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

Abbreviated title: Modern and ancient cryptogamic weathering

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Abstract

Specific micro-weathering features and biochemically-derived residues formed by living organisms can be used as biomarkers to infer the presence of biological communities within sedimentary units of ancient ecosystems. We examined basaltic soil minerals from modern cryptogamic ground covers (CGCs) in Iceland and compared these to two lower Palaeozoic fossil systems. Nine biologically-mediated weathering features (BWFs) were identified in modern soils including micron-scale surface trenching and penetrative tunnels, which are attributed to the actions of bacteria, fungi, and exudates. Specific BWFs are associated with Fe residues, and with Fe-rich bio-precipitated nodules. Further, putative comparable features and Fe enrichment are identified in palaeosols from the upper Silurian (Llansteffan; south Wales) and the Lower Devonian (Rhynie chert, Scotland). Although we are cautious about attributing biological affinity to individual isolated features, results demonstrate the potential of using multiple BWF types as a collective together with their chemical signatures as new proxies to understand community structure and interactions in early terrestrial ecosystems . This new information is the first evidence of interactions between ancient CGC-like organisms with substrate/soil inorganic components in the fossil record, and demonstrates the ability of CGC-like biospheres to contribute to mineral weathering, soil development and biogeochemical cycling during the lower Palaeozoic.

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

The colonization of the terrestrial realm by primitive plants, lichens (and lichen-like symbiotic relationships), and microbial organisms (e.g., fungi, bacteria, algae) during the Early to Mid-Palaeozoic had profound influence on the geochemistry of the atmosphere and ocean (Berner & Kothavala 2001; Lenton et al. 2012), the structure of sedimentary systems (Gibling & Davies 2012; McMahon & Davies 2018), and soil development (Mergelov et al. 2018; Mitchell et al. 2016). Laboratory studies demonstrate that modern analogues of early land plants (i.e., bryophytes), lichens and associated micro-organisms (e.g., mycorrhizal fungi, bacteria) significantly influence weathering and cation mobilization from rocks (Mergelov et al. 2018; Quirk et al. 2015; Field et al. 2012; Lenton et al. 2012), beginning with the formation of microscopic bio-dissolution features through organism/soil interactions (Li et al. 2016; Bonneville et al. 2009). Such features can be characteristic of certain classes of organism or interaction and, where found in palaeosols, can (in principle) provide novel insights into the nature of early communities, the interactions of their biotic components, and their broader impacts on the environment (Mitchell et al. 2016). However the character of biologically-induced micro-weathering features associated with mixed cryptogamic vegetation types is poorly understood. Here, we use imaging and chemical analytical techniques to characterize the microscopic biologically-mediated weathering features (BWFs) that form in soils under cryptogamic ground cover (CGC) vegetation on primordial land surfaces in Iceland.

Modern CGCs are communities dominated by bryophytes (mosses, liverworts, hornworts), lichens, fungi, algae and bacteria (Elbert et al. 2012; Belnap & Lange 2001); they are widely recognised as the closest modern analogues of the oldest plant-based terrestrial ecosystems of the Early Palaeozoic (Edwards et al. 2015), with evidence of liverwort-like cryptospores (Strother 2016) and molecular clock estimates (Morris et al. 2018) potentially pushing their origin back to the Cambrian. We compare BWFs forming today on basalt regolith in Iceland to features observed in two fossil systems with different characteristics; first, we compare with the 407 Ma Rhynie chert (lower Devonian; Scotland, UK), which is one of the earliest preserved terrestrial plant ecosystems (Edwards et al. 2017). The fossiliferous chert beds at Rhynie formed as a silica sinter in a geothermal wetland, resulting in the exceptional preservation of the biota (Channing 2018). This palaeobiota resembles modern CGCs in many respects, but there are recognised differences in the nature of the plants (e.g., no liverworts; Edwards et al. 2017) and fungal components (e.g. no Basidiomycota) and in some of the known interactions (Mitchell et al. 2016). Second, we compare to slightly older palaeosols (upper Silurian) that developed on a lowland floodplain typical of the Old Red Sandstone from South Wales (Chapel Point Calcrete Member, Llansteffan; Wales, UK) (Brasier et al. 2014). Although no fossils are known from this site, the palaeosol is considered to have formed under CGC vegetation that would be comparable to that of the Rhynie chert. Our goals are to use the physical and chemical characteristics of modern BWFs to help identify sites of biologically-mediated weathering in the fossil/sedimentological record, to understand the nature of the vegetation that occupied palaeosols where fossilized remains are absent or sparse, and to identify new biogeochemical markers associated with BWFs. This new information will contribute to our understanding of the roles that early colonizing terrestrial organisms played in weathering, soil development, biogeochemical nutrient cycling and landscape architecture.

Geological setting and methods

Fieldwork

Modern CGC sampling - Iceland

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

Llansteffan palaeosols (Old Red Sandstone)

Samples of upper Silurian (Pridoli; 420 Ma) palaeosols were collected from Llansteffan, South Wales (Fig. 1b). Palaeosols belong to the Chapel Point Calcretes Member at the top of the Moors Cliff Formation (Morrisey et al. 2012; Wright & Marriott 1996) and developed in mudstone-dominated ephemeral fluvial channel and floodplain settings (Brasier et al. 2014). The palaeosols are documented as vertisol type (Wright & Marriott 1996) and contain pedogenic calcrete indicating development under a seasonal semi-arid to sub-humid climate (Marriott et al. 2009). Samples were collected from the palaeosurface of palaeosol profiles (i.e., the top of the palaeosol bed) to ensure collection of material as close to the presumed soil surface as possible. The outer ~10 cm surface of the exposure was removed to avoid potential modern contamination and sedimentary samples were taken from freshly exposed areas.

Museum collections and imaging and analysis

Rhynie chert

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

Light Microscopy, Scanning Electron Microscopy, and Electron Dispersive Spectroscopy

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

Results

Grain weathering features in modern CGCs

SEM revealed nine surficial and penetrative grain features that probably developed by biologically-mediated weathering (Fig. 2; Supplemental A). Surficial rounded elongate tracks (type 1) are the commonest feature (Figs 2 a & b); these exhibit elongate surface troughs with rounded sides and edges, usually on the order of 5μm wide, and of variable lengths. The troughs are concave up to ~300 nm depth and track along the grain surface rather than penetrating. Rounded elongate tracks are often associated with residue infill (Fig. 2 a, b). Bowl features (type 2; Fig. 2 c) are a series of concave surficial ~1-2μm wide bowl-shaped depressions, no deeper than ~200 nm, with rounded edges. These often appear to connect as linear structures (Fig. 2 c) across the grain surface. Borings (type 3; Fig. 2 d) penetrate grains up to ~10μm depth. These features are both straight and curved, forming perpendicularly to the grain surface (Fig. 2 d). These have rounded edges and some residue infill (Fig. 2 d). Wedge elongate tracks (type 4; Fig. 2 e) are linear surface features similar to rounded elongate tracks, but they instead have angular edges and a ‘wedge’ shaped tip. These features are sometimes associated with residue infill (Fig 2. e). Pitting features (type 5) are commonly associated with the attachment point of bryophyte rhizoids (Fig 2. f) and show surface etchings associated with crystallographic orientations. Asymmetric holes (type 6) (Figs 2 g-h) are commonly found in groups; they are often associated with other features (e.g., wedge shaped tracks; Fig. 2 e) and fungal hyphae (Figs 2 g & h). Holes are ~2 μm in diameter and are asymmetrical; there are a series of smaller holes within a larger depression (e.g., Fig. 2 g). Holes have smooth, curved edges. Some have residue infill (Fig. 2 e), and some are associated with extra-polymeric substances (EPS) from local fungal hyphae (Fig. 2 h). Study of thin sections reveals networks of internal dichotomous tunnels (type 7) (Figs 2 I & j). The tunnels appear to be of two types; irregular (Fig. 2 i) which develop singular tunnels of variable widths (although there appears to be some connections between tunnels; Fig. 2 i), have infill, and a wedge-shaped tip; and regular (Fig. 2 j), which are a dichotomous network, have constant widths, no infill, and penetrate grains up to 50 µm from a single surficial penetration point. Tramlines (type 8; Fig. 2 k) are composed of two parallel marks on the grain surface and are associated with the surficial attachment points of fungal hyphae. Cut networks (type 9; Figs 2 l & m) are a linear arrangement of curved depressions. Individual cuts are between 4 -10 µm wide and form elongate networks up to 60 µm in length. They are often associated with fungal hyphae (Fig. 2 m), and some have residue infill (Fig. 2 l).

Grain weathering features in fossil material

Rhynie chert

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

Llansteffan palaeosols

We have also identified numerous grain features in the Llansteffan palaeosols (Figs 3 e-j) which are similar to BWFs observed in modern CGCs. Grains are dominated by quartz, plagioclase, calcite, and clays. Large (~5-10 µm) and small (<3 µm) surficial asymmetric holes are present (Figs 3 e, f, h, i), which are often associated with elongate surface tracks (Figs 3 e & f). Elongate tracks also exist independently, sometimes as long as 80 µm and develop crossing networks (Fig. 3 g). Some features also have a fine-grained residue infill (e.g., Figs 3 f & i). There are also parallel tramlines, reminiscent of tramlines on modern grains (e.g., Figs 2 k & 3 j).

Chemistry of residues

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

Modern CGC grain residue composition

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

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

Llansteffan palaeosol grains residue composition

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

Discussion

Are the grain features biologically-mediated?

Modern CGC grain weathering features

We have identified numerous surficial and internal features on modern CGC soil grains (e.g., Fig. 2) that we propose are biologically-mediated in origin. Supportive of this are features such as smooth edges, constant diameters, and rounded ends (e.g., Figs 2 a, b, d, g, h) which are suggestive of a biological origin (Jongmans et al. 1997; Hoffland et al. 2002), whereas mechanical structural alteration (e.g., cracks) have sharp, non-rounded edges (e.g., Fig. 2 j). In addition, if the features were the product of chemical weathering (i.e., the action of hydrolysis-like dissolution reactions), they would have regularly shaped and oriented etch-pits because chemical dissolution occurs preferentially along specific crystallographic plains and boundaries (Landeweert et al. 2001); our features, bar rhizoid pitting (type 5), do not show these structures.

Surficial weathering features

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

We propose that the surficial BWFs identified here represent different stages of the surficial weathering process (Fig. 5 a). Firstly, initial hypha-grain attachment (stage 1) develops a set of parallel weathered tramlines (type 8) (e.g., Fig. 2 k) marking the outer width of the hyphae, and exudates produced by the hypha bio-weather of the grain surface. After the hypha is established on the grain surface for a period of time, in-situ bio-weathering results in concave depressions that mark the shape and size of the hypha, or elongate tracks, and the eventual development of a weathered residue (Figs 5 a & 2 a, b, e). Once the hypha dies, is removed or moves on, these features are left on the grain surface as a bio-marker of previous fungal hypha colonization. The stage at which the hypha is capable of weathering is most likely dependent on the time of colonization, the energy available to promote weathering by any mutualistic symbiotic partnership, and the chemical composition/hardness of the grain. Thus, we are confident that these are biological in origin.

Internal weathering features

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

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

Comparison of modern BWFs with fossil grain features

Because of the similar morphological traits (Figs 2 & 3) and chemical trends (irrespective of parent chemistry; Fig. 4) with BMFs in modern CGCs, we propose that fossil grain features are biologically-mediated. We discount a physical/abiotic origin; biologically-mediated tunnels and bio-penetration (e.g., Figs 3 c & d) are morphologically distinct from common physical features (e.g., quartz conchoidal fracture and cracks (Figs 2 j & 3 c), physically-derived inclusions (Fig. 3 d) lacking terminal crystals (e.g., Mcloughlin et al. 2010), and typical chemical weathering features following specific predefined chemical and crystallographic boundaries (e.g., denticulated margins; Velbel 1989). Further, it is unlikely that these weathering features have been produced by ‘modern’ organisms because of the method of collection (see methods). Consequently, we are confident the features were formed before diagenesis and are useful for comparative studies.

The Rhynie chert (Figs 3 a-d) has comparable features reminiscent of modern BWFs, including surficial bowl features (Figs 2 c &3 a), surficial tramlines and cuts (Figs 2 k-m & 3 b-c), and penetrating tunnels (Figs 2 i-j & 3 c-d). Bowl features (Fig. 2 c) are analogous to concave etchings created by bacteria and develop by the excretion of EPS promoting in-situ bio-dissolution (Thorseth et al. 1995). The circular ‘bowl’ shape could suggest development by coccoid-type bacteria, and that chains are created by numerous parallel colonies (Thorseth et al. 1995). We postulate that bacterial colonies were adhering to grain surfaces in the Rhynie chert, secreting EPS and promoting the development of distinctive bowl-shaped features (Thorseth et al. 1995) (Fig. 3 a). Filamentous cyanobacteria are known in the Rhynie chert in microbial mats on sediment surfaces (Strullu-Derrien 2018; Krings et al. 2007) and as coccoid cyanobacteria in the postulated cyanolichen Winfrenatia (Taylor et al. 1997). The shape and size of the bowls suggests they could have been formed by spherical coccoid photobionts from cyanolichens (e.g., Taylor et al. 1997), and indicate that this grain may have been part of a lichen CGC-hosting substrate. It also seems likely that fungi, particularly of a symbiotic affinity, were interacting with mineral grains. Rhynie chert BWFs are analogous to tramlines (type 8) and cuts (type 9; Fig. 3 b) of modern CGC BWFs (Figs 2 k & l). Cut (type 9) features in the Rhynie chert are both angular and round (Fig. 3 b), possibly analogous to hypha-derived wedge elongate tracks (type 4) in modern CGCs (Fig. 2 e). Based on our assumptions of the attachment and weathering process (e.g., Fig. 5), this could indicate that both non-symbiotic and symbiotic fungi interacted with grains in the Rhynie chert. There is evidence of free-living saprotrophic zoosporic fungi in the Rhynie chert ecosystem which were likely adaptations during patchy resource availability (Strullu-Derrien et al. 2017). These organisms could be responsible for surficial weathering features. The shape and size of possible filamentous penetration (Figs 3 c & d) and the comparative morphology to modern features (e.g., Figs 3 e, i, j) indicates they may be from mutualistic fungal hypha interactions which would have the energy requirements for internal penetration (Harrison 2005). There are numerous examples of mutualism (mycorrhizal fungi) with Rhynie chert plants; in Horneophyton lignieri (Strullu-Derrien et al. 2014), Aglaophyton major (Remy et al. 1994), and possibly in Nothia aphylla (Krings et al. 2007). These observations indicate that mycorrhizal-driven mineral weathering was occurring in the Rhynie chert system.

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

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

Fe-rich nodules and bio-precipitation

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

Interestingly, there is evidence of bio-precipitation from lichen relationships; these include iron oxides/hydroxides and forsterite (Gorbushina et al. 2001) bio-precipitation from organic acids secreted by lichen mycobionts (Adamo & Violante 2000), and Fe hydroxide and clay-rich coatings (e.g., Arocena et al. 2003) in biogenic rock varnishes caused by lichenized cyanobacterium (Krumbein & Jens 1981). Whether this was caused by plant symbiotic fungi or lichenized fungi is still unclear, however comparison with modern processes could provide an indication. This provides new evidence of fungal interactions in the upper Silurian Llansteffan palaeosols, an extension of current knowledge of biomarkers (e.g., Gorbushina et al. 2004; Gadd 2007), and that CGC-like organisms were not only in existence but were responsible for biologically-mediated weathering processes.

BWF residue, clay, and early Palaeozoic soils

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

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

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

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

As well as smectite-rich vertisol development, there is a general increase in the proportion of mudstones in the terrestrial sedimentological record through the early Palaeozoic (e.g., Gibling & Davies 2012; McMahon & Davies 2018; Davies et al. 2017), presumed to be due to expanding primitive land biotas since the late Proterozoic/early Cambrian enhancing the production of pedogenic clay minerals (e.g., contrasting views in Kennedy et al. 2006 and Tosca et al. 2010). Results here and in Mitchell et al. (2016) indicate that biologically-mediated weathering of minerals and subsequent biogenic smectite development by primitive CGC organisms is a likely driver of this change. In addition, the stabilization of land surfaces by the interactions of early terrestrial organisms with soil grains (e.g., entwining by rhizoids and symbionts; Mitchell et al. 2016) and exudates (e.g., soil aggregation; Galloway et al. 2017) will have contributed to the evolution of extensive muddy floodplains and a change in fluvial system architecture (e.g., Davies & Gibling 2010). This illustrates the profound affect that evolving early Palaeozoic plant-dominated biospheres had on landscapes.

3. Conclusions

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

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Figure captions

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

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

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

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

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

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

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

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