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Characterization of kerogenous films and taphonomic modes of the Sirius Passet Lagerstätte, Greenland

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ABSTRACT
The Sirius Passet Lagerstätte (northern Greenland) is an exceptionally well-preserved early Cambrian faunal community containing a diverse array of stem-group euarthropods, lobopodians, worms, sponges, and the iconic Halkieria. Material collected in situ during recent expeditions has yielded a range of fossil specimens that are preserved as two-dimensional, reflective films. Here we document in detail, for the first time from the Sirius Passet, compressed, kerogenous fossil films characteristic of Burgess Shale-type (BST) preservation. The carbon structure and the taphonomic mode associated with these films were investigated using Raman spectroscopy. Our analysis confirms that these reflective films are kerogenous, showing a higher D1 (disordered) band and G (graphite) band intensity and area, indicating a greater concentration of disordered carbon compared to the surrounding matrix. The spectral characteristics of the fossils denote moderately ordered kerogenous matter, indicating that the transitional Buen Formation that hosts the Sirius Passet was thermally altered at a peak temperature of 409 ± 50 °C. Phyllosilicate minerals are associated with the films, but they are not anatomical or taxon-specific, suggesting that the higher thermal maturation of the kerogen in the Sirius Passet produced a uniform distribution of minerals. This is unlike the kerogenous films in the Burgess Shale Lagerstätte (British Columbia, Canada) that have been metamorphosed at a lower temperature of 335 ± 50 °C and typically show an anatomically specific phyllosilicate distribution. Preservation as kerogenous films, however, is not continuous, and the presence of other taphonomic modes not indicative of BST preservation suggests that the Sirius Passet represents a unique and complex deposit.

INTRODUCTION
The extraordinary snapshot of communities preserved in Konservat-Lagerstätten has significantly influenced our understanding of the early evolution of animal life in the Cambrian period. Taphonomic investigations have identified several preservational modes in Lagerstätten (Briggs, 2003). In the Cambrian, the most celebrated deposits are those that exhibit Burgess Shale–type (BST) preservation (Gaines, 2014), defined as the exceptional preservation of non-mineralizing organisms as two-dimensional carbonaceous compressions (Butterfield, 1995). This preservational style occurs in fine-grained marine sediments and is characteristic of a number of early Paleozoic (Gaines, 2014) and Proterozoic deposits (Anderson et al., 2011). Despite nearly three decades of intensive research into the topic, the taphonomic processes that led to BST preservation is still a matter of debate. Several hypotheses have been proposed, ranging from the simple absence of bioturbation and dysoxic or anoxic conditions, to the role of clays in inhibiting autolytic decay, early aluminosilicate diagenesis, pyrite mineralization involving sulfate- and iron-reducing bacteria, Fe²⁺ ions adsorbing on organic tissues to delay degradation, and the sealing of sediments by pervasive carbonate cements (see the review by Gaines, 2014).

However, the presence of clay minerals (or rather their greenschist facies metamorphic equivalents, such as illite and chlorite) is likely a result of diageneis/metamorphism (Powell, 2003; Butterfield et al., 2007; Page et al., 2008), and the association of iron-bearing minerals in unweathered fossil material may be too sporadic to have been considered a key factor in BST preservation (Gaines, 2014), although resulting from related processes and microbial decomposition (Berner, 1984; Schiffbauer et al., 2014).

The Sirius Passet in Greenland, is one of the most important and potentially the oldest Cambrian Lagerstätten (Budd, 2011). The majority of documented fossils from Sirius Passet were collected as talus material, and preservation is variable (Peel and Ineson, 2011). Trilobites are preserved as complete molds showing a veneer of authigenic silica (Strang et al., 2016a), whereas other less-mineralized taxa are preserved in slight relief, replicated by silica and clay minerals, with some specimens displaying three-dimensional phosphatized digestive tracts, and a single taxon (Campanamuta mantonae Budd, 2011) preserving three-dimensional muscle fibers (Budd, 2011; Peel, 2016). Remains of organic matter, on the other hand, were thought to have been lost, if originally present at all, as a result of the relatively high grade of metamorphism (greenschist facies) that the Sirius Passet has experienced (Budd, 2011). Some fossils however, collected both in situ and as talus during more recent expeditions (2009 and 2011), are seemingly preserved as thin, reflective films and resemble, at least superficially, fossil films seen in BST deposits (Vinther et al., 2011). The composition and mode of preservation of these films though have been given no attention. Based on 14 specimens, we have employed Raman spectroscopy and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) elemental mapping to investigate the composition and the taphonomic modes of fossils from the Sirius Passet Lagerstätte preserved as two-dimensional reflective films. Raman spectra from three Burgess Shale (British Columbia, Canada) specimens (all from the Walcott Quarry Member) were also analyzed for comparison.

RESULTS
In hand specimen, organisms preserved as films from the Sirius Passet are notoriously difficult to recognize, and are best observed underwater with high-angle reflected white light, where they appear as reflective films and stand out conspicuously from the non-reflective sedimentary matrix (Fig. 1). Unlike the Burgess Shale (Butterfield et al., 2007), there appears to be no further distinction of individual morphological features in terms of reflectivity; rather, entire fossils are uniformly reflective and polarized light appears to have little or no effect. The majority of fossil films are covered to a varying degree by iron oxide and oxyhydroxide coatings (Fig. 1).

Raman analysis demonstrates that there was a degree of homogeneity across the host rock and the 14 Sirius Passet fossil specimens, with all spectra exhibiting a strong carbon signal (with the exception of some point spectra directed at the iron oxide and oxyhydroxide coatings). The majority of point spectra also exhibit vibrational modes at 200 cm⁻¹ and 464 cm⁻¹ attributed to quartz, and a vibrational mode at 262 cm⁻¹ attributed to...
muscovite, suggesting that all fossils analyzed were closely associated with phyllosilicates. The vibrations of quartz and muscovite, however, were not fossil-specific and appear to be consistently present across both the fossil films and the surrounding matrix. Iron oxides are commonly observed here in association with kerogenous films (Fig. 1). The mineralogy of the iron coatings is variable. The coatings contained a range of vibrational modes, although all were indicative of iron oxides and/or oxyhydroxides. For example, the coating on Isoxys (Fig. 1I) exhibits diagnostic vibrational modes at 220 cm⁻¹, 296 cm⁻¹, 410 cm⁻¹ and 610 cm⁻¹ indicating hematite (α-Fe₂O₃) while the veneer on Siriocaris (Fig. 1E) exhibits hematite in part, but also vibrations at 299 cm⁻¹ and 385 cm⁻¹ diagnostic of goethite (α-FeOOH). The pervasive presence of iron oxides and/or oxyhydroxides most likely reflects modern oxidative weathering of the samples.

After baseline correction and deconvolution, carbonaceous material (CM) from the fossil films can be resolved into five bands, D1, G, D2, D3 and D4 (D—disordered, G—graphite; Figs. 2A–2C). All Raman spectra from the fossil films display D3 and D4 bands and have a well-developed D1 band that is typically more intense (mean intensity ratio of D and G bands, Iₓ/Iᵧ, of 1.07) than the G band, and with a larger area (mean Aₓ/Aᵧ ratio of 1.26) than the G band. The mean Rₓ/Aₓ ratio of the reflective films is 0.527 ± 0.0106 (Table DR1 in the GSA Data Repository¹). The CM in the sedimentary matrix can also be deconvoluted into five bands; however, the D3 band, which in amorphous CM emerges with increased disorder, is not identifiable in some matrix spectra (Table DR1). The D1 band is generally equal to the G band in intensity (mean Iₓ/Iᵧ ratio of 1.00); however, the D1 band generally exhibits a larger area (mean Aₓ/Aᵧ ratio of 1.18). The mean R² ratio of the reflective films is 0.513 ± 0.015. In sample DH074, where acquisition times and accumulations of spectra were kept constant, the CM in the fossil films displayed a higher mean D1 and G band intensity and area compared with the CM in the sedimentary matrix (Figs. 2D and 2E). Statistical tests show that there is a significant difference in the intensity and area of the D1 and G bands in the fossil films and the sedimentary matrix (both Mann-Whitney tests with a p value <0.05). Using Equation 2 in the Data Repository [Ty = −445° Rₓ + 641 (±50 °C); Bysaacs et al., 2002], the peak thermal paleotemperature calculated for the Sirius Passet deposit is 409 ± 50 °C. The kerogen in the Burgess Shale is less ordered than the Sirius Passet, with a higher mean Rₓ ratio of 0.686 ± 0.012, a higher mean Iₓ/Iᵧ ratio of 1.52, and a greater mean Aₓ/Aᵧ ratio of 3.20, all indicative of less-ordered material (Sforna et al., 2014). The peak thermal paleotemperature calculated for the Walcott Quarry Member of the Burgess Shale Lagerstätte is 335 ± 50 °C (see the Data Repository).

Raman spectra results were supported by elemental mapping analyses of taxa using energy-dispersive X-ray spectroscopy (see the Data Repository). In many of the analyzed specimens, carbon of the fossil films is indistinguishable from the matrix, which is perhaps not surprising given the host rock also contains CM. Indeed, many elements (e.g., Si, Al, K) in the fossils were also indistinguishable from the surrounding matrix, supporting the relative uniform mineralogy suggested by Raman spectra. Some specimens, for example Isoxys (Fig. II; Fig. DR4A), and an element from an undescribed priapulid (Fig. 1H; Fig. DR4B), do show

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¹GSA Data Repository item 2018107, materials and methods, Tables DR1–DR3, and Figures DR1–DR11, is available online at http://www.geosociety.org /datarepository/2018/ or on request from editing@geosociety.org.
subtle elevated levels of carbon (Fig. DR4) in comparison to the surrounding matrix. Some films also show an increase in silica as well as carbon, although this is not so obvious for all specimens (Fig. DR4). Elemental mapping of a coating on a specimen of *Siriocaris* and *Isoxys* (Fig. DR4) shows elevated levels of iron and sulfur that most likely indicate the presence of pyrite or secondary jarosite, now largely altered to Fe-bearing oxides.

**DISCUSSION**

The preservation of fossils as carbonaceous remains in Cambrian Lagerstätten has been of considerable interest since organic remains were first liberated from the Burgess Shale nearly 30 years ago (Butterfield, 1990). Mechanisms that delay the degradation or destruction of organisms are viewed as one of the most important taphonomic factors that lead to the exquisite preservation seen in Lagerstätten (Gaines, 2014). However, perhaps of equal importance yet less frequently explored, is the subsequent metamorphic history and peak thermal paleotemperatures experienced by Lagerstätten. Organic matter is structurally susceptible to heating during burial and metamorphism, and an increase in temperature results in the irreversible maturation of organic matter into kerogens and eventually graphite in a process that potentially impairs the morphology of organic remains (Beyssac et al., 2002; Schopf et al., 2005; Schibbauer et al., 2012). It has been suggested that the Sirius Passet experienced a metamorphic grade high enough to eradicate all signs of carbonaceous remains (Budd, 2011), but this has not been previously tested. Our results indicate that there is CM in the Sirius Passet and that the primary mode of preservation of these films was as carbonaceous compressions. The large majority of spectra acquired display a well-developed D1 band (full width at half maximum [FWHM] < 70 cm$^{-1}$) that is slightly more intense than the G band. These spectral characteristics are indicative of moderately ordered CM (Sforna et al., 2014) bearing a metamorphic signature corresponding to a peak temperature of ~400 °C. The low RD3 and RD4 ratios (0.015 and 0.02, respectively) calculated from the deposit are also consistent with a relatively high peak temperature (Sforna et al., 2014, Fig. DR3).

This carbonaceous signal is not necessarily diagnostic for the organic material in the fossil films, as the surrounding sedimentary matrix also contains CM. Although the spectra from the matrix generally show lower values of $I_p/I_G$, $A_G/A_D$, and $R_G$, overall the structure and crystallinity of the CM in the matrix and fossil films is very similar (Figs. DR1 and DR2). This is not surprising, given that the structural order of CM at this metamorphic grade is predominantly controlled by temperature (Beyssac et al., 2002) and that the carbon in the fossil films and the sedimentary matrix underwent the same thermal alteration. However, in spite of this overall degree of structural homogeneity, some features of the collected spectra can give an indication concerning a differential abundance of CM between the fossil films and the surrounding matrix. The Sirius Passet fossil films consistently show a greater D1 and G band intensity and area in relation to the surrounding sedimentary matrix (Figs. 2D and 2E), suggesting a greater concentration of CM within the fossil.

The Sirius Passet has been considered to lie within the spectrum of BST preservation (Budd, 2011), although the lack of previously documented kerogenous remains and the presence of muscle fibers preserved in three dimensions has resulted in Gaines (2014) tentatively excluding the deposit from known BST deposits, awaiting further study. The presence of two-dimensional kerogenous films in the Sirius Passet does satisfy the umbrella definition of BST preservation (Butterfield, 1995), but there are distinct taphonomic differences. For example, the vast majority of Burgess Shale fossils preserve no significant third dimension, indicating a complete loss of cellular tissues (Butterfield et al., 2007). This contrasts sharply with the Sirius Passet where, to date, the majority of documented organisms are preserved in three dimensions (Budd, 2011). Fossils of the Burgess Shale also show tissue-specific variation in the elemental composition of phyllosilicate templates (Orr et al., 1998; Page et al., 2008). This anatomically specific phyllosilicate distribution was interpreted as reflecting differences in maturation pathways between morphologically specific kerogen types (Butterfield et al., 2007; Page et al., 2008). The reflective kerogenous films analyzed here from the Sirius Passet, on the other hand, show no specific tissue-related mineral variation and are instead homogeneous (Fig. 1). The distribution of phyllosilicates and CM in fossils of the Burgess Shale creates a contrast that assists with the differentiation of morphological features within the fossil organism. In the case of the Sirius Passet, exposure to temperatures of ~400 °C could have led to complete overprinting of kerogen maturation pathways; such that phyllosilicate minerals that arose during early diagenesis in an anatomically specific fashion were homogenized during progressive metamorphism producing a uniform phyllosilicate distribution and carbonaceous film, impeding the discrimination of specific anatomical features. Muscovite is consistently associated with carbonaceous films (also present in the host rock) in the Sirius Passet and it is a typical end-member mineral in a trend where clay minerals are progressively replaced by chlorite and eventually by the more thermally stable muscovite (Powell, 2003; Butterfield et al., 2007). As such, relative to the Burgess Shale, the reflective films in the Sirius Passet provide an example of organisms preserved as carbonaceous films that have been exposed to progressively higher temperatures during metamorphism.

Preservation as kerogenous films, however, is discontinuous and the presence of different preservational modes in the Sirius Passet presumably, to some degree, reflects differences in the general composition of the organisms’ original tissues and/or their variable susceptibility to decay. For example, the silica death mask has only been identified in trilobites (Strang et al., 2016a), phosphatization may be restricted to digestive tracts (Peel, 2016; Strang et al., 2016b), replication by silica and phyllosilicate minerals with slight topographic relief appears to be predominantly observed in large euarthropods and lobopods (e.g., Budd, 2011), three-dimensional muscle fibers have only been documented from a single taxon (Budd, 2011), and kerogenization has only been observed in particular faunal elements (e.g., no large euarthropods have been observed preserved as reflective films; Fig. 1). The presence of compressed kerogenized films and phosphatized digestive tracts is similar to other BST deposits (Gaines, 2014). However, the combination of these films and the presence of organisms preserved in three dimensions exhibiting silica veneers and muscle fibers are unique to Cambrian Lagerstätten. Three-dimensional muscles, for example, have only been described from specimens of *Myoscolex* from the Emu Bay Shale in South Australia, where they are preserved by phosphate (Paterson et al. 2016). It is possible that the muscle fibers in *Campananumata* were also primarily preserved by phosphate and secondarily replaced by silica during diagenesis. This is also evident in the gut of *Campananumata*, where phosphate and silica are in close association (Strang et al., 2016b), with the former possibly representing residual material. Yet, the taphonomic processes operating in the Emu Bay Shale are not considered to be BST, as kerogenized fossil films are yet to be documented (Paterson et al., 2016). Thin sheets of phyllosilicate minerals have also been mentioned as potentially replacing organic matter in euarthropod taxa (Budd, 2011), although this remains to be documented in detail. The topographic relief of the fossils and their close association with abundant trace fossils (Peel and Ineson, 2011) is also unlike typical BST deposits. This combination of preservational styles, displaying similarities to BST and non-BST deposits, highlights the complex set of taphonomic modes present in the Sirius Passet.

**CONCLUSIONS**

Reflective films in the Sirius Passet Lagerstätte are preserved as kerogenous compressions. They display spectral characteristics that are indicative of moderately ordered kerogenous matter that was heated to a peak temperature of 409 ± 50 °C. The carbon in the Burgess Shale Lagerstätte is less ordered and was thermally matured at a lower peak temperature of
335 ± 50 °C. Phyllosilicate minerals are associated with the films, but are not taxon- or anatomically specific, suggesting that the higher thermal maturation of the kerogen in the Sirius Passet produced a uniform distribution of minerals. While the preservation of organisms as kerogenous films is reminiscent of BST preservation, the Sirius Passet exhibits a range of taphonomic modes, including silica veneers, large organisms with slight topographic relief, and three-dimensional muscle fibers that are not typical of BST preservation.

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