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Evidence for microbially mediated silver enrichment in a middle Cambrian Burgess Shale-type deposit, Mackenzie Mountains, northwestern Canada

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Abstract: The Selwyn basin and Mackenzie platform of northwestern Canada house an array of mineral deposits and prospects that are rich in silver, including Neoproterozoic red-bed or Kupferschiefer-type Cu and lower Paleozoic sedimentary exhalative (SEDEX) and Zn-Pb deposits. Within this overall metallogenic setting, the middle Cambrian (Drumian) Rockslide Formation was deposited under a largely oxic water column on the platform-to-basin slope along the eastern side of the Selwyn basin. The formation includes an interval termed the Ravens Throat River Lagerstätte which is a localized Burgess Shale-type calcareous mudstone about 2 m thick that preserves soft-bodied fossils. The mudstone contains comparatively large amounts of organic carbon preserved as thin carbonaceous laminae and discontinuous seams, representing benthic microbial mats, the remains of cyanobacteria and algae that were living in the water column, fecal pellets, large coprolites, and degraded animal tissues. The upper part of the Rockslide Formation, including the fossiliferous interval, contains elevated concentrations of Ag, up to 0.47 ppm. Some of the Ag in the mudstone occurs as aggregates of elemental particles ~10 µm in size preferentially on the carbonaceous material comprising the coprolites. This localized enrichment suggests bioaccumulation of Ag nanoparticles or Ag⁺ from the water column by microorganisms on the coprolites or degrading organic matter in them. The source of the Ag may have been from penecontemporaneous SEDEX metallogeny or from broadly related subsurface fluids in the Selwyn Basin that enriched the overlying seawater.

Key words: noble metals, environmental microbiology, geochemistry, taphonomy, microbial ecology

Introduction

Sedimentary strata host a variety of mineral deposits, and shales in particular play a key role in certain kinds of mineralization, especially by copper, zinc, lead and silver (Hitzman et al. 2010; Emsbo et al. 2016). One of the most famous mineral deposits hosted in shales is the Kupferschiefer in central Europe, which in addition to Cu also contains large amounts of Ag (e.g., Oszczepalski et al. 2019). Shales also play a major role in the preservation of hydrothermal ore deposits, especially sedimentary exhalative (SEDEX) deposits or, the more recently recognized clastic dominant (CD) type (Leach et al. 2010; Magnall et al. 2020). CD-type deposits are moderate to high grade Zn-Pb-

Ag ores typically in pyritic and carbonaceous shales (Goodfellow and Lydon 2007; Emsbo et al. 2016).

Burgess Shale-type (BST) Lagerstätten are early Paleozoic mudstones containing soft-tissue preservation, exemplified by the Burgess Shale of southeastern British Columbia (e.g., Butterfield 1995; Muscente et al. 2017). These deposits may be enriched in metalliferous minerals formed during taphonomic and early diagenetic processes. Minerals that may be associated with kerogenized BST fossils include pyrite, apatite, aluminosilicates, monazite, barite, calcite and dolomite (e.g., Broce and Schiffbauer 2017). In addition, Cu associated with chalcopyrite has been found in the arthropod *Marrella* from the Burgess Shale and interpreted to be the remnant of hemocyanin blood (Pushie et al. 2014). While several BST deposits occur in mineral districts (e.g., Steiner et al. 2001), there have been no reports of Ag enrichment.

Silver is a natural soluble component in modern seawater and marine sediments, and Ag concentrations in muds in modern oceans usually increase with water depth, until ceasing at depths >2500 m. Modern sands, normal shales, and oxic marine sediments have average concentrations of 0.08 ppm to 0.1 ppm, while black shales and anoxic sediments are slightly enriched between 0.13 ppm and 1.54 ppm (McKay and Pedersen 2008). Elevated Ag concentrations are not restricted to anoxic sediments, however, as suboxic sediments from the mid to lower slope of the Pacific continental margin of Canada have also shown elevated Ag concentrations between 0.22 ppm and 0.36 ppm (McKay and Pedersen 2008). This distribution of Ag in modern sediments implies that Ag in the oceans may be linked to biogenic particle flux, especially diatoms (e.g., McKay and Pedersen 2008; Wagner et al. 2013). These results are mostly based on studies conducted on the Eastern Pacific margin, where dissolved oxygen is lower, and sedimentary Ag is better conserved than in the Southern Ocean (Wagner et al. 2013). In any case, the Ag geochemical cycling in marine environments remains poorly understood (Wagner et al. 2013).

A multitude of mineral deposits and prospects, ranging in age from the Neoproterozoic to Mesozoic, is found in the Mackenzie Mountains of northwestern Canada (Ootes et al. 2013). Silver occurs in a variety of these, one of the more important ones being the Prairie Creek carbonate-hosted Mississippi Valley-type Zn-Pb deposit in lower and middle Paleozoic dolostones (Paradis 2007; Stavinga et al. 2017). In addition, there are several Neoproterozoic to upper Cambrian SEDEX deposits that preserve elevated Ag in the Selwyn Basin, a Paleozoic marine embayment of the ancestral Pacific Ocean, Panthalassa, into the shallow-water Mackenzie Platform. The Anvil District, of Cambrian age, is the most prominent of these deposits (Godwin et al. 1982; Pigage 2004).

The middle Cambrian Rockslide Formation was deposited on the eastern side of the Selwyn Basin, and at one locality, the Ravens Throat River Lagerstätte, there is extraordinary preservation of soft-bodied fossils (Kimmig and Pratt 2015, 2016). Here, we report the discovery of small particles of native Ag on organic carbon films, making it the first record of Ag enrichment in BST deposits. We characterize the mineralogy and trace-element geochemistry of the host strata and explore the possible biogeochemical processes leading to silver enrichment.

Geologic setting

The Rockslide Formation of the Mackenzie Mountains is a middle Cambrian (*Plagiura-Poliella* Biozone to late *Bolaspidella* or *Lejopyge laevigata* Biozone; Wuliuan–Drumian), deeper water succession of shale, lime mudstone, calcareous mudstone, and

dolomitic limestone, locally with debris flows of lime mudstone clasts with variable amounts of quartz sand. It was deposited on the slope along the eastern flank of the Selwyn Basin, the off-shelf facies of the Mackenzie Platform, over a geographic area several hundred kilometres wide (Gabrielse et al. 1973; Fritz 1979; Pratt 1989). The lower part of the Rockslide Formation is correlative with intra-platform basinal shales of the Mount Cap Formation located along the eastern side of the Mackenzie Mountains and in the Mackenzie River valley (Dixon and Stasiuk 1998; MacNaughton et al. 2013; Handkamer 2020). These strata yield rare examples of BST preservation (Butterfield and Nicholas 1996). To the north in the Misty Creek embayment, the Rockslide Formation grades into a thick succession of turbiditic deposits belonging to the Hess River Formation (Cecile 1982; Chevrier and Turner 2013). Towards the west the Rockslide Formation is overlain by deeper water shaly limestones of the Rabbitkettle Formation (Pratt 1992; Gordey and Anderson 1993).

The Ravens Throat River Lagerstätte (Fig.1) is the only known outcrop in the Rockslide Formation that contains BST fossils (Kimmig and Pratt 2015). It is located near the headwaters of the Ravens Throat River (63°10'N, 127° 55'W), about 50 km west of the type section. The Rockslide Formation there is 175 m thick. It is underlain by Ediacaran to lower Cambrian sandstones of the Backbone Ranges Formation and thin-bedded limestones of the Sekwi Formation, and is overlain by sandy dolomites belonging to the Avalanche Formation.

At the Ravens Throat River locality, the lower half of the Rockslide Formation onlaps a synsedimentary listric fault scarp cutting the Backbone Ranges Formation. A change in dip of the lower Rockslide Formation at 19 m above base shows that the fault experienced a second phase of movement (Kimmig and Pratt 2015). The dip of succeeding strata is uniform, indicating that rotation along the fault had ceased. The fossiliferous beds consist of two units of brownish green-weathering, planar-laminated calcareous mudstone, ~2 m thick at 135 m and ~1 m thick at 164 m above base of the formation (Fig. 2); the lower one contains most of the fossils of soft-bodied animals, along with hyolithid mollusc shells, polymeroid trilobites, and agnostoid arthropods, as well as large coprolites (Kimmig and Pratt 2015, 2018). Bioturbation is common although not apparent on weathered or split surfaces (Pratt and Kimmig 2019). The host rock is composed of quartz, illite, chlorite, calcite, and dolomite (Kimmig and Pratt 2016). Pyrite cubes are common (Fig. 3a, b).

Materials and methods

Kimmig and Pratt (2018) interpreted black organic patches, greenish-brown when weathered, in the lower fossiliferous interval of the Ravens Throat River Lagerstätte as compacted coprolites (Fig. 4). They are circular in outline and range from 8 mm to 37 mm in diameter, the majority being between 10 mm and 20 mm across (Fig. 4a, b). The patches have the shape of a disc 0.5–1 mm thick, representing a compressed agglomeration of unidentifiable carbonaceous material, fragments of worm cuticle, arthropod valves, carbonaceous flakes, and mud. The flakes are more or less uniform in size in each patch, but vary from patch to patch from ~1 to 5 mm in size and up to 0.5 mm thick. There are also isolated flakes scattered on many bed surfaces. Many of the patches have hyoliths, polymeroid trilobites, and agnostoid arthropods located on them. These associated fossils are preserved articulated and appear to be in feeding position (Kimmig and Pratt 2018).

About 150 coprolite specimens were collected during four field campaigns (1983, 1998, 2004, and 2012) mostly from the scree slope, with a few via excavation

of the cliff exposure. Additionally, 64 lithological samples of fossiliferous calcareous mudstone, non-fossiliferous lime-mudstone and dolomitic siltstone from the Ravens Throat River locality were collected from the outcrop and six samples were taken from fossil bearing specimens collected off the scree slope in 2012. Seventy polished thin sections representing all lithologies, as well as each layer of the lower fossil bed, were prepared. Thin sections and specimens for mineral analysis were carbon-coated and analyzed with a JEOL JXA-8600 Superprobe. For trace-element analysis unweathered samples were chosen from each bed of the lower fossiliferous horizon, as well as representative samples from the other lithological units. Samples of ~1x2 cm were cut from the same hand samples that were used for thin section preparation, powdered to ~10 µm particle size using a Siebtechnik disc mill, stored in 50 ml centrifuge tubes, and analyzed at the commercial laboratories of the Saskatchewan Research Council, Saskatoon, using a PerkinElmer SCIEX Elan DRC II quadrupole inductively coupled plasma mass spectrometer (ICP-MS), and either the PerkinElmer Optima 4300DV or Optima 5300DV inductively coupled plasma optical emission spectroscopy (ICP-OES) instruments for Cr and Sr concentrations, with an external precision generally better than ±10% (2σ). Standards used for the analyses were ASR 109 and DCB01 for ICP-MS and ICP-OES analyses. An aliquot of powder was digested in a Teflon tube hot-block digestion system using a mixture of ultra-pure concentrated acids: HF, HNO₃, HClO₄. The residue was dried down and re-dissolved in dilute HNO₃ prior to analysis by ICP-MS and ICP-OES.

Enrichment factors (EF) were determined by normalizing selected trace elements to Al, which represents a proxy for the detrital fraction, and comparing those ratios to 'average shale'. The EF is equal to $(\text{Element}/\text{Al})_{\text{sample}}/(\text{Element}/\text{Al})_{\text{shale}}$, where the ratio in the numerator is that for the shale in question, and the ratio in the denominator is that for a 'typical' shale (Tribovillard et al. 2006; using data from Turekian & Wedepohl 1961; Wedepohl 1971).

Biomarker analysis was conducted at the University of Göttingen Organic Geochemistry Lab using catalytic hydropyrolysis (for detailed methods see Blumenberg et al. 2015).

Coprolite specimens are housed in the Royal Tyrrell Museum of Palaeontology, Drumheller, Alberta (TMP prefix).

Results

The fossiliferous calcareous mudstones beds contain up to 0.43 ppm Ag, which is about four times higher than the Ag content in the underlying unfossiliferous lime mudstone (0.08–0.14 ppm; Table 1). The overlying dolomitic siltstone is also enriched with an average content of 0.47 ppm. No native Ag or Ag-bearing minerals were seen in polished thin sections.

The trace-element data for the fossil beds and the other lithofacies (Table 1), in the context of the EF to account for the detrital bias (Table 2; Kimmig and Pratt 2016), show variable enrichment of most elements, but none of the major metals (Cu, Pb and Zn) which usually co-occur with Ag, are enriched, or show a correlation with Ag. By contrast, the calcareous mudstone overall is variably depleted in Cu (avg. EF = 0.33), Pb (avg. EF = 0.17) and Zn (avg. EF = 0.76), compared to 'typical' shale, whereas Ag is enriched (avg. EF = 6.17).

The thirteen coprolite specimens selected for microprobe analysis contained no worm cuticle or arthropod valves. Five specimens were observed that preserved native

Ag as aggregates or clusters of particles on the carbonaceous surfaces (Fig. 4c, d). Individual particles are $\sim 10\ \mu\text{m}$ across, and aggregates range up to $\sim 300\ \mu\text{m}$ in size. Their distribution on the coprolite shows no pattern. Samples from both the outcrop (Fig. 4c) and the scree slope (Fig. 4d) contain these Ag particles. Several specimens of hyoliths, bivalved arthropods, trilobites, and macrophytic algae belonging to *Margaretia dorus* were also analyzed with the microprobe, but none preserved visible Ag. The Ag is not associated with pyrite. The pyrite is mostly euhedral, suggesting it originated in later diagenetic stages (Fishman et al. 2019).

Biomarker analysis revealed no surviving biomarkers or aromatic hydrocarbons that would discriminate a contribution from animals, acritarchs, eukaryotic algae, or other microbial sources.

Discussion

Ag enrichment in the calcareous mudstones of the Ravens Throat River Lagerstätte is on average 6x higher than ‘average shale’ values (0.07 ppm, Wedepohl 1971), with a maximum recorded value of 0.43 ppm (Table 1, 2). Unfortunately, there are no published Ag values for any of the other Cambrian units in the Mackenzie Mountains for comparison, but there is some data looking more broadly at Cambrian shales in the Canadian Cordillera (Supplement Data Table 1) available through the Sedimentary Geochemistry and Paleoenvironments Project (Farrell et al. 2021). The data suggest many shales do not have any silver enrichments, including the BST-bearing Mural Formation in the southern Cordillera (Sperling et al. 2018). However, the Cambrian samples in ‘map unit Csh’ and the Road River Group in the Richardson trough have Ag values that range from 0.1 to 1.5 ppm and 0.1 to 3.2 ppm, respectively (Supplement Data Table 1), values higher than the Rockslide Formation samples (0.08 to 0.47 ppm, Table 1). In addition to these units, black shales worldwide have been recognized to preserve large amounts of Ag (e.g., Lipinski et al. 2003; Khanchuk et al. 2011), but there is overall little information of Ag in sediments outside of economically viable deposits.

Elevated Ag levels, however, have not been detected in sediments or fossils of other BST deposits. Nevertheless, syndepositional or syngenetic association of Ag with fossils and organic matter has been reported, albeit very rarely. Some late Permian fish up to about 10 cm in length are preserved as Ag in the German Kupferschiefer of northern Hessen (Deecke 1923; Wanderer 1932; Brandt 2012). In these specimens, elemental Ag preferentially replaced the soft tissue and scales and fins before substantial decay. By contrast, soft-bodied fossils in the Ravens Throat River Lagerstätte do not exhibit Ag mineralization, and it is only present on the carbonaceous matter comprising the coprolite patches. The Kupferschiefer is considered to have been deposited under anoxic bottom waters (Wedepohl 1994; Paul 2006). Whereas trace-element analysis, as well as the presence of extensive bioturbation, indicate that the fossiliferous calcareous mudstone of the Ravens Throat River Lagerstätte was deposited under an oxic to occasionally dysoxic water column (Kimmig and Pratt 2016, 2018; Pratt and Kimmig 2019). It has long been held that oxygen-limited conditions, at least in the sediment, are a requirement for soft-tissue preservation (e.g., Allison 1988; Sagemann et al. 1999; Babcock et al. 2001). Heterotrophic bacterial activity leads to bottom-water anoxia if surface productivity is high enough or mixing of the water column is limited, but this does not stop decay because the reaction changes to a slower anaerobic one (Allison 2001; Briggs 2003). Nonetheless, decay can cease, as evidenced by BST deposits, and preservation of biogenetic metals is possible, as has been

proposed for the Burgess Shale (Pushie et al. 2014). This shows that there is potential for further examples of preservation of biogenic matter other than organic tissues.

Some of the aggregates of small Ag particles bear a resemblance to pyrite framboids (e.g., Wilkin and Barnes 1997). This suggests the possibility that the Ag may be pseudomorphous after pyrite. Pyrite replacement by Ag, however, seems to be more likely in high temperature ore deposits (e.g., Simanenko et al. 2015; Grant et al. 2018), and the pyrite Ravens Throat River Lagerstätte is generally cubic, whereas the Ag is somewhat rounded in shape. The localization of the Ag particles on the coprolites and absence of an association with pyrite cubes are evidence that Ag precipitation took place relatively early while the organic matter was reactive, and is unrelated to pyrite formation.

Source of the silver

During the middle Cambrian the Ravens Throat River Lagerstätte was located near the Equator on a north-facing tropical platform-to-basin slope. If mid-latitude currents formed a large clockwise gyre in Panthalassa of the northern hemisphere, this could have generated upwelling along present-day western Laurentia (Servais et al. 2014), which would have led to free entry of oceanic waters into the Selwyn Basin. Thus, it is probable that some of the Ag in the Ravens Throat River Lagerstätte originated directly from oceanic seawater, although it is unclear how much of it might have originated from surface productivity (production of organic matter by phytoplankton). Microscopic organic particles in the water column may have incorporated Ag in one way or another. But, as the Ravens Throat River Lagerstätte was deposited under mainly oxic conditions, suggested by redox-sensitive trace elements, extensive bioturbation, and the presence of a relatively diverse benthic fauna (Kimmig and Pratt 2015, 2016, 2018; Pratt and Kimmig 2019), it is unlikely that all the Ag present in the sediment originated in this way, because Ag preservation is favored by suboxic to anoxic conditions (McKay and Pedersen 2008). Due to this there must have been other sources for the Ag, such as erosion of exposed Ag deposits or influx of Ag-bearing brines.

Of the known Ag-bearing ore deposits in the region, only the Zn-Pb-Ag SEDEX deposits of the Anvil District to the west in the Yukon, still in the Selwyn Basin, are similar in age to the Rockslide Formation (Pigage, 1991; Ootes et al. 2013). The Ag content in these deposits ranges from 36 to 84 g/t (Goodfellow 2007). The younger (Early Devonian) SEDEX deposit at Macmillan Pass also contains significant amounts of Ag, ranging from 38 to 80 g/t (Goodfellow 2007). However, it is unlikely that physical transport of sediments derived from erosion of ore bodies from an already formed deposit ~350-400 km away is the source of the Ag, because there is no evidence for uplift and erosion of the deposit during that time. Moreover, in contrast to both these deposits, the Ravens Throat River Lagerstätte is not enriched in Cu, Zn or Pb. While this could also suggest that the enrichment was independent of the fluids responsible for the Anvil District, it is possible that the Ag came from conduits under the Selwyn Basin and were carried by currents to the Ravens Throat River locality. Considering the long age span of these mineral deposits, there could have been considerable potential for Ag to enter the marine environment via metalliferous fluids moving up along basement faults.

Like the Kicking Horse Rim and the onlapping of the Burgess Shale against the Cathedral Escarpment, the Ravens Throat River Lagerstätte is associated with a syndepositional fault. Brine seeps have been implicated as a possible factor in BST

preservation, as brines greatly reduce the decay rates of organisms immersed in them (Powell et al. 2006; Parsons-Hubbard et al. 2008; P. Johnston et al. 2009; K. Johnston et al. 2009). Stacey et al. (2021) suggested that the brines that dolomitized the Cathedral Formation ascended through regional faults in the middle to possibly late Cambrian, although an alternative explanation is younger fault-related fluid flow (Vandeginste et al. 2005). However, not only is the fault at the Ravens Throat River locality listric in nature, rather than originating in the underlying units or the basement, the uniform dip of the Rockslide Formation above 19 m above base indicates that it was inactive by the time of deposition of the fossil-bearing calcareous mudstone. In addition, the underlying beds are not enriched in Ag, and there is no evidence for metal deposition along the fault. Warm, dilute brines could still have discharged into the seawater via fractures or faults in the underlying strata in a manner similar to how SEDEX and lithogene deposits formed (Lydon 1995; Graybeal and Vikre 2010; Manning and Emsbo 2018). Localized bottom-hugging brines might have been a factor in limiting the distribution of Ag enrichment (e.g., Sangster 2002).

Instead of being dispensed into seawater, the Ag could have been introduced into the stratigraphy by fluids via faults long after lithification. For example, the Prairie Creek deposit is hosted by the Ordovician Whittaker Formation, whereas mineralization at Macmillan Pass is much younger. With both scenarios, however, elevated levels of Pb might be expected because it is a primary component in those deposits (Ootes et al. 2013), which is not the case with the Ravens Throat River Lagerstätte.

Another possibility for fluid flow in the region could have been during the Cretaceous–Cenozoic Laramide orogeny and formation of the Mackenzie Mountains. This being said, no Ag-rich deposits are known in the region from this time interval (Ootes et al. 2013). Similarly, the Mountain River emerald deposit in the Mackenzie Mountains suffered its deformation during the Cretaceous–Cenozoic, but fluid inclusion date the deposit forming brines to the Devonian to middle Mississippian (Hewton et al. 2013). There is no published information on Ag content of modern groundwater in the area of the Ravens Throat River Lagerstätte or the Mackenzie Mountains for that matter, but in nearby surface waters it appears low in general (Golder Associates 2015). Thus, it is unlikely that the Ag concentrations would have been high enough for hydrological processes to enrich the upper part of the Rockslide Formation.

Based on this, a post-depositional hydrothermal origin of the Ag is unlikely, as the underlying lime mudstones have a broadly similar lithological composition as the fossiliferous host rock but are not enriched, and there is no evidence of a permeability boundary between the two intervals which could have led to stratigraphically compartmentalized fluid flow. Furthermore, the fine-grained nature of the sediment, mostly composed of clay-size particles, would have led to reduced permeability (Dewhurst et al., 1999). Additionally, there is also no evidence of metamorphism in the host rock, or other kinds of secondary mineralization in the fossiliferous interval or the coprolites from meteoric waters (Kimmig and Pratt 2016).

Organic role in silver concentration

While the fossiliferous and overlying strata are enriched in Ag, it is not clear in which form it is preserved, as no obvious Ag particles have been recognized in petrographic thin sections or with the microprobe. It could be a combination of Ag nitrates, sulfides, other sulfur compounds, fluorides, or nanoparticles of elemental Ag. Nevertheless,

because Ag is preserved in elemental form preferentially in the coprolites, this suggests that Ag accumulated under the influence of organic activity in some way, either by being passively trapped, actively scavenged from the water column, a combination of both, or ingested through prey.

The role of microorganisms in the reduction and accumulation of noble metals has been documented in modern bacteria, algae and fungi (e.g., Reith et al. 2007; Prasad and Elumalai 2013) and is thought to have been important in the formation of some ore deposits (Lovley 1993; Kashefi et al. 2001; Southam et al. 2009; Heinrich 2015; Frimmel 2018). Whereas most of these studies concentrated on Au, it has been observed that microbially mediated accumulation of Ag can occur in a similar way (e.g., Zierenberg and Schiffman 1990; Lovley 1993; Klaus-Joerger et al. 2001; Prasad and Elumalai 2013). Bacterial mediation involves metabolic processes in the form of enzymatically catalyzed reactions (Gupta et al. 1999; Reith et al. 2007), and depending on the species, the Ag can be stored within or outside, through cation efflux, the organism (Gupta et al. 1999; Pugazhenthiran et al. 2009). In contrast to bacteria, algae and fungi accumulate noble metals via passive biosorption (Sadowski et al. 2008; Prasad and Elumalai 2009; Devi and Joshi 2015; Kathiraven et al. 2015), and store the Ag within the organism.

Preservation of microorganisms in the fossil record is dependent on the degree of diagenetic alteration and thermal maturation, often causing the preserved fossils to look markedly different than their original form during life, and have different chemical signals (Li J. et al. 2013, 2014; Li Y.-L. et al. 2013). Experimental taphonomy studies on bacteria have shown that calcified specimens have a tendency to keep their overall morphology even when high temperatures are applied, whereas non-calcified specimens, which would be expected in BST deposits, lose their original form and appear as unidentifiable organic residues (Li et al. 2014; Robin et al. 2015). It is difficult to compare experimental results with natural occurring examples in the stratigraphic record (e.g., Vandenbroucke and Largeau 2007), but because the particles of Ag are larger than bacteria, the clusters of Ag might be related to masses of bacterial cells, and it is possible that individual particles might have lost their original shape over time, perhaps due to recrystallization.

Although Ag is toxic to most organisms, some living species have high tolerances and some can even bioaccumulate it safely. In modern marine habitats, some benthic macrophytic algae are known to bind dissolved Ag and tolerate elevated concentrations (Langston and Burt 1994; Fleeger et al. 2003). Similarly, some invertebrates, such as brine shrimp belonging to *Artemia*, the bryozoan *Victorella*, gastropods such as *Littorina littorea*, and certain nereid polychaetes, can bioaccumulate considerable amounts of heavy metals without symptoms of toxicity (Fisher 1995; Ratte 1999). Moreover, some crustaceans, such as freshwater *Daphnia magna*, may even require a certain amount of Ag in their diet (Rangwala and Keating 2008).

An alternative to a biofilm of microorganisms accumulating Ag on the coprolites is that it bioaccumulated in the coprolite-producer, which was probably a predatory worm (Kimmig and Pratt 2018). This explanation is unlikely because the coprolites do not preserve remains of the producer which is interpreted to have vacated its burrow after defecation. On the other hand, the producer could have defecated the Ag which had been in its prey. In the samples lacking arthropod exoskeleton and worm cuticle this may have included priapulid worms, or the producer might have rejected Ag particles it ingested and expelled them as part of pseudofeces, a phenomenon that has been observed in oysters, which also may be able to accumulate trace elements selectively (Abbe and Anders 1990; Sanders et al. 1990). Modern fish accumulate most

of the Ag they ingest in their livers and gills (e.g., Hogstrand et al. 1996). Similarly, experiments on earthworms and marine gastropods and annelids also show that Ag is incorporated in their soft tissues (Ramskov et al. 2015; Courtois et al. 2021). However, bioaccumulation in the prey does not appear to explain the fact that the Ag crystals are in clusters and in elemental form, and that not all coprolites exhibit Ag enrichment.

Another possibility is that digested tissues were reactive upon being defecated or, as biodegradation proceeded on or just under the seafloor, which made available appropriate ligands. That the distribution of Ag aggregates is patchy and not all coprolites exhibit them suggests that this is a less likely explanation.

At present, the most likely mechanism is that biofilms composed of specific microorganisms, either bacterial or fungal, that were locally forming on the feces either passively captured elemental Ag nanoparticles or bound Ag^+ from the water column which later transformed to the elemental form. How nanoparticles might have grown to be the larger crystal-like particles, or how the cation transformed to elemental Ag, is unclear. Other microorganisms in the environmental setting, benthic or planktic, may have also provided dispersed organic matter whose ligands bound Ag, which is why the concentration of Ag is elevated in the rock overall.

Conclusions

The middle Cambrian Ravens Throat River Lagerstätte in the Rockslide Formation of the Mackenzie Mountains, northwestern Canada, is known for its BST fossils and abundant coprolites. These fossils are preserved in a calcareous mudstone deposited on the flank of the Selwyn Basin. This rock type is enriched in silver, but lacks concomitant enrichment in Pb, Cu, and Zn which are usually linked in Ag-bearing mineral deposits. Specifically, large coprolites preferentially preserve aggregates of micrometer-scale particles or crystals of elemental Ag. This suggests that microbial activity on or organic matter in the coprolite extracted the Ag from the water column.

The presence of SEDEX deposits in this region suggests that the elevated Ag concentrations may have been derived from localized sources, such that Ag-bearing fluids may have issued onto the seafloor via syndepositional faults, or passed through a SEDEX deposit, or marine currents brought Ag-enriched seawater into the embayment.

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Competing interests statement

The authors declare there are no competing interests.

Contributors' statement

JK designed and led the study. JK and BRP completed fieldwork and collected all specimens used in the study. JK and BRP photographed the specimens. JK completed all analyses. JK and BRP created the figures. JK and BRP wrote the manuscript, discussed and agreed in interpretation of the data.

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Data availability statement

The data that support the findings of this study are available in the Table and figures of this article.

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Figures

Fig. 1. Map of northwestern Canada showing the main regional tectonic features and the larger Ag-bearing deposits (dot symbol) broadly in the vicinity of the Cambrian Ravens Throat River Lagerstätte (star symbol). Modified from Kimmig and Pratt (2015). Location of Mineral deposits and geologic information from Goodfellow (2007) and Ootes et al. (2013).

Fig. 2. Generalized stratigraphy of the middle Cambrian (Drumian) Rockslide Formation in the Ravens Throat River area, Northwest Territories. Gray-coloured intervals contain Burgess Shale-type soft-bodied fossils; coprolites are limited to the

lower fossil bed. Modified from Kimmig and Pratt (2016).

Fig. 3. Photomicrographs (plane-polarized light) of the fossil-bearing calcareous mudstone. (a) Finely laminated claystone with burrows (disrupted laminae), seams and flakes of organic carbon (black arrows), scattered silt grains (white), and pyrite euhedra (black). (b) Finely laminated claystone as in (a), with two compacted trilobite sclerites (center-left, white), overlying a lime mudstone lens composed of calcite microspar. Black arrows indicate burrows.

Fig. 4. (a) Photograph with reflected light of coprolite containing Ag immersed in alcohol (TMP 2013.101.0084). Light-gray object in lower left is an obliquely oriented hyolithid mollusc; dark object in lower right is an enrolled agnostoid arthropod. (b) Photograph with reflected light of coprolite containing Ag immersed in alcohol (TMP 2013.101.0079). Object oriented slightly oblique is a hyolith. (c) SEM backscattered electron photomicrograph of elemental Ag (clusters of white particles or crystals) in carbonaceous coprolite (dark) (TMP 2013.101.0084). (d) SEM backscattered electron photomicrograph of elemental Ag (clusters of white particles or crystals) in carbonaceous coprolite (dark) (TMP 2013.101.0079). Arrows in (c) and (d) indicate silver.

Fig. 5. Microprobe energy dispersive X-ray spectroscopy spectra of coprolite on mudstone bedding surfaces (TMP 2013.101.0084). (a) Silver aggregate. (b) Matrix organic carbon and rock.

Tables

Table 1. Trace element data of selected beds in the Rockslide Formation at the Ravens Throat River Lagerstätte. Height is above base of the Rockslide Formation. The samples between +134.35 and +136.76 m are from the lower fossiliferous interval, while the one at +164 m is from the upper fossiliferous interval. The six scree samples come from the lower fossiliferous interval. Data published in Kimmig and Pratt (2016) indicated by *.

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Supplement Data Set. Silver occurrences in the Canadian Cordillera.

Fig. 1. Map of northwestern Canada showing the main regional tectonic features and the larger Ag-bearing deposits (dot symbol) broadly in the vicinity of the Cambrian Ravens Throat River Lagerstätte (star symbol). Modified from Kimmig and Pratt (2015). Location of Mineral deposits and geologic information from Goodfellow (2007) and Ootes et al. (2013).

146x146mm (300 x 300 DPI)

Fig. 3. Photomicrographs (plane-polarized light) of the fossil-bearing calcareous mudstone. (a) Finely laminated claystone with burrows (disrupted laminae), seams and flakes of organic carbon (black arrows), scattered silt grains (white), and pyrite euhedra (black). (b) Finely laminated claystone as in (a), with two compacted trilobite sclerites (center-left, white), overlying a lime mudstone lens composed of calcite microspar. Black arrows indicate burrows.

Fig. 4. (a) Photograph with reflected light of coprolite containing Ag immersed in alcohol (TMP 2013.101.0084). Light-gray object in lower left is an obliquely oriented hyolithid mollusc; dark object in lower right is an enrolled agnostoid arthropod. (b) Photograph with reflected light of coprolite containing Ag immersed in alcohol (TMP 2013.101.0079). Object oriented slightly oblique is a hyolith. (c) SEM backscattered electron photomicrograph of elemental Ag (clusters of white particles or crystals) in carbonaceous coprolite (dark) (TMP 2013.101.0084). (d) SEM backscattered electron photomicrograph of elemental Ag (clusters of white particles or crystals) in carbonaceous coprolite (dark) (TMP 2013.101.0079). Arrows in (c) and (d) indicate silver.

Fig. 5. Microprobe energy dispersive X-ray spectroscopy spectra of coprolite on mudstone bedding surfaces (TMP 2013.101.0084). (a) Silver aggregate. (b) Matrix organic carbon and rock.

Facies	Height m	Sc ppm	V ppm	U Ppm	Th ppm	Pb ppm	Mo ppm	Cu ppm	Co ppm	Ni ppm	Zn ppm	Cr ppm	Ag ppm
Dolomitic limestone	190	7.2*	72.8*	4.38*	6.63*	14.8*	1.56*	18.2*	64.2*	26.5*	43*	40*	0.47
Calcareous mudstone	164	12.5*	107*	2.27*	9.12*	4.6*	0.43*	8.2*	31.9*	25.3*	64*	62*	0.36
Calcareous mudstone	scree	10.9	124	2.72	10.30	2.58	0.84	2.7	20.9	18.5	45	79	0.38
Calcareous mudstone	scree	11.3	141	3.06	10.50	5.17	0.71	8.7	57.3	24.7	56	75	0.40
Calcareous mudstone	scree	7.0	83.8	1.67	4.99	2.08	0.42	21.9	35.5	39.0	41	49	0.27
Calcareous mudstone	scree	9.4	119	2.16	9.09	2.41	0.56	3	23.4	19.7	48	72	0.39
Calcareous mudstone	scree	10.4	112	2.28	7.61	2.15	0.34	3.1	13.9	21.2	53	67	0.40
Calcareous mudstone	scree	7.3	51.9	2.56	9.08	6.84	0.54	2.8	37.1	28.6	53	80	0.22
Calcareous mudstone	136.76	10.3*	106*	2.73*	9.80*	2.41*	0.58*	5.2*	111*	23.3*	61*	74*	0.37
Calcareous mudstone	136.21	11.4*	121*	3.19*	11.40*	2.25*	0.71*	4.3*	29.6*	21.6*	60*	75*	0.41
Calcareous mudstone	136.06	7.9*	69.2*	2.75*	5.74*	2.69*	0.74*	50.1*	76.4*	53.2*	64*	48*	0.42
Calcareous mudstone	135.76	12.1*	119*	2.89*	10.00*	1.93*	0.63*	6.6*	34.4*	25.5*	73*	73*	0.24
Calcareous mudstone	135.14	12.8*	123*	3.03*	10.30*	1.85*	0.22*	21.3*	82.7*	25.4*	61*	81*	0.41
Calcareous mudstone	134.79	12.2*	122*	3.50*	10.70*	2.36*	0.52*	11.5*	46.1*	23.1*	68*	77*	0.42
Calcareous mudstone	134.63	13.0*	128*	3.46*	10.80*	2.50*	0.47*	12*	33.7*	29.5*	74*	77*	0.39
Calcareous mudstone	134.51	11.2*	121*	2.89*	9.58*	2.32*	0.71*	5.9*	50.9*	30.0*	78*	71*	0.37
Calcareous mudstone	134.42	11.5*	123*	3.46*	10.30*	3.01*	0.42*	15.2*	37.8*	35.2*	89*	73*	0.39
Calcareous mudstone	134.35	14.1*	141*	4.34*	12.10*	3.74*	1.08*	4.5*	17.2*	26.9*	61*	81*	0.43
Lime mudstone	133	4.2*	36.9*	2.14*	1.64*	5.39*	0.88*	14.4*	68.4*	19.8*	19*	11*	0.08
Debris flow	79	5.2*	67.2*	2.44*	4.3*	11.60*	2.16*	10.0*	34.8*	18.5*	70*	27*	0.22
Lime mudstone	60	2.8*	169*	2.03*	2.05*	5.69*	1.85*	17.2*	18.1*	19.8*	36*	15*	0.14
Black shale	5	7.2*	234*	6.32*	4.24*	13.00*	6.07*	16.3*	22.0*	33.6*	141*	44*	0.21
Detection limits		0.1	0.1	0.02	0.02	0.02	0.01	0.1	0.02	0.1	1	1	0.02

TABLE 1 Trace element data of selected beds in the Rockslide Formation at the Ravens Throat River Lagerstätte. Height is above base of the Rockslide Formation. The samples between +134.35 and +136.76 m are from the lower fossiliferous interval, while the one at +164 m is from the upper fossiliferous interval. The six scree samples come from the lower fossiliferous interval. Data published in Kimmig and Pratt (2016) indicated by *.

Facies	Height m	Al ppm	(Cu/Al) x 10 ⁴	EF	(Zn/Al) x 10 ⁴	EF	(Pb/Al) x 10 ⁴	EF	(Ag/Al) x 10 ⁴	EF
Dolomitic limestone	190	42923.08	4.24	0.83	10.02	0.93	3.45	1.52	0.11	13.83
Calcareous mudstone	164	76213.61	1.08	0.21	8.40	0.78	0.60	0.27	0.05	5.96
Calcareous mudstone	scree	82033.31	0.33	0.06	5.49	0.51	0.31	0.14	0.05	5.85
Calcareous mudstone	scree	84679.55	1.03	0.20	6.61	0.62	0.61	0.27	0.05	5.96
Calcareous mudstone	scree	56100.20	3.90	0.77	7.31	0.68	0.37	0.16	0.05	6.08
Calcareous mudstone	scree	76740.84	0.39	0.08	6.25	0.58	0.31	0.14	0.05	6.42
Calcareous mudstone	scree	80445.57	0.39	0.08	6.59	0.61	0.27	0.12	0.05	6.28
Calcareous mudstone	scree	74623.85	0.38	0.07	7.10	0.66	0.92	0.41	0.03	3.72
Calcareous mudstone	136.76	76212.00*	0.68*	0.13*	8.00*	0.75*	0.32*	0.14*	0.05	6.13
Calcareous mudstone	136.21	78329.00*	0.55*	0.11*	7.66*	0.72*	0.29*	0.12*	0.05	6.61
Calcareous mudstone	136.06	49220.25*	10.18*	2.00*	13.00*	1.22*	0.55*	0.24*	0.09	10.77
Calcareous mudstone	135.76	79387.50*	0.83*	0.16*	9.20*	0.86*	0.24*	0.11*	0.03	3.82
Calcareous mudstone	135.14	81504.50*	2.61*	0.51*	7.48*	0.70*	0.23*	0.10*	0.05	6.35
Calcareous mudstone	134.79	78329.00*	1.47*	0.29*	8.68*	0.81*	0.30*	0.13*	0.05	6.77
Calcareous mudstone	134.63	82563.00*	1.45*	0.28*	8.96*	0.84*	0.30*	0.13*	0.05	5.96
Calcareous mudstone	134.51	80446.00*	0.73*	0.14*	9.70*	0.91*	0.29*	0.13*	0.05	5.81
Calcareous mudstone	134.42	79916.75*	1.90*	0.37*	11.14*	1.04*	0.38*	0.16*	0.05	6.16
Calcareous mudstone	134.35	86267.75*	0.52*	0.10*	7.07*	0.66*	0.43*	0.19*	0.05	6.29
Lime mudstone	133	18629.99	7.73	1.52	10.20	0.95	2.89	1.28	0.04	5.42
Debris flow	79	26992.32	3.70	0.73	25.93	2.41	4.30	1.90	0.08	10.29
Lime mudstone	60	18259.51	9.42	1.85	19.72	1.83	3.12	1.38	0.08	9.68
Black shale	5	50121.03	3.25	0.64	28.13	2.62	2.59	1.15	0.04	5.29

TABLE 2 Enrichment factors (EF) for selected trace elements of selected beds in the Rockslide Formation at the Ravens Throat River Lagerstätte. Height is above base of the Rockslide Formation. The samples between +134.35 and +136.76 m are from the lower fossiliferous interval, while the one at +164 m is from the upper fossiliferous interval. The six scree samples come from the lower fossiliferous interval. Data published in Kimmig and Pratt (2016) indicated by *.