UNIVERSITY OF LEEDS

This is a repository copy of *Marine anoxia and sedimentary mercury enrichments during the Late Cambrian SPICE event in northern Scotland*.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/146235/

Version: Accepted Version

Article:

Pruss, SB, Jones, DS, Fike, DA et al. (2 more authors) (2019) Marine anoxia and sedimentary mercury enrichments during the Late Cambrian SPICE event in northern Scotland. Geology, 47 (5). pp. 475-478. ISSN 1943-2682

https://doi.org/10.1130/G45871.1

© 2019 Geological Society of America. This is an author produced version of a paper published in Geology. Uploaded in accordance with the publisher's self-archiving policy.

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

White Rose university consortium
Universities of Leeds, Sheffield & York

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk/

Publisher: GSA
Journal: GEOL: Geology
DOI:10.1130/G45871.1

Marine anoxia and sedimentary mercury enrichments during the Late Cambrian SPICE event in northern Scotland

Sara B. Pruss[1], David S. Jones[2], David A. Fike[3], Nicholas J. Tosca[4], and Paul B. Wignall[5]

[1]*Department of Geosciences, Smith College, Northampton, Massachusetts 01063, USA*

[2]*Department of Geology, Amherst College, Amherst, Massachusetts 01002, USA*

[3]*Department of Earth & Planetary Sciences, Washington University in St. Louis, St. Louis, Missouri 63130, USA*

[4]*Department of Earth Sciences, University of Oxford, Oxford OX1 3AN, UK*

[5]*The School of Earth Sciences, Leeds University, Leeds, West Yorkshire LS2 9JT, UK*

ABSTRACT

Elevated mercury concentrations in ancient sedimentary rocks are used as a fingerprint for large igneous province (LIP) volcanism because there is a tight association between known LIPs and coeval sedimentary Hg anomalies. While nonvolcanic processes of sedimentary Hg enrichment, including redox variations, have been demonstrated in modern settings, interpretations of ancient sedimentary Hg records have focused on LIP volcanism. Here, we document a link between sedimentary Hg enrichment and marine redox changes during the late Cambrian Steptoean positive isotopic carbon excursion (SPICE) event, a time with no known LIP. We report a new occurrence of the SPICE event from the Eilean Dubh Formation of northern Scotland, which preserves a series of coeval Hg enrichments. Abundant glauconite, a redox-

sensitive iron-bearing mineral, co-occurs stratigraphically with the SPICE and Hg enrichments but is rare to absent from the rest of the section, and bioturbation is low in strata spanning the SPICE. We suggest that local Hg enrichments were driven by changing marine redox conditions during the SPICE event, rather than emplacement of a LIP. Redox oscillations should be considered as an additional control on Hg enrichments in the geologic record.

INTRODUCTION

Enrichments of Hg concentrations in ancient sedimentary rocks have been used as a fingerprint of large igneous province (LIP) volcanism. All five major mass extinction events and many Mesozoic oceanic anoxic events (OAEs) are linked to sedimentary Hg anomalies; many are also synchronous with known LIP activity (e.g., Sanei et al., 2012; Percival et al., 2015; Thibodeau et al., 2016). For some extinctions, a documented LIP culprit is lacking, although Hg anomalies are observed (Jones et al., 2017; Racki et al., 2018). While it is possible that in some cases the geologic record of massive volcanism is not preserved, a broader suite of nonvolcanic processes may generate sedimentary Hg enrichments (e.g., Shen et al., 2019; Them et al., 2019). Previous investigations of the relationship between Hg (normalized to total organic carbon [TOC]) and redox conditions during intervals of LIP volcanism yielded an equivocal or no relationship between Hg/TOC and other redox proxies (Grasby et al., 2013; Percival et al., 2015); however, those studies only examined the effect of Hg as it relates to TOC. Given that Hg abundance can be tied to redox conditions and authigenic mineral formation in the present-day environment (Emili et al., 2011), we provide a more systematic examination of this proxy through the late Cambrian Steptoean positive isotopic carbon excursion

(SPICE) event. **[[Note: Informal divisions of the geologic time scale have been set lowercase throughout, while formally defined periods are set in uppercase.]]**

Sedimentary Hg accumulation has been intensively studied in Holocene systems, because Hg is toxic to animals and its methylated form, monomethylmercury (MeHg), bioaccumulates in higher-order taxa (Morel et al., 1998). In laboratory experiments designed to mimic marine anoxic events, Hg and MeHg were removed from the water column and delivered to surface sediments by Fe and Mn oxyhydroxides, which scavenge Hg under oxic conditions (Gagnon et al., 1997). Hg is, however, liberated from surface sediments when oxygen is absent (Emili et al., 2011); bottom waters that have experienced low-oxygen conditions have locally elevated Hg and MeHg concentrations and can subsequently experience Hg drawdown through authigenic mineral formation when oxygen is present again (Emili et al., 2011), thereby enriching the sedimentary Hg inventory. These observations offer an interpretive framework for Hg cycling in the geologic past. Here, we apply this framework to Upper Cambrian marine strata from northern Scotland.

The Cambrian Period was characterized by large shifts in the carbon isotopic record of carbonates (Maloof et al., 2005; Smith et al., 2015). Perhaps the most studied Cambrian excursion is the SPICE, first recognized in western North America as a large positive carbon isotope excursion in biologically depauperate carbonates of the Furongian (late) Cambrian interval (Saltzman et al., 1998). This excursion also occurs globally in Furongian strata (Glumac and Walker, 1998; Saltzman et al., 2000; Gill et al., 2011). In Laurentia, the SPICE is found during an interval of coupled marine regression-transgression (Saltzman et al., 2004), which has led some workers to propose that this isotopic excursion was related to tectonic changes (Glumac and Walker, 1998) and enhanced organic carbon burial (Saltzman et al., 2000). The extinction of trilobites associated with the SPICE (Palmer, 1984) has been linked to low-oxygen conditions (Gill et al., 2011) and/or warm ocean temperatures (Elrick et al., 2011). Sedimentological, paleontological, and geochemical data all suggest significant, perhaps global, environmental perturbation, although the ultimate cause of the carbon isotopic excursion and redox changes is unclear.

METHODS

We collected samples at meter-scale intervals from rocks of the Upper Cambrian Eilean Dubh Formation and Lower Ordovician Sailmhor Formation, northern Scotland. Then, 1 to 2 g aliquots of powder were collected from each sample and analyzed for $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ (carb—carbonate) using a Gas Bench II coupled to a Delta V Advantage mass spectrometer at Washington University, St. Louis, Missouri, USA. Results are reported in permil relative to the Vienna Peedee belemnite (VPDB) standard in delta notation. Reproducibility of standards was 0.1‰ for $\delta^{18}O$ and 0.05‰ for $\delta^{13}C$. Carbonate content of whole-rock powders was determined by mass loss following dissolution with hydrochloric acid. Carbon content of insoluble residue was measured with a Costech ECS 4010 elemental analyzer, with relative standard deviation of TOC measurements <4.5%. Hg was measured on whole-rock powders with a Teledyne Leeman Labs Hydra II_C mercury analyzer, with relative standard deviation <10%. TOC and Hg analyses were done at Amherst College, Amherst, Massachusetts. Powder X-ray diffraction was performed at Oxford University (UK) on hand-ground decarbonated residues. Samples were mounted as a slurry mixed with anhydrous ethanol on a low-background scattering silicon crystal substrate and analyzed using a Panalytical Empyrean Series 2 diffractometer operating at 40 kV and 40 mA with a Co Kα source. Samples were analyzed while being continuously rotated, and data were acquired from 5° to 85° 2θ using a step size of 0.026°. Diffraction data were reduced using HighScore Plus software, and mineral identification was based on correspondence to the International Center for Diffraction Data Powder Diffraction File 4+ database (http://www.icdd.com/index.php/pdf-4/). The amount and fractions of clay were measured. Glauconite abundance in marine strata is a qualitative proxy for ancient bottom-water oxygen levels, with high concentrations indicating redox oscillations (Tang et al., 2017). We determined the abundance of glauconite in samples deposited before, during, and after the SPICE event. We calculated the percent of glauconite from whole rock using glauconite concentration in decarbonated residues and insoluble residue concentration in the whole rock.

RESULTS

We identified a previously unrecognized manifestation of the SPICE event in the Eilean Dubh Formation in northern Scotland, and we present accompanying Hg and mineralogical data here (Fig. 1). The Eilean Dubh Formation lacks many useful biostratigraphic fossils, but strata below it record the Redlichiid-Olenellid extinction carbon isotope excursion (ROECE) and Drumian carbon isotope excursion (DICE) events (Faggetter et al., 2018); the Cambrian-Ordovician boundary, defined by conodonts (Huselbee and Thomas, 1998), occurs ~70 m above the Eilean Dubh excursion, placing the excursion firmly within the Furongian. From a baseline value of ~–0.3‰, the onset of the $\delta^{13}C$ excursion occurs at ~39.7 m above the base of the exposed section, reaches

DOI:10.1130/G45871.1

values of 2.7‰, and returns to −1.0‰ at 70 m. Facies through this event lack bioturbation and include stromatolitic and thrombolitic limestone and ribbon and laminated limestone and dolostone. Below the SPICE, background Hg concentration is ~1.0 ppb; the largest Hg enrichments begin at 42.9 m, with additional peaks through the SPICE and up to 76.3 m (Fig. 1).

Because Hg is commonly bound to organic matter, we normalized Hg concentration to TOC (Sanei et al., 2012) through the SPICE interval. Hg/TOC values are elevated through the SPICE (Fig. 1). We excluded data with TOC ≤0.006% (wt%; cf. Grasby et al., 2016). TOC values range from 0.003% to 0.132% throughout the SPICE, but they do not covary with Hg (Fig. 2; see also Fig. DR1 in the GSA Data Repository[1]). We used the mineralogical data to normalize Hg to clay abundance (Fig. 1; Fig. DR1). Hg concentration has a stronger correlation with clay concentration than with TOC (Fig. DR1), suggesting that Hg binding to clay minerals may be more important than to organic matter in these rocks. Nonetheless, there is secular variability in the Hg/clay ratio, with very low background Hg/clay values below and above the SPICE and enriched Hg/clay values within the SPICE (Fig. 1). The occurrence of the Hg peaks within the SPICE interval, regardless of the normalization used, strongly suggests a secular change in Hg accumulation and burial during the SPICE.

DISCUSSION

Mineralogical Constraints on Redox Conditions

Various geochemical proxies have been developed to evaluate redox conditions in ancient strata, including those based on trace-element abundance and isotopic composition such as Cr, Fe, S, Mo, and U (Gill et al., 2011; Dahl et al., 2014; Planavsky et al., 2014). A common technique used to reconstruct paleoredox conditions is the reactive iron proxy, which measures ratios of highly reactive Fe (FeHR) to total iron (FeT). Sediments deposited beneath oxic water can be distinguished from sediments deposited under anoxic water columns based on their FeHR/FeT ratios (Raiswell and Canfield, 1998). This proxy has been primarily applied to fine-grained siliciclastic sediments, but because the SPICE in Scotland is hosted in strata with a mean carbonate content of 90% (Table DR1), we developed an alternate mineralogical approach to reconstructing redox conditions in the Eilean Dubh Formation.

The presence and/or abundance of authigenic minerals can constrain the redox conditions of a particular depositional environment. For example, laboratory experiments show that greenalite [$(Fe^{2+}, Fe^{3+})_{2–3}Si_2O_5(OH)_4$] forms in anoxic water columns, providing constraints on the origin of iron formation (Tosca et al., 2016). More recently, studies of fossils replaced by glauconite and/or apatite have linked these mineralogies to redox oscillations (Pruss et al., 2017). Glauconite is an authigenic mixed-valence iron-bearing phyllosilicate that forms in marine sediments under fluctuating redox conditions (Odin and Létolle, 1980; O'Brien et al., 1990). Redox constraints on glauconite formation have been well studied in modern systems (Odin and Létolle, 1980; O'Brien et al., 1990). For example, glauconite is common in modern distal shelf deposits (Odin and Matter, 1981), where fluctuating local oxygen minimum zones drive the redox oscillations necessary for glauconite formation. Strata deposited during the SPICE are enriched in glauconite relative to underlying and overlying strata (Fig. 1). Glauconite is absent from rocks below 37 m but makes up more than 2% (±1.0 wt%) of the whole rock, and up to 20% of the noncarbonate fraction in many samples deposited during the SPICE.

Glauconite content generally remains far below 2% in strata above the SPICE, except for sample 106.7.

A potential complication with utilizing glauconite abundances as a redox proxy is that they can occur as either an authigenic or detrital component in rocks. While glauconite requires oscillating redox conditions to form, its abundance may reflect transport of allochthonous grains (Chafetz and Reid, 2000), in which case its presence would not provide direct evidence for redox conditions at the site where it was ultimately deposited. However, our lithostratigraphic data demonstrate that glauconite enrichment occurred in shallow carbonate environments with minimal terrigenous input (Fig. DR1; Table DR1). Moreover, while some detrital phases (e.g., quartz, K-feldspar) are present in these rocks, they are neither more nor less abundant during the glauconite-bearing SPICE interval (Table DR1; Fig. DR2). Whether the product of authigenic cement formation or intrabasinal transport, we interpret the observed increase in glauconite in strata spanning the SPICE as reflecting redox oscillations in the local marine environment at the time of deposition; the sediments in which the glauconite formed must have experienced low-oxygen conditions for at least some of their depositional history (O'Brien et al., 1990). The absence of bioturbation in laminated limestone and dolostone through the SPICE interval provides independent evidence for low oxygen, perhaps periodically, through this part of the section. This inferred redox oscillation is consistent with the redox control of Hg enrichments in sediments observed in laboratory experiments and in Holocene environments (Emili et al., 2011). Taken together, we interpret the Eilean Dubh SPICE event to have co-occurred with low-oxygen conditions

Publisher: GSA
Journal: GEOL: Geology
DOI:10.1130/G45871.1

that oscillated with more oxic ones, allowing for glauconite formation and enhanced sedimentary Hg accumulation.

Local Manifestations of Global Trends in Anoxia?

Multiple lines of independent evidence reported elsewhere suggest that the SPICE broadly co-occurred with low-oxygen conditions **[[Cite relevant references here?** Nearly synchronous positive excursions in $\delta^{13}C$ and $\delta^{34}S$ and Mo depletion may reflect the expansion of anoxic deeper waters (Gill et al., 2011), although anoxia may have been time transgressive at basinal and global scales (Schiffbauer et al., 2017). The heterogeneity of the sulfur isotopic record (Hurtgen et al., 2009; Gill et al., 2011), interpreted to record changes in the global marine sulfate pool, points to low sulfate concentrations in the global ocean, which may be linked to lower overall oxygen levels. The U isotope record suggests a shift from oxic to transiently low-oxygen conditions during the SPICE (Dahl et al., 2014), consistent with elevated pyrite and organic carbon burial (Saltzman et al., 2011) and/or warmer ocean temperatures (Elrick et al., 2011).

The Hg proxy in marine sedimentary rocks may provide a way to track the local redox changes in sedimentary successions. In the Eilean Dubh Formation, Hg abundance increases (up to ~35 ppb) during the onset and throughout the SPICE but is low or absent in the rest of the section. When controlled for TOC and clays, two sedimentary sinks for Hg, these peaks remain. This suggests that the Hg proxy is sensitive to local redox conditions, perhaps better constraining the timing of local anoxia than more global proxies. Local expressions of anoxia are important to constrain, because the onset of anoxia may be time transgressive within and/or between basins. In the Eilean Dubh Formation, Hg abundance indicates an initial development of local low-oxygen

DOI:10.1130/G45871.1

conditions at the onset of SPICE, with a peak in development during the falling limb of the event. Here, it appears Hg abundance may track the onset and duration of low-oxygen conditions, followed by a subsequent local oxygenation event; such patterns may be useful for monitoring local redox conditions in other basins and at other times in geologic history.

CONCLUSIONS

There is a strong and well-documented relationship between LIPs and sedimentary Hg enrichment throughout the geologic record. However, our observations for the SPICE in the Eilean Dubh Formation suggest that Hg enrichments do not necessarily reflect excess Hg loading from a large volcanic source. Given the association between Hg enrichment and glauconite formation, we argue for a redox control on Hg accumulation during the SPICE in Scotland. Furthermore, many intervals for which LIPs have been implicated in elevated Hg also co-occur with redox oscillations (Sanei et al., 2012; Racki et al., 2018), underscoring the need to better understand the relationship between Hg and redox.

ACKNOWLEDGMENTS

We acknowledge the assistance of M. Kopicki, L. Lim, H. Grotzinger, E. Swislow, R. Chinitz, T. Browne, and K. Clayton in laboratory preparation and analysis of samples. E. Roth provided field assistance, and L. Faggetter provided field and laboratory assistance. Smith College and Amherst College are acknowledged for partial support of this research. Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research (to Pruss).

REFERENCES CITED

Chafetz, H.S., and Reid, A., 2000, Syndepositional shallow-water precipitation of glauconitic minerals: Sedimentary Geology, v. 136, p. 29–42, https://doi.org/10.1016/S0037-0738(00)00082-8.

Dahl, T.W., Boyle, R.A., Canfield, D.E., Connelly, J.N., Gill, B.C., Lenton, T.M., and Bizzarro, M., 2014, Uranium isotopes distinguish two geochemically distinct stages during the later Cambrian SPICE event: Earth and Planetary Science Letters, v. 401, p. 313–326, https://doi.org/10.1016/j.epsl.2014.05.043.

Elrick, M., Rieboldt, S., Saltzman, M.R., and McKay, R.M., 2011, Oxygen-isotope trends and seawater temperature changes across the late Cambrian Steptoean positive carbon-isotope excursion (SPICE event): Geology, v. 39, p. 987–990, https://doi.org/10.1130/G32109.1.

Emili, A., Koron, N., Covelli, S., Faganeli, J., Acquavita, A., Predonzani, S., and De Vittor, C., 2011, Does anoxia affect mercury cycling at the sediment-water interface in the Gulf of Trieste (northern Adriatic Sea)? Incubation experiments using benthic flux chambers: Applied Geochemistry, v. 26, p. 194–204, https://doi.org/10.1016/j.apgeochem.2010.11.019.

Faggetter, L.E., Wignall, P.B., Pruss, S.B., Sun, Y., Raine, R.J., Newton, R.J., Widdowson, M., Joachimski, M.M., and Smith, P.M., 2018, Sequence stratigraphy, chemostratigraphy and facies analysis of Cambrian Series 2–Series 3 boundary strata in northwestern Scotland: Geological Magazine, v. 155, p. 865–877, https://doi.org/10.1017/S0016756816000947.

Gagnon, C., Pelletier, É., and Mucci, A., 1997, Behaviour of anthropogenic mercury in coastal marine sediments: Marine Chemistry, v. 59, p. 159–176, https://doi.org/10.1016/S0304-4203(97)00071-6.

Gill, B.C., Lyons, T.W., Young, S.A., Kump, L.R., Knoll, A.H., and Saltzman, M.R., 2011, Geochemical evidence for widespread euxinia in the later Cambrian ocean: Nature, v. 469, p. 80–83, https://doi.org/10.1038/nature09700.

Glumac, B., and Walker, K.R., 1998, A late Cambrian positive carbon-isotope excursion in the Southern Appalachians: Relation to biostratigraphy, sequence stratigraphy, environments of deposition, and diagenesis: Journal of Sedimentary Research, v. 68, p. 1212–1222, https://doi.org/10.2110/jsr.68.1212.

Grasby, S.E., Sanei, H., Beauchamp, B., and Chen, Z., 2013, Mercury deposition through the Permo–Triassic biotic crisis: Chemical Geology, v. 351, p. 209–216, https://doi.org/10.1016/j.chemgeo.2013.05.022.

Grasby, S.E., Beauchamp, B., and Bond, D., 2016, Mercury anomalies associated with three extinction events (Capitanian crisis, latest Permian extinction and the Smithian/Spathian extinction) in NW Pangea: Geological Magazine, v. 153, p. 285–297, https://doi.org/10.1017/S0016756815000436.

Hurtgen, M.T., Pruss, S.B., and Knoll, A.H., 2009, Evaluating the relationship between the carbon and sulfur cycles in the later Cambrian ocean: An example from the Port au Port Group, western Newfoundland, Canada: Earth and Planetary Science Letters, v. 281, p. 288–297, https://doi.org/10.1016/j.epsl.2009.02.033.

Huselbee, M.Y., and Thomas, A.T., 1998, *Olenellus* and conodonts from the Durness Group, NW Scotland, and the correlation of the Durness succession: Scottish Journal of Geology, v. 34, p. 83–88, https://doi.org/10.1144/sjg34010083.

Jones, D.S., Martini, A.M., Fike, D.A., and Kaiho, K., 2017, A volcanic trigger for the Late Ordovician mass extinction? Hg data from South China and Laurentia: Geology, v. 45, p. 631–634, https://doi.org/10.1130/G38940.1.

Maloof, A.C., Schrag, D.P., Crowley, J.L., and Bowring, S.A., 2005, An expanded record of early Cambrian carbon cycling from the Anti-Atlas margin, Morocco: Canadian Journal of Earth Sciences, v. 42, p. 2195–2216, https://doi.org/10.1139/e05-062.

Morel, F.M.M., Kraepiel, A.M.L., and Amyot, M., 1998, The chemical cycle and bioaccumulation of mercury: Annual Review of Ecology and Systematics, v. 29, p. 543–566, https://doi.org/10.1146/annurev.ecolsys.29.1.543.

O'Brien, G.W., Milnes, A.R., Veeh, H.H., Heggie, D.T., Riggs, S.R., Cullen, D.J., Marshall, J.F., and Cook, P.J., 1990, Sedimentation dynamics and redox iron-cycling: Controlling factors for the apatite-glauconite association on the East Australian continental margin, *in* Notholt, A.J.G., and Jarvis, I., eds., Phosphorite Research and Development: Geological Society [London] Special Publication 52, p. 61–86, https://doi.org/10.1144/GSL.SP.1990.052.01.06.

Odin, G.S., and Létolle, R., 1980, Glauconitization and phosphatization environments: A tentative comparison, *in* Bentor, Y.K., ed., Marine Phosphorites: Society of Economic Paleontologists and Mineralogists (SEPM) Special Publication 29, p. 227–237.

Odin, G.S., and Matter, A., 1981, De glauconiarum origine: Sedimentology, v. 28, p. 611–641, https://doi.org/10.1111/j.1365-3091.1981.tb01925.x.

Palmer, A.R., 1984, The biomere problem: Evolution of an idea: Journal of Paleontology, v. 58, p. 599–611, https://doi.org/10.2307/1304904?refreqid=search-gateway:4b0209cceeccada3bdd9f059fc28852e.

Percival, L.M.E., Witt, M.L.I., Mather, T.A., Hermoso, M., Jenkyns, H.C., Hesselbo, S.P., Al-Suwaidi, A.H., Storm, M.S., Xu, W., and Ruhl, M., 2015, Globally enhanced mercury deposition during the end-Pliensbachian extinction and Toarcian OAE: A link to the Karoo-Ferrar large igneous province: Earth and Planetary Science Letters, v. 428, p. 267–280, https://doi.org/10.1016/j.epsl.2015.06.064.

Planavsky, N.J., Reinhard, C.T., Wang, X., Thomson, D., McGoldrick, P., Rainbird, R.H., Johnson, T., Fischer, W.W., and Lyons, T.W., 2014, Low Mid-Proterozoic atmospheric oxygen levels and the delayed rise of animals: Science, v. 346, p. 635–638, https://doi.org/10.1126/science.1258410.

Pruss, S.B., Dwyer, C.H., Smith, E.F., Macdonald, F.A., and Tosca, N.J., 2017, Phosphatized early Cambrian archaeocyaths and small shelly fossils (SSFs) of southwestern Mongolia: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 513, p. 166–177, https://doi.org/10.1016/j.palaeo.2017.07.002.

Racki, G., Rakociński, M., Marynowski, L., and Wignall, P.B., 2018, Mercury enrichments and the Frasnian-Famennian biotic crisis: A volcanic trigger proved?: Geology, v. 46, p. 543–546, https://doi.org/10.1130/G40233.1.

Raine, R.J., 2009, The Durness Group of NW Scotland: A Stratigraphical and Sedimentological Study of a Cambro-Ordovician Passive Margin Succession [Ph.D. thesis]: Birmingham, UK, University of Birmingham, 270 p.

Raiswell, R., and Canfield, D.E., 1998, Sources of iron for pyrite formation in marine sediments: American Journal of Science, v. 298, p. 219–245, https://doi.org/10.2475/ajs.298.3.219.

Saltzman, M.R., Runnegar, B., and Lohmann, K.C., 1998, Carbon isotope stratigraphy of Upper Cambrian (Steptoean Stage) sequences of the eastern Great Basin: Record of a global oceanographic event: Geological Society of America Bulletin, v. 110, p. 285–297, https://doi.org/10.1130/0016-7606(1998)110<0285:CISOUC>2.3.CO;2.

Saltzman, M.R., Ripperdan, R.L., Brasier, M., Lohmann, K., Robison, R., Chang, W., Peng, S., Ergaliev, E., and Runnegar, B., 2000, A global carbon isotope excursion (SPICE) during the late Cambrian: Relation to trilobite extinctions, organic-matter burial and sea level: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 162, p. 211–223, https://doi.org/10.1016/S0031-0182(00)00128-0.

Saltzman, M.R., Cowan, C.A., Runkel, A.C., Runnegar, B., Stewart, M.C., and Palmer, A.R., 2004, The late Cambrian SPICE ($\delta^{13}C$) event and the Sauk II-Sauk III regression: New evidence from Laurentian basins in Utah, Iowa and Newfoundland: Journal of Sedimentary Research, v. 74, p. 366–377, https://doi.org/10.1306/120203740366.

Saltzman, M.R., Young, S.A., Kump, L.R., Gill, B.C., Lyons, T.W., and Runnegar, B., 2011, Pulse of atmospheric oxygen during the late Cambrian: Proceedings of the

National Academy of Sciences of the United States of America, v. 108, p. 3876–3881, https://doi.org/10.1073/pnas.1011836108.

Sanei, H., Grasby, S.E., and Beauchamp, B., 2012, Latest Permian mercury anomalies: Geology, v. 40, p. 63–66, https://doi.org/10.1130/G32596.1.

Schiffbauer, J.D., Huntley, J.W., and Fike, D.A., 2017, Decoupling biogeochemical records, extinction, and environmental change during the Cambrian SPICE event: Science Advances, v. 3, p. 1–7, https://doi.org/10.1126/sciadv.1602158.

Shen, J., Algeo, T.J., Chen, J., Planavsky, N.J., Feng, Q., Yu, J., and Liu, J., 2019, Mercury in marine Ordovician/Silurian boundary sections of South China is sulfide-hosted and non-volcanic in origin: Earth and Planetary Science Letters, v. 511, p. 130–140, https://doi.org/10.1016/j.epsl.2019.01.028.

Smith, E.F., Macdonald, F.A., Petach, T.A., Bold, U., and Schrag, D.P., 2015, Integrated stratigraphic, geochemical, and paleontological late Ediacaran to early Cambrian records from southwestern Mongolia: Geological Society of America Bulletin, v. 128, p. 442–468, https://doi.org/10.1130/B31248.1.

Tang, D., Shi, X., Ma, J., Jiang, G., Zhou, X., and Shi, Q., 2017, Formation of shallow-water glaucony in weakly oxygenated Precambrian ocean: An example from the Mesoproterozoic Tieling Formation in North China: Precambrian Research, v. 294, p. 214–229, https://doi.org/10.1016/j.precamres.2017.03.026.

Them, T.R., II, Jagoe, C.H., Caruthers, A.H., Gill, B.C., Grasby, S.E., Gröcke, D.R., Yin, R., and Owens, J.D., 2019, Terrestrial sources as the primary delivery mechanism of mercury to the oceans across the Toarcian oceanic anoxic event (Early Jurassic):

Earth and Planetary Science Letters, v. 507, p. 62–72, https://doi.org/10.1016/j.epsl.2018.11.029.

Thibodeau, A.M., Ritterbush, K., Yager, J.A., West, A.J., Ibarra, Y., Bottjer, D.J., Berelson, W.M., Bergquist, B.A., and Corsetti, F.A., 2016, Mercury anomalies and the timing of biotic recovery following the end-Triassic mass extinction: Nature Communications, v. 7, p. 11147, https://doi.org/10.1038/ncomms11147.

Tosca, N.J., Guggenheim, S., and Pufahl, P.K., 2016, An authigenic origin for Precambrian greenalite: Implications for iron formation and the chemistry of ancient seawater: Geological Society of America Bulletin, v. 128, p. 511–530, https://doi.org/10.1130/B31339.1.

FIGURE CAPTIONS

Figure 1. Map showing measured section near Durness, Scotland (modified from Raine, 2009). Base of section is 58°37′35.33″N, 4°47′50.90″W. All data are presented in Table DR1 (see footnote 1).

Figure 2. Stratigraphic column of Upper Cambrian upper Eilean Dubh Formation measured at Balnakeil Bay in northern Scotland, with accompanying geochemical data: carbon isotopes (VPDB [Vienna Peedee belemnite]), Hg abundance (ppb), Hg/TOC (TOC—total organic carbon; ppb/wt%), Hg/clay (ppb/wt%), and glauconite abundance (wt% relative to whole rock [WR]) are shown.

[1]GSA Data Repository item 2019xxx, **[[Please provide DR title(s) and brief descriptions here.]]**, is available online at

http://www.geosociety.org/datarepository/2019/, or on request from editing@geosociety.org.