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1 **Biologically-mediated weathering in modern cryptogamic ground covers and the lower**
2 **Palaeozoic fossil record**

3 *Abbreviated title: Modern and ancient cryptogamic weathering*

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16 **Abstract**

17 Specific micro-weathering features and biochemically-derived residues formed by living
18 organisms can be used as biomarkers to infer the presence of biological communities within
19 sedimentary units of ancient ecosystems. We examined basaltic soil minerals from modern
20 cryptogamic ground covers (CGCs) in Iceland and compared these to two lower Palaeozoic
21 fossil systems. Nine biologically-mediated weathering features (BWFs) were identified in
22 modern soils including micron-scale surface trenching and penetrative tunnels, which are
23 attributed to the actions of bacteria, fungi, and exudates. Specific BWFs are associated with
24 Fe residues, and with Fe-rich bio-precipitated nodules. Further, putative comparable features

25 and Fe enrichment are identified in palaeosols from the upper Silurian (Llansteffan; south
26 Wales) and the Lower Devonian (Rhynie chert, Scotland). Although we are cautious about
27 attributing biological affinity to individual isolated features, results demonstrate the potential
28 of using multiple BWF types as a collective together with their chemical signatures as new
29 proxies to understand community structure and interactions in early terrestrial ecosystems .
30 This new information is the first evidence of interactions between ancient CGC-like
31 organisms with substrate/soil inorganic components in the fossil record, and demonstrates the
32 ability of CGC-like biospheres to contribute to mineral weathering, soil development and
33 biogeochemical cycling during the lower Palaeozoic.

34

35 **Supplementary material:** [A: Fieldwork geomorphological information, B: Triplot SEM-
36 EDS data] is available at

37

38 The colonization of the terrestrial realm by primitive plants, lichens (and lichen-like
39 symbiotic relationships), and microbial organisms (e.g., fungi, bacteria, algae) during the
40 Early to Mid-Palaeozoic had profound influence on the geochemistry of the atmosphere and
41 ocean (Berner & Kothavala 2001; Lenton *et al.* 2012), the structure of sedimentary systems
42 (Gibling & Davies 2012; McMahon & Davies 2018), and soil development (Mergelov *et al.*
43 2018; Mitchell *et al.* 2016). Laboratory studies demonstrate that modern analogues of early
44 land plants (i.e., bryophytes), lichens and associated micro-organisms (e.g., mycorrhizal
45 fungi, bacteria) significantly influence weathering and cation mobilization from rocks
46 (Mergelov *et al.* 2018; Quirk *et al.* 2015; Field *et al.* 2012; Lenton *et al.* 2012), beginning
47 with the formation of microscopic bio-dissolution features through organism/soil interactions
48 (Li *et al.* 2016; Bonneville *et al.* 2009). Such features can be characteristic of certain classes
49 of organism or interaction and, where found in palaeosols, can (in principle) provide novel

50 insights into the nature of early communities, the interactions of their biotic components, and
51 their broader impacts on the environment (Mitchell *et al.* 2016). However the character of
52 biologically-induced micro-weathering features associated with mixed cryptogamic
53 vegetation types is poorly understood. Here, we use imaging and chemical analytical
54 techniques to characterize the microscopic biologically-mediated weathering features (BWFs)
55 that form in soils under cryptogamic ground cover (CGC) vegetation on primordial land
56 surfaces in Iceland.

57 Modern CGCs are communities dominated by bryophytes (mosses, liverworts,
58 hornworts), lichens, fungi, algae and bacteria (Elbert *et al.* 2012; Belnap & Lange 2001); they
59 are widely recognised as the closest modern analogues of the oldest plant-based terrestrial
60 ecosystems of the Early Palaeozoic (Edwards *et al.* 2015), with evidence of liverwort-like
61 cryptospores (Strother 2016) and molecular clock estimates (Morris *et al.* 2018) potentially
62 pushing their origin back to the Cambrian. We compare BWFs forming today on basalt
63 regolith in Iceland to features observed in two fossil systems with different characteristics;
64 first, we compare with the 407 Ma Rhynie chert (lower Devonian; Scotland, UK), which is
65 one of the earliest preserved terrestrial plant ecosystems (Edwards *et al.* 2017). The
66 fossiliferous chert beds at Rhynie formed as a silica sinter in a geothermal wetland, resulting
67 in the exceptional preservation of the biota (Channing 2018). This palaeobiota resembles
68 modern CGCs in many respects, but there are recognised differences in the nature of the
69 plants (e.g., no liverworts; Edwards *et al.* 2017) and fungal components (e.g. no
70 Basidiomycota) and in some of the known interactions (Mitchell *et al.* 2016). Second, we
71 compare to slightly older palaeosols (upper Silurian) that developed on a lowland floodplain
72 typical of the Old Red Sandstone from South Wales (Chapel Point Calcrete Member,
73 Llansteffan; Wales, UK) (Brasier *et al.* 2014). Although no fossils are known from this site,
74 the palaeosol is considered to have formed under CGC vegetation that would be comparable

75 to that of the Rhynie chert. Our goals are to use the physical and chemical characteristics of
76 modern BWFs to help identify sites of biologically-mediated weathering in the
77 fossil/sedimentological record, to understand the nature of the vegetation that occupied
78 palaeosols where fossilized remains are absent or sparse, and to identify new biogeochemical
79 markers associated with BWFs. This new information will contribute to our understanding of
80 the roles that early colonizing terrestrial organisms played in weathering, soil development,
81 biogeochemical nutrient cycling and landscape architecture.

82

83 **Geological setting and methods**

84 *Fieldwork*

85 *Modern CGC sampling - Iceland*

86 Modern CGCs and soils were collected from localities in Iceland (Fig. 1a). Iceland is
87 unique because of the variety of basal and early-colonizing CGC organisms and its relatively
88 primordial land surfaces (e.g., recent lava flows, aeolian-derived ejecta/scoria). Samples were
89 obtained from a variety of geomorphological localities containing an assortment of CGC
90 organisms (see *supplemental A*). Sampling was achieved by taking 8 cm x 2.5 cm micro-
91 cores through CGCs and underlying soil. Micro-cores were housed in plastic vials and treated
92 with a fixative (10% formalin).

93

94 *Llansteffan palaeosols (Old Red Sandstone)*

95 Samples of upper Silurian (Pridoli; 420 Ma) palaeosols were collected from
96 Llansteffan, South Wales (Fig. 1b). Palaeosols belong to the Chapel Point Calcretes Member
97 at the top of the Moors Cliff Formation (Morrisey *et al.* 2012; Wright & Marriott 1996) and
98 developed in mudstone-dominated ephemeral fluvial channel and floodplain settings (Brasier
99 *et al.* 2014). The palaeosols are documented as vertisol type (Wright & Marriott 1996) and

100 contain pedogenic calcrete indicating development under a seasonal semi-arid to sub-humid
101 climate (Marriott *et al.* 2009). Samples were collected from the palaeosurface of palaeosol
102 profiles (i.e., the top of the palaeosol bed) to ensure collection of material as close to the
103 presumed soil surface as possible. The outer ~10 cm surface of the exposure was removed to
104 avoid potential modern contamination and sedimentary samples were taken from freshly
105 exposed areas.

106 *Museum collections and imaging and analysis*

107 *Rhynie chert*

108 We studied both sediment cores and thin sections of Rhynie chert; cores and some
109 thin sections were loaned from the University of Aberdeen, where some cores were made into
110 thin sections within the Imaging and Analysis Centre (IAC) at the Natural History Museum
111 (London). The cores are from core 97/3 of Trewin & Wilson 2004. Cores were studied to
112 expand the investigation into sedimentary units surrounding the fossiliferous chert beds. The
113 nature of the lithology (silicified sinter) suggests that contamination by modern organisms is
114 near impossible, and that grains within the siliceous matrix show primary information.

115

116 *Light Microscopy, Scanning Electron Microscopy, and Electron Dispersive Spectroscopy*

117 Thin sections of Rhynie chert were studied with a Nikon Eclipse LV100ND
118 compound light microscope housed within the Dept. Earth Sciences at the Natural History
119 Museum (London). Modern Iceland CGC soil grains and Rhynie chert core sediments were
120 imaged using a Leo 1455 variable pressure scanning electron microscope (SEM) within the
121 IAC at the Natural History Museum (London). Scanning electron microscopy energy
122 dispersive X-ray spectroscopy (SEM-EDS) was used to establish chemical compositions
123 within the Advanced Imaging of Materials (AIM) Facility at Swansea University (UK) on a
124 Zeiss Evo WSEM and a Zeiss Crossbeam 540 FIB-SEM; major elements (Si, Al, Fe, Mg, Ca,

125 K, Na, P, Ti) were obtained and normalized via standard methods (*see Supplemental B*).

126

127 **Results**

128 *Grain weathering features in modern CGCs*

129 SEM revealed nine surficial and penetrative grain features that probably developed by
130 biologically-mediated weathering (Fig. 2; *Supplemental A*). Surficial rounded elongate tracks
131 (type 1) are the commonest feature (Figs 2 a & b); these exhibit elongate surface troughs with
132 rounded sides and edges, usually on the order of 5 μ m wide, and of variable lengths. The
133 troughs are concave up to ~300 nm depth and track along the grain surface rather than
134 penetrating. Rounded elongate tracks are often associated with residue infill (Fig. 2 a, b).
135 Bowl features (type 2; Fig. 2 c) are a series of concave surficial ~1-2 μ m wide bowl-shaped
136 depressions, no deeper than ~200 nm, with rounded edges. These often appear to connect as
137 linear structures (Fig. 2 c) across the grain surface. Borings (type 3; Fig. 2 d) penetrate grains
138 up to ~10 μ m depth. These features are both straight and curved, forming perpendicularly to
139 the grain surface (Fig. 2 d). These have rounded edges and some residue infill (Fig. 2 d).
140 Wedge elongate tracks (type 4; Fig. 2 e) are linear surface features similar to rounded
141 elongate tracks, but they instead have angular edges and a ‘wedge’ shaped tip. These features
142 are sometimes associated with residue infill (Fig 2. e). Pitting features (type 5) are commonly
143 associated with the attachment point of bryophyte rhizoids (Fig 2. f) and show surface
144 etchings associated with crystallographic orientations. Asymmetric holes (type 6) (Figs 2 g-h)
145 are commonly found in groups; they are often associated with other features (e.g., wedge
146 shaped tracks; Fig. 2 e) and fungal hyphae (Figs 2 g & h). Holes are ~2 μ m in diameter and
147 are asymmetrical; there are a series of smaller holes within a larger depression (e.g., Fig. 2 g).
148 Holes have smooth, curved edges. Some have residue infill (Fig. 2 e), and some are
149 associated with extra-polymeric substances (EPS) from local fungal hyphae (Fig. 2 h). Study

150 of thin sections reveals networks of internal dichotomous tunnels (type 7) (Figs 2 I & j). The
151 tunnels appear to be of two types; irregular (Fig. 2 i) which develop singular tunnels of
152 variable widths (although there appears to be some connections between tunnels; Fig. 2 i),
153 have infill, and a wedge-shaped tip; and regular (Fig. 2 j), which are a dichotomous network,
154 have constant widths, no infill, and penetrate grains up to 50 μm from a single surficial
155 penetration point. Tramlines (type 8; Fig. 2 k) are composed of two parallel marks on the
156 grain surface and are associated with the surficial attachment points of fungal hyphae. Cut
157 networks (type 9; Figs 2 l & m) are a linear arrangement of curved depressions. Individual
158 cuts are between 4 -10 μm wide and form elongate networks up to 60 μm in length. They are
159 often associated with fungal hyphae (Fig. 2 m), and some have residue infill (Fig. 2 l).

160

161 *Grain weathering features in fossil material*

162 *Rhynie chert*

163 We have identified comparable features from sedimentary grains and thin sections in
164 the Rhynie chert (Figs 3 a-d). Grains here are dominated by quartz, micas, and Ca-K
165 feldspars, with minimal clays. 2-3 μm linear networks of surficial bowl-like depressions are
166 observed on grain surfaces (Fig. 3 a). There are also 100-500 nm wide wedge-shaped surficial
167 features, some of which are angular, and some of which are curved (e.g., Fig. 3 b). We have
168 also identified apparent in-situ tunnel-like features from thin sections (Figs 3 c & d) which
169 originate from organic material which commonly surrounds grains. There also appears to be
170 filamentous remains within some grains, some of which have wedge-shaped tips (Fig. 3 c).

171

172 *Llansteffan palaeosols*

173 We have also identified numerous grain features in the Llansteffan palaeosols (Figs 3 e-j)
174 which are similar to BWFs observed in modern CGCs. Grains are dominated by quartz,

175 plagioclase, calcite, and clays. Large (~5-10 μm) and small (<3 μm) surficial asymmetric
176 holes are present (Figs 3 e, f, h, i), which are often associated with elongate surface tracks
177 (Figs 3 e & f). Elongate tracks also exist independently, sometimes as long as 80 μm and
178 develop crossing networks (Fig. 3 g). Some features also have a fine-grained residue infill
179 (e.g., Figs 3 f & i). There are also parallel tramlines, reminiscent of tramlines on modern
180 grains (e.g., Figs 2 k & 3 j).

181

182 *Chemistry of residues*

183 A number of modern CGC grain features contain a residue (e.g., Figs 2 a, b, d, e, I & L).
184 We have analysed the comparative composition of residue infill with that of 'clean' areas of
185 the host grain (i.e., areas which have not undergone weathering) via SEM-EDS; results are
186 compared in a series of A-CNK-FM and Al-Si-Fe ternary diagrams (Fig. 4) for major cations
187 (definition in figure caption). Chemical information can be found in *supplemental B*.

188

189 *Modern CGC grain residue composition*

190 Chemical compositions of a variety of weathered residues were compared (Fig. 4).
191 A-CNK-FM plots (Fig. 4 a) display a general trend for all features towards the FM apex
192 when comparing 'clean' areas to residue compositions, indicating enrichment in Fe and/or
193 Mg. This is the case for tunnels (type 7), wedge elongate tracks (type 4), cuts (type 9), and
194 rounded elongate tracks (type 1). Residues of asymmetric holes (type 6) indicate a slight
195 enrichment in CNK, but otherwise an almost homogeneous chemistry to the 'clean' values.
196 Some rounded elongate tracks (type 1) are ~40% more enriched in FM compared with 'clean'
197 areas (Fig. 4 a). Also plotted are compositional comparisons of a fungal hypha attached to a
198 soil grain (Figs 4 a, e, f), indicating Fe and Mg enrichment in the hypha itself, EPS, and
199 probable hyphae-derived bio-precipitates in comparison to 'clean' areas. Al-Si-Fe plots (Fig.

200 4 b) indicate residue is enriched in Fe rather than Mg. There is also a general trend away from
201 the Al and Si apexes in comparison to Fe (Fig. 4 b).

202

203 *Llansteffan palaeosol grains residue composition*

204 Figures 4 C and D illustrate a chemical comparison of grain residues and palaeosol mud-
205 and claystones composition. Residue is associated with potential asymmetric holes (type 6),
206 cuts (type 9), rounded elongate tracks (type 1), and dissolution (type 5). A-CNK-FM plots
207 (Fig. 4 c) indicate that the composition of mud/claystones overlaps significantly with that of
208 the residue composition. There is low CNK in all samples, between 0 and 60% Al, and
209 between 20 and 96% FM (Fig. 4 c). Of the residue values, asymmetric holes (type 6) have the
210 lowest FM, whereas elongate tracks (type 1) have the highest (between 84 and 96%). This
211 plot again suggests an accumulation of Fe and/or Mg in residues (in specific features). The
212 Si-Al-Fe plot (Fig. 4 d) indicates a different trend. Mud/claystone samples are located nearer
213 the Si apex, as well as residues belonging to asymmetric holes (type 6), cuts (type 8), and
214 dissolution (type 5). Other asymmetric holes and elongate rounded tracks (type 1) are
215 compositionally similar to clay/mudstone samples (Fig. 4 d). Residue associated with
216 networks of elongate tracks (Fig. 3 g) plot at the Fe apex, clarifying that enrichment is in Fe
217 rather than Mg.

218

219 **Discussion**

220 *Are the grain features biologically-mediated?*

221 *Modern CGC grain weathering features*

222 We have identified numerous surficial and internal features on modern CGC soil
223 grains (e.g., Fig. 2) that we propose are biologically-mediated in origin. Supportive of this are
224 features such as smooth edges, constant diameters, and rounded ends (e.g., Figs 2 a, b, d, g, h)

225 which are suggestive of a biological origin (Jongmans *et al.* 1997; Hoffland *et al.* 2002),
226 whereas mechanical structural alteration (e.g., cracks) have sharp, non-rounded edges (e.g.,
227 Fig. 2 j). In addition, if the features were the product of chemical weathering (i.e., the action
228 of hydrolysis-like dissolution reactions), they would have regularly shaped and oriented etch-
229 pits because chemical dissolution occurs preferentially along specific crystallographic plains
230 and boundaries (Landeweert *et al.* 2001); our features, bar rhizoid pitting (type 5), do not
231 show these structures.

232

233 *Surficial weathering features*

234 The width and shape of rounded and wedge elongate tracks (Figs 2 a, b, e) and tunnel
235 features (Figs 2 i & j) indicate they are developed by filamentous organisms, probably fungi
236 or bacteria. A fungal origin is supported by the proximal presence of hypha (e.g., Fig. 2 g, h,
237 k, m) and in-situ evidence of hypha forming tramlines on the grain surface (Fig. 3 k).
238 Surficial rounded elongate track-like features are common in growth experiments (e.g., on
239 feldspars; Hoffland *et al.* 2004) caused by ectomycorrhizal (Bonneville *et al.* 2009),
240 arbuscular mycorrhizal (symbiont of liverwort *Marchantia sp.*; Quirk *et al.* 2015), and
241 saprotrophic (Li *et al.* 2016) fungi, which supports a fungal origin. The nature of any
242 symbiotic association in our soils is unclear, however it seems likely that mutualistic
243 associations (e.g., lichen-like) between fungi and photosynthetic organisms (plants, algae,
244 cyanobacteria), and the transfer of energy from one organism to another (e.g., for
245 carbohydrates and nutrients), is a plausible driver of weathering (Hoffland *et al.* 2004).

246 We propose that the surficial BWFs identified here represent different stages of the
247 surficial weathering process (Fig. 5 a). Firstly, initial hypha-grain attachment (stage 1)
248 develops a set of parallel weathered tramlines (type 8) (e.g., Fig. 2 k) marking the outer width
249 of the hyphae, and exudates produced by the hypha bio-weather of the grain surface. After

250 the hypha is established on the grain surface for a period of time, in-situ bio-weathering
251 results in concave depressions that mark the shape and size of the hypha, or elongate tracks,
252 and the eventual development of a weathered residue (Figs 5 a & 2 a, b, e). Once the hypha
253 dies, is removed or moves on, these features are left on the grain surface as a bio-marker of
254 previous fungal hypha colonization. The stage at which the hypha is capable of weathering is
255 most likely dependent on the time of colonization, the energy available to promote
256 weathering by any mutualistic symbiotic partnership, and the chemical composition/hardness
257 of the grain. Thus, we are confident that these are biological in origin.

258

259 *Internal weathering features*

260 We propose that biologically-mediated internal weathering is represented by different
261 features observed through internal imaging of soil components and grains. Grain attachment
262 focused at the hypha tip (stage 1) creates a network of parallel ‘cuts’ (Figs 2 l & 5 b), where
263 the cut orientation represents the hypha travelling direction (Figs 2 l & 5 b). Targeted tip-
264 driven weathering results in hole (type 6) development; these holes are numerous and are
265 often found proximal to fungal hyphae (e.g., Figs 2 g & h). Individual holes within the larger
266 depression probably indicate numerous penetration attempts. Comparative holes with
267 inwards-penetrating walls have been discussed in Hoffland *et al.* (2004) and others, and are
268 judged to be caused by biophysical and biochemical weathering by mutualistic/symbiotic
269 hyphae (e.g., Hoffland *et al.* 2004; van Scholl *et al.* 2008; Jongmans *et al.* 1997). When full
270 penetration is successful, borings (type 3) are produced (stage 4; Figs 2 d & 5 b) and
271 eventually can form tunnels (Figs 2 i & j). This process is dependent on the duration and rate
272 of bio-weathering; future studies should attempt to quantify this. The tunnels identified in this
273 study are comparable to biotic tubular alteration textures outlined in Furnes *et al.* 2007, which
274 are further formalised as *Tubulohyalichnus* ichnotaxta in McLoughlin *et al.*, 2008.

275 Comparable terrestrial tunnel features (type 7) are known from the literature; examples
276 include the penetration of feldspars by ectomycorrhizal fungi which create rounded
277 bifurcating networks of open, 3-10 μm wide tubular pores (e.g., Landeweert *et al.* 2001; van
278 Scholl *et al.* 2008; Berner & Cochrain 1998). Tunnels (type 7) form by a combination of
279 nanometer-scale bio-mechanical forcing and chemical alteration from the excretion of low
280 molecular weight organic anions (LMWOA's, e.g., oxalate, citrate; Hoffland *et al.* 2004,
281 Bonneville *et al.* 2009). LMWOA's contribute to the mobilization of nutrients (e.g., Mg, Ca,
282 K), and chelation of cations (Landeweert *et al.* 2001; Bonneville *et al.* 2009) from the grain,
283 creating elemental gradients (depletions) on bio-weathered areas at the hyphal-mineral
284 interface. Hyphal LMWOA production has substantial carbon costs indicating
285 mutualistic/symbiotic organisms (including fungi) have a weathering incentive over free-
286 living (e.g., cyanobacteria; Staudigel *et al.* 1995) and saprotrophic organisms (Gadd 2010;
287 Hoffland *et al.* 2004). Therefore it is most likely that symbionts in mutualistic associations
288 develop penetrating internal features, whereas surficial features are most likely developed by
289 those not in symbiotic relationships or those with less energy. This new information not only
290 recognizes different bio-weathering features and strategies of formation, but also provides a
291 framework for recognising BMWFs in the fossil record and their potential responsible
292 (symbiotic, parasitic, free-living) organisms (e.g., fungi/cyanobacteria).

293

294 ***Comparison of modern BWFs with fossil grain features***

295 Because of the similar morphological traits (Figs 2 & 3) and chemical trends
296 (irrespective of parent chemistry; Fig. 4) with BMFs in modern CGCs, we propose that fossil
297 grain features are biologically-mediated. We discount a physical/abiotic origin; biologically-
298 mediated tunnels and bio-penetration (e.g., Figs 3 c & d) are morphologically distinct from
299 common physical features (e.g., quartz conchoidal fracture and cracks (Figs 2 j & 3 c),

300 physically-derived inclusions (Fig. 3 d) lacking terminal crystals (e.g., Mcloughlin *et al.*
301 2010), and typical chemical weathering features following specific predefined chemical and
302 crystallographic boundaries (e.g., denticulated margins; Velbel 1989). Further, it is unlikely
303 that these weathering features have been produced by ‘modern’ organisms because of the
304 method of collection (see methods). Consequently, we are confident the features were formed
305 before diagenesis and are useful for comparative studies.

306 The Rhynie chert (Figs 3 a-d) has comparable features reminiscent of modern BWFs,
307 including surficial bowl features (Figs 2 c & 3 a), surficial tramlines and cuts (Figs 2 k-m & 3
308 b-c), and penetrating tunnels (Figs 2 i-j & 3 c-d). Bowl features (Fig. 2 c) are analogous to
309 concave etchings created by bacteria and develop by the excretion of EPS promoting in-situ
310 bio-dissolution (Thorseth *et al.* 1995). The circular ‘bowl’ shape could suggest development
311 by coccoid-type bacteria, and that chains are created by numerous parallel colonies (Thorseth
312 *et al.* 1995). We postulate that bacterial colonies were adhering to grain surfaces in the
313 Rhynie chert, secreting EPS and promoting the development of distinctive bowl-shaped
314 features (Thorseth *et al.* 1995) (Fig. 3 a). Filamentous cyanobacteria are known in the Rhynie
315 chert in microbial mats on sediment surfaces (Strullu-Derrien 2018; Krings *et al.* 2007) and
316 as coccoid cyanobacteria in the postulated cyanolichen *Winfrenatia* (Taylor *et al.* 1997). The
317 shape and size of the bowls suggests they could have been formed by spherical coccoid
318 photobionts from cyanolichens (e.g., Taylor *et al.* 1997), and indicate that this grain may
319 have been part of a lichen CGC-hosting substrate. It also seems likely that fungi, particularly
320 of a symbiotic affinity, were interacting with mineral grains. Rhynie chert BWFs are
321 analogous to tramlines (type 8) and cuts (type 9; Fig. 3 b) of modern CGC BWFs (Figs 2 k &
322 l). Cut (type 9) features in the Rhynie chert are both angular and round (Fig. 3 b), possibly
323 analogous to hypha-derived wedge elongate tracks (type 4) in modern CGCs (Fig. 2 e). Based
324 on our assumptions of the attachment and weathering process (e.g., Fig. 5), this could

325 indicate that both non-symbiotic and symbiotic fungi interacted with grains in the Rhynie
326 chert. There is evidence of free-living saprotrophic zoosporic fungi in the Rhynie chert
327 ecosystem which were likely adaptations during patchy resource availability (Strullu-Derrien
328 *et al.* 2017). These organisms could be responsible for surficial weathering features. The
329 shape and size of possible filamentous penetration (Figs 3 c & d) and the comparative
330 morphology to modern features (e.g., Figs 3 e, i, j) indicates they may be from mutualistic
331 fungal hypha interactions which would have the energy requirements for internal penetration
332 (Harrison 2005). There are numerous examples of mutualism (mycorrhizal fungi) with
333 Rhynie chert plants; in *Horneophyton lignieri* (Strullu-Derrien *et al.* 2014), *Aglaophyton*
334 *major* (Remy *et al.* 1994), and possibly in *Nothia aphylla* (Krings *et al.* 2007). These
335 observations indicate that mycorrhizal-driven mineral weathering was occurring in the
336 Rhynie chert system.

337 Asymmetric holes (e.g., Figs 3 e, f & i), reminiscent of holes in modern CGC
338 weathering (Figs 2 g & h) are present on Llansteffan palaeosol grains suggesting fungal
339 weathering also in late Silurian CGC-like biospheres. The presence of surficial rounded
340 elongate tracks (Figs 3 e, f, g & j) and tramlines (Fig. 3 i), analogous to features in modern
341 soils (Figs 2 a, b, k; Li *et al.* 2016; Bonneville *et al.* 2009; Hoffland *et al.* 2004) are most
342 likely also the product of fungal hyphae colonizing the surface of grains (Fig. 5 a).

343 By identifying several BWFs and interpreting them as collective evidence in the fossil
344 material provides a robust indication of the former presence of specific organisms and modes
345 of weathering. These observations suggest an assortment of CGC-like organisms (e.g., fungal
346 hyphae (either mycorrhizal/saprotrophic, plant symbiont/lichenized), bacterial colonies) were
347 adhering themselves to, penetrating, and weathering mineral grains in early Palaeozoic
348 terrestrial systems. In particular, this study extends our knowledge of CGC-like biospheres to
349 the late Silurian, furthers our understanding of weathering and soil development, and adds a

350 new proxy for the identification of CGCs and their organisms in the sedimentological/fossil
351 record.

352

353 ***Fe-rich nodules and bio-precipitation***

354 We have observed Fe-rich nodular precipitates in association with fungal hyphae in
355 modern CGCs (e.g., Figs 2 h & 4 e). The chemical composition of precipitated nodules, as
356 well as the composition of various biological features associated with the precipitates (hypha
357 EPS; Figs 4 a & b) indicates the highest concentrations of Fe are in EPS exudates and the bio-
358 precipitated nodule (Fig. 4 b). This is consistent with hyphal exudates promoting the
359 production of Fe-rich bio-precipitates (e.g., Figs 2 h & 4 e), which is well documented and
360 supported in the literature; occurrences include the fungal biomineralization of iron
361 oxyhydroxide minerals (Oggerin *et al.* 2016), fungal and bacterial slime biomineralization of
362 Mn oxides (Akhtar & Kelso 1992), and bio-precipitation of Fe, Mn and Zn by fungal oxalic
363 acid exudates (Gadd 1999). We propose that Fe accumulation documented here can be used
364 as a biomarker for biologically-mediated weathering (particularly by fungi) in the fossil
365 record. Weathered residues associated with elongate tracks in fossil material are enriched in
366 Fe (Figs 4c & d), and values are comparable with fungal-derived Fe-rich bio-precipitates in
367 modern CGC soils (e.g., Figs 4 a, b & e), which indicates that bio-precipitation is
368 independent of soil mineral 'parent' chemistry (e.g., Fig. 4). Combined with the comparable
369 morphological traits of fossil structures with BWFs created by fungal hyphae in modern CGC
370 soils, the Fe-rich nodule and residue chemistry lends support to the fungal bio-precipitation
371 hypothesis. However to complement this data, further understanding of weathering by fungi
372 on substrates of different chemistries is sought.

373 Interestingly, there is evidence of bio-precipitation from lichen relationships; these
374 include iron oxides/hydroxides and forsterite (Gorbushina *et al.* 2001) bio-precipitation from

375 organic acids secreted by lichen mycobionts (Adamo & Violante 2000), and Fe hydroxide
376 and clay-rich coatings (e.g., Arocena *et al.* 2003) in biogenic rock varnishes caused by
377 lichenized cyanobacterium (Krumbein & Jens 1981). Whether this was caused by plant
378 symbiotic fungi or lichenized fungi is still unclear, however comparison with modern
379 processes could provide an indication. This provides new evidence of fungal interactions in
380 the upper Silurian Llansteffan palaeosols, an extension of current knowledge of biomarkers
381 (e.g., Gorbushina *et al.* 2004; Gadd 2007), and that CGC-like organisms were not only in
382 existence but were responsible for biologically-mediated weathering processes.

383

384 ***BWF residue, clay, and early Palaeozoic soils***

385 Modern CGC biologically-mediated weathering residues all display an enrichment of Fe
386 and Mg (Fig. 4 a), specifically Fe (Fig. 4 b), compared with ‘parent’ values, due in part to Fe-
387 rich bio-precipitates. Clay, probably of smectite variety (concurrent with residue and soil
388 compositions from Mitchell *et al.* 2016) is present and is supported by an Fe-rich chemistry,
389 variable (but generally high) Al and Si, and fine-grained, shrink-swell physical structures
390 (e.g., Fig. 2 a & d).

391 Mud-claystone Llansteffan palaeosol chemical compositions are similar to residues (Figs
392 4 c-d). It is possible that residues contribute to/are responsible for a) mud-clay buildup in
393 palaeosols, and b) the specific Fe rich composition (Figs 4 c-d). Smectite is a dominant
394 component of vertisols (shrink-swell palaeosols) in alluvial units in the Old Red Sandstone of
395 south Wales (e.g, Marriott & Wright 1996; Wright & Marriott 1996; Hillier *et al.* 2007;
396 Marriott & Wright 2004), including the Llansteffan palaeosols. No palaeobotanic remains
397 have been found in the Llansteffan palaeosols, however a diverse and varied flora is known in
398 other areas of the Lower Old Red Sandstone (including rhyniophytoids (e.g., *Cooksonia*),
399 rhyniophytes, plants with tracheophytic and bryophytic characters, *Prototaxites* and

400 *Pachytheca*, and probable coalified banded tubes reminiscent of fungal hyphae (Morris *et al.*
401 2011; Barclay 2005), indicating that CGC-like organisms were present. Probable fungi-
402 derived BWFs and residues (Figs 3 e-j) in the Llansteffan paleosols suggests that a) there
403 were CGC-like organisms colonizing the soil surface at some point during their development,
404 b) the affirmation of the presence of hyphae-like organisms from other ORS units of south
405 Wales (Morris *et al.* 2011) and c) biologically-mediated weathering by CGC-like organisms
406 was potentially contributing towards smectite development within palaeosols and the early
407 Palaeozoic sedimentary system.

408 Smectite clays are also found in the Rhynie chert sedimentary system (e.g., Trewin &
409 Rice 1992; Trewin *et al.* 2003). Despite the proposition that the Rhynie chert smectite is the
410 result of hydrothermal alteration (e.g., Trewin *et al.* 2003), our results demonstrate the clear
411 possibility of an alternative hypothesis for the smectite. This hypothesis however requires
412 further study, and a detailed chemical analysis of Old Red Sandstone (including the Rhynie
413 chert) smectite clays needs to be obtained.

414 As well as smectite-rich vertisol development, there is a general increase in the
415 proportion of mudstones in the terrestrial sedimentological record through the early
416 Palaeozoic (e.g., Gibling & Davies 2012; McMahon & Davies 2018; Davies *et al.* 2017),
417 presumed to be due to expanding primitive land biotas since the late Proterozoic/early
418 Cambrian enhancing the production of pedogenic clay minerals (e.g., contrasting views in
419 Kennedy *et al.* 2006 and Tosca *et al.* 2010). Results here and in Mitchell *et al.* (2016)
420 indicate that biologically-mediated weathering of minerals and subsequent biogenic smectite
421 development by primitive CGC organisms is a likely driver of this change. In addition, the
422 stabilization of land surfaces by the interactions of early terrestrial organisms with soil grains
423 (e.g., entwining by rhizoids and symbionts; Mitchell *et al.* 2016) and exudates (e.g., soil
424 aggregation; Galloway *et al.* 2017) will have contributed to the evolution of extensive muddy

425 floodplains and a change in fluvial system architecture (e.g., Davies & Gibling 2010). This
426 illustrates the profound affect that evolving early Palaeozoic plant-dominated biospheres had
427 on landscapes.

428

429 **3. Conclusions**

430 Here we have identified nine biologically-mediated weathering features (BWFs) on modern
431 soil grains associated with cryptogamic ground covers (CGCs). Both multi-organism physical
432 markings, biologically-derived weathering residues (e.g., Mitchell *et al.* 2016) and Fe-rich
433 nodular bio-precipitates are useful as biomarkers to recognize the former presence of CGCs
434 and their associated organismal weathering in the fossil record. Comparable features
435 observed in the upper Silurian Llansteffan palaeosols and Lower Devonian exceptionally
436 preserved Rhynie chert not only indicate that BMWFs can be a useful proxy for identifying
437 fossil CGCs, but also that the former presence of specific CGC-inhabiting organisms (e.g.,
438 mycorrhizal fungi, cyanobacteria) can be determined. This can potentially improve our
439 understanding of Lower Palaeozoic terrestrial environments, circumventing the need to rely
440 on a plant macrofossil record that is essentially missing before the lower Silurian (e.g.,
441 Tomescu & Rothwell 2006; Gastaldo & Demko 2011), and provides information pertaining
442 to ancient plant-soil interactions and biogeochemical cycles. However, we propose that
443 caution is exercised when identifying BWFs in the fossil record, as these features are best
444 interpreted as a collective rather than as isolated features (similar collective methods are used
445 for interpreting microbially-induced sedimentary structures; Davies *et al.* 2016). This method
446 could extend the record of CGC-like organisms and environments beyond the current
447 documented age from body fossils and palynological data; to test this theory, BWFs should
448 be sought in terrestrial sedimentary lithologies from the Cambrian and Proterozoic.

449

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462

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688

689 **Figure captions**

690 **Fig. 1.** Sample locations of modern CGCs in Iceland and Llanseffan palaeosols in the Old
691 Red Sandstone. **(a):** CGC areas in Iceland. K = Krafla Fires, Sn = Snæfellsjökull, So =
692 Solheimajökull glacier, C = central desert, G = Geysir area. Grey areas show icecaps.

693 Adapted from Mitchell et al. 2016. **(b)**: Location of Llansteffan in South Wales, UK. Adapted
694 from Wight & Marriott 2007.

695 **Fig. 2.** Weathering features on modern CGC soil grains obtained via SEM. Nine features
696 have been identified (seven surficial **(a-c, e-h, k-m)** and two internal **(d, i-j)**): Type 1 rounded
697 elongate tracks **(a, b)**, type 2 bowls **(c)**, type 3 borings **(d)**, type 4 wedge elongate tracks **(e)**,
698 type 5 pitting **(f)**, type 6 asymmetrical holes **(e, g, h)**, type 7 tunnels **(i, j)**, type 8 tramlines
699 **(k)**, and type 8 cut networks **(l, m)**.

700 **(a)**: Example of a rounded elongate track with infill weathered residue (white arrow). **(b)**:
701 Numerous rounded elongate tracks with infill weathered residue (white arrow). **(c)**: Surficial
702 concave bowl-shaped depressions (white arrow). **(d)**: Borings (black arrows), some have
703 infill weathered residue (white arrow). **(e)**: Wedge elongate track with distinctive wedge-
704 shaped tip (black arrow), this particular example has infill residue. Asymmetrical holes are
705 also present (white arrow). **(f)**: Surficial pitting (white arrow) where a bryophyte rhizoid is in
706 grain contact (black arrow). **(g)**: Asymmetrical holes (white arrows); holes appear to be
707 numerous smaller holes in a larger singular depression. Also shown is a fungal hyphae (black
708 arrow) and Fe-rich precipitates (grey arrow). **(h)**: Asymmetric holes (white arrows); these
709 examples are also associated with a fungal hyphae (black arrow), extra polymeric substances
710 (EPS; grey arrow), and Fe-rich precipitates (red arrow). **(i)**: Irregular tunnels (thin section).
711 This example has infill and a wedge-shaped tip (black arrow). There is also connecting
712 tunnels between main tunnels (grey arrow). **(j)**: Example of regular dichotomous tunnels
713 (white arrow). Tunnels are bifurcating and originate at the grain surface from a single point,
714 are devoid of infill, and have constant widths. Black arrow indicates a crack for comparison.
715 **(k)**: Parallel tramlines (white arrows) caused by attachment of a fungal hyphae (black arrow).
716 **(l)**: Networks of cuts (black arrows); this example shows the tracks moving from left to right.
717 **(m)**: Cuts (white arrows); also shown is a fungal hypha (black arrow).

718 **Fig. 3.** Probable biologically-mediated grain weathering features from the fossil record. **(a-**
719 **d):** Lower Devonian Rhynie chert. **(e-j):** Upper Silurian Llansteffan palaeosols. **A-b, e-j**
720 SEM images, c-d thin section optical microscope images. **(a):** Chain of elongate bowl-like
721 depressions (white arrow). **(b):** Wedge-shaped (white arrows) and curved (black arrow) track
722 marks on the surface of quartz grains. **(c):** Examples of possible filaments penetrating grains
723 (black and white arrows). Black arrow shows feature with wedge tip, white arrow shows
724 rounded, and red arrow shows natural conchoidal fracture in grain for comparison. **(d):**
725 Organic material which appears to be penetrating grain (red arrow). Grey arrows in (c-d)
726 indicate organic rinds on grains. White arrow indicates mineral inclusion. **(e):** Series of holes
727 (black arrow) and rounded elongate tracks (white arrow) on grain from Llansteffan
728 palaeosols. **(f):** Asymmetric hole (white arrow) and elongate track (black arrow), both with
729 infill residue. **(g):** Networks of elongate track marks (black arrows) on grain surface. **(h):**
730 Large asymmetric holes (black arrows) on a grain surface. **(i):** Asymmetric hole (black
731 arrow). **(j):** Surface grain features including an elongate track (black arrow) and parallel
732 tramlines (white arrow).

733 **Fig. 4.** Compositional ternary diagrams for modern CGC soil grains from Iceland **(a and b)**
734 and from grains from the Llansteffan paleosols **(c and d)** comparing residues with 'clean'
735 grain areas. **(a) and (c):** A-CNK-FM ternary plot, which is equivalent to $Al_2O_3 -$
736 $(CaO+Na_2O+K_2O) - (FeO+MgO)$ compositions. **(b) and (d):** Al-Si-Fe ternary plot, which is
737 equivalent to $Al_2O_3 - SiO_2 - FeO$ compositions. Values are averages of numerous analyses
738 from the same feature. In A and B: Ka = kaolinite, Il = illite, Fs = feldspar, pyx = pyroxene,
739 Am = amphibole, Bi = biotite, Sm = smectite. E: SEM image of modern fungal hyphae (white
740 arrow), EPS (grey arrow) and Fe-rich nodules (black arrow) on grain surface; these
741 correspond to grey and black points on **(a)** and **(b)** under fungal hypha features. **(f):**
742 Simplified schematic features in **(e)**. **(g):** SEM image of the often complex arrangement of

743 biologically-mediated weathering features; these correspond to green points in A and B. Cuts
744 (white arrow), elongate tracks (black arrow), borings (grey arrow), holes (red arrow). Ternary
745 plots adapted from Nesbitt & Young (1989).

746 **Fig. 5.** Proposed developmental stages of surficial **(a)** and internal **(b)** biologically-mediated
747 weathering features.