 metamorphic grade increases (Figure 10; Henne and Craw, 2012). This increase in maturity  
635 of CM with metamorphic grade occurred in parallel with mobilization of gold and associated

636 elements from the metamorphic pile (Figure 10; Pitcairn et al., 2006, 2010). Hence, there  
637 may be a genetic relationship between CM and gold during the evolution of these rocks.

638

639 In P-P facies rocks, CM 1 coexists with framboidal pyrite (Figure 5, 6). Both CM and pyrite  
640 are dispersed through these low grade (P-P) rocks, and are generally in close proximity at the  
641 micron to millimetre scale (Figure 5, 6). This pyrite is of diagenetic origin, and the presence  
642 of the reductive organic matter that became CM 1 probably facilitated deposition of that  
643 pyrite. At the same time, the combination of authigenic pyrite and CM facilitated localized  
644 enrichment of Au within the pyrite (Large et al., 2011, 2012). Large et al. (2012) conducted  
645 LA-ICP-MS on framboidal pyrite in P-P samples from Fiddlers Flat, and detected 0.5 – 10  
646 ppm Au and 1000 - 8000 ppm As (Figure 10; Large et al., 2012). In terms of implications of  
647 framboidal pyrite for gold mineralization, Vilor (1983) proposed that gold is deposited from  
648 seawater by interaction with hydrogen sulfide, and is adsorbed by organic detritus. Bacteria  
649 are thought to contribute to this process (Zhang et al., 1997). If we assume these processes  
650 occurred during formation of the framboidal pyrite in the lowest grade P-P samples, CM 1  
651 may have been associated with the extraction or adsorption of gold from seawater.

652

653 The diagenetic pyrite recrystallized to coarser grained pyrite, and ultimately transformed to  
654 pyrrhotite during progressive metamorphism to greenschist facies (Figure 7, 10; Henne and  
655 Craw, 2012; Large et al., 2011, 2012). CM 2 and CM 3 were deposited from metamorphic-  
656 hydrothermal fluids during this same transition. The scale of mobility of the carbon required  
657 to cause the observed localized enrichment of CM in veins is unknown, but may be only  
658 millimetres (Figure 8B) (Henne and Craw, 2012). However, associated Au and As contents  
659 are very similar in the matrices of P-P, P-A, and lower GS facies rocks (Table 1; Pitcairn et  
660 al., 2006), so there is no evidence to support a link between changes in CM type and gold  
661 mobilization. CM 2 is equivalent to the CM referred to as graphite by Henne and Craw  
662 (2012), who proposed that this CM was mobilized and deposited prior to gold mobilization  
663 and deposition.

664

665 Pyrrhotite is the principal sulfide mineral in the amphibolite facies rocks, and both pyrite and  
666 pyrrhotite can be present in different rock-types throughout the metamorphic transition from  
667 P-P (Figure 10; Pitcairn et al., 2010). Gold and other trace elements were released from pyrite  
668 into metamorphic-hydrothermal fluids during upper greenschist facies metamorphism, in the  
669 transition to pyrrhotite that was completed by amphibolite facies (Figure 10; Pitcairn et al.,

670 [2006, 2010](#)). The metamorphic-hydrothermal fluids that formed CM 3 in late metamorphic  
671 shears were undoubtedly related to the gold-bearing fluids generated during prograde  
672 metamorphism, but no gold deposition is observed to have coincided with the deposition of  
673 CM 3. Instead, gold deposition occurred at slightly lower temperatures, in structurally-  
674 controlled fluid flow zones, with the less well crystallized CM 4 ([Figure 9; Table 3](#)).

675

676 Previous workers have suggested that CM may have some relationship with deposition of  
677 gold and other sulfide minerals in the Victorian gold province of Australia and elsewhere (e.g.  
678 [Bierlein et al., 2001](#)). Given the clear association between CM 4, sulfide minerals and gold at  
679 the Macraes mine, it is necessary to consider if CM 4 is associated with gold deposition at  
680 that site. There are potentially four different relationships between CM 4 and gold deposition  
681 that need to be considered.

682

683 (1) CM 4 is pre-existing *in-situ* CM that reacted with metal-bearing fluid flowing through a  
684 primary organic-rich layer ([Cox et al., 1995; McKeag and Craw, 1989](#)). Deposition of gold  
685 and sulfide minerals may have been via formation of gold-organic compounds that were  
686 subsequently oxidized to form metallic gold (e.g., [Radtke and Scheiner, 1970](#)). Alternatively,  
687 CM in host rocks may have acted as a reducing agent for fluid carrying gold as bisulfide  
688 complexes, resulting in gold precipitation via a reaction like Equation [6] ([Craw, 2002,](#)  
689 [2007; Zoheir, 2008](#)).

690



692

693 (2) CM 4 was deposited from the mixing of CO<sub>2</sub>-rich and organic-rich or methane (CH<sub>4</sub>)-  
694 rich fluids during deposition of sulfide minerals, and the sulfide mineral deposition facilitated  
695 gold deposition within those sulfide grains (e.g., [Craw 2002](#)).

696 (3) Some CM 4 was precipitated from fluids prior to gold mineralization and caused the  
697 deposition of gold *via* mechanisms such as equation [6] ([Craw, 2002; 2007](#)).

698 (4) CM 4 was precipitated from fluids prior to, during, or after, gold mineralization, but had  
699 no direct causal role in gold precipitation. In this case, the CM may reflect only the focussing  
700 of fluid, rather than have a direct chemical role for CM in gold transport or deposition. For  
701 example, the CM may have had only a structural role that focused the hosting shear zone  
702 ([Upton and Craw, 2008](#)).

703

704 The evidence collected in this study, combined with previous work, shows clearly that  
705 mineralization-related CM 4 material is different from the CM 3 in host rocks, and that  
706 essentially precludes the first of the above scenarios. Our data are as yet insufficient to  
707 distinguish among the other three possible scenarios. Further work using additional  
708 techniques such as thermodynamic modelling and detailed chemical mapping using  
709 synchrotron and laser-ablation techniques are underway to further distinguish among the  
710 scenarios outlined above.

711

## 712 **6. Conclusions**

713 The combination of petrographic analysis and acquisition of Raman spectra revealed four  
714 types of carbonaceous material (CM) of varying maturity and origins in the Otago Schist. In  
715 P-P and P-A grade rocks, low maturity CM 1 coexists with framboidal pyrite and is proposed  
716 to have an *in-situ*, sedimentary origin. This CM may have been involved in sedimentary  
717 processes that produced the source of Au for gold deposits in the Otago region. CM 2, which  
718 also has low crystallinity, is also found in low grade samples and is interpreted, on the basis  
719 of its presence as large flakes in veins, to have been deposited by fluids. At the highest  
720 metamorphic grades studied (lower GS), well organized CM 3 is interpreted to have been  
721 deposited from fluids after the peak of deformation because black bands that contain CM 3  
722 cross cut the foliation. Less-well crystallized CM 4 from mineralized rocks is associated with  
723 sulfide minerals, and is interpreted to have a fluid-mediated history although the details are  
724 poorly understood.

725

726 Based on the above discussion, various carbonaceous materials with different origins may  
727 have had different roles in the formation of the gold deposit. Further, the strong association of  
728 CM 1 with gold-bearing sulfide minerals suggests that CM may have played a role in pre-  
729 concentrating the gold source. CM 4 at the deposit site may have been involved in gold  
730 deposition, but in the Otago Schist region, the detailed mechanism of gold deposition is still  
731 poorly understood.

732

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985 **Figures captions**

986 **Figure 1** Geological map of the Otago Schist in New Zealand (modified from [Henne and](#)  
987 [Craw, 2012](#) and [Pitcairn et al., 2005](#)); the highlighted areas with black boxes are sampling  
988 locations, i.e. Lake Hawea, Flddlers Flat and Golden Bar.

989  
990 **Figure 2** The two vibrational modes that may be displayed by single-crystal graphite. E2g is  
991 an in-plane optical vibration model and only this model is Raman active (modified from  
992 [Reich and Thomsen, 2004](#)).

993  
994 **Figure 3** (A) Raman spectrum of graphite (modified after [Wopenka and Pasteris, 1993](#)); (B)  
995 Raman spectrum of disordered CM (modified after [Wopenka and Pasteris, 1993](#)); (C) Raman  
996 spectrum of CM 1 from FF-16; (D) Raman spectrum of CM 2 from FF-12-A; (E) Raman  
997 spectrum of CM 3 from TC-01; (F) Raman spectrum of CM 4 from GB-04-A; The numbers  
998 in brackets are peak positions/average peak positions (see [Figure 1](#)) in  $\text{cm}^{-1}$ .

999  
1000 **Figure 4** Plot of (A)  $R1=D/G$  (intensity ratio); (B)  $R2= D/G$  (width ratio); (C)  $R3= (D+D1)/$   
1001  $(D+D1+G+D2+D3)$  (area ratio); (D)  $R4= S1/(S1+S2+S3)$  (area ratio). These ratios are  
1002 plotted against the estimated ranked metamorphic grade, from P-P to lower GS facies (P-P:  
1003 Prehnite-Pumpellyite facies; P-A: Pumpellyite-Actinolite facies; GS: Lower Greenschist  
1004 facies); the error bars shown are one standard deviation, taken from multiple measurements  
1005 of CM in the same samples.

1006  
1007 **Figure 5** Petrographic photomicrographs of CM 1 in framboidal pyrite in lower P-P facies in  
1008 reflected light (FF-16).

1009  
1010 **Figure 6** Petrographic photomicrographs of CM 1 in upper P-P facies (FF-15); (A)  
1011 backscatter electron (BSE) image of CM 1 and pyrite; (B) reflected light image of CM 1,  
1012 pyrite and chalcopyrite.

1013  
1014 **Figure 7** Photomicrographs of CM 2 in P-A and GS facies samples in reflected light and  
1015 SEM-BSE; (A) Strip-shaped CM 2 and framboidal pyrite in reflected light; (B) Strip-shaped  
1016 CM 2 and framboidal pyrite in BSE from FF-04, P-A facies; (C) Flaky CM 2 in carbonate

1017 veins in BSE from FF-13, P-A facies; (D) Flaky CM 2 elongated parallel the foliation with  
1018 pyrite and chalcopyrite in reflected light from FF-12-A, GS facies.

1019

1020 **Figure 8** Photomicrographs of CM 3 from P-A facies (LH-01); (A) CM 3 grain in reflected  
1021 light; (B) black bands (dark) consisting of CM 3 in transmitted light; (C) black bands (dotted  
1022 line) consisting of CM 3 in reflected light.

1023

1024 **Figure 9** Photomicrographs of CM 4 in reflected light (from GB-04-A, lower GS facies) in  
1025 mineralized sheared rock, Golden Bar pit, Macraes mine. (A) Mica-rich shears (dark)  
1026 surround disrupted fragments of quartz (pale grey). White sulfides, including a large fractured  
1027 arsenopyrite grain (centre) are scattered through the sheared rock. These sulfides contain  
1028 particulate and solid solution Au ([Large et al. 2012](#)). (B) CM 4 particles are scattered through  
1029 the sheared rock with the auriferous sulfides.

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1031 **Figure 10** Relationships between CM, Au and As with increasing metamorphic grade in the  
1032 Otago Schist (P-P: Prehnite-Pumpellyite facies; P-A: Pumpellyite-Actinolite facies; GS:  
1033 Lower Greenschist facies; AMP: Amphibolite facies). The first column is the representative  
1034 Raman spectra of four types of CM from our studies compared to X-ray diffraction and  
1035 reflectance of CM ([after Henne and Craw, 2012](#); [Landis 1971](#); [McKeag and Craw 1989](#)). The  
1036 second column is the sulfides transformation investigated by [Pitcairn et al., \(2010\)](#). The third  
1037 column is trace metal concentration variations from [Pitcairn et al., \(2006\)](#) and [Large et al.,](#)  
1038 [\(2012\)](#).

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1040 **Figure 11** A comparison of Raman spectra results and FTIR results (The Raman spectrum of  
1041 crystalline graphite is modified from [Wopenka and Pasteris, 1993](#); FTIR results were  
1042 investigated by [Pitcairn et al., 2005](#)).

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