

1 **Cadmium Sulphide in a Mesoproterozoic terrestrial environment**

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5 **ABSTRACT**

6 Cadmium sulphide mineralization occurs in grey-black shales of the late Mesoproterozoic Stoer Group,  
7 northwest Scotland. Cd is strongly redox-controlled, and normally concentrated in anoxic marine  
8 sediments or epigenetic mineralization involving organic matter. However the Stoer Group was  
9 deposited in a terrestrial environment, including lacustrine deposits of shale. At the limited levels of  
10 atmospheric oxygenation in the Mesoproterozoic (~10% of present), the near-surface environment  
11 could have fluctuated between oxic and anoxic, allowing fractionation of Cd from Zn, and the formation  
12 of Cd sulphide rather than Cd-bearing sphalerite. This occurrence emphasizes the importance of the  
13 Stoer Group as a record of the Mesoproterozoic terrestrial environment.

14 **KEYWORDS:** cadmium, greenockite, Mesoproterozoic, Torridonian, oxygenation, Scotland

15 **Running Head:** Mesoproterozoic cadmium sulphide

16

17 **Introduction**

18 We report Cd sulphide mineralization in the Mesoproterozoic of Scotland. The occurrence of Cd  
19 sulphides in rocks deposited in a terrestrial environment is unusual, and we discuss this in the context of  
20 the limited oxygenation of the Mesoproterozoic atmosphere.

21 Cadmium is a trace element normally found substituting for Zn in the Zn sulphide mineral sphalerite.  
22 However it may, rarely, form the Cd sulphide greenockite, especially in anoxic environments (Ripley et  
23 al. 1990, Lesven et al. 2010, Fleurance et al. 2013). Thus, in sedimentary rocks, Cd is found enriched in  
24 sphalerite-bearing deposits such as Mississippi Valley-type ores (Schwartz 2000, Ye et al. 2012) and in  
25 marine black shales (e.g. Ripley et al. 1990, Perkins & Foster 2004, Falk et al. 2006, Fleurance et al.  
26 2013).

27 Cadmium is a highly redox-sensitive element (van Geen et al. 1995, Rosenthal et al. 1995, Thomson et al.  
28 2001, Pailler et al. 2002, Chaillou et al. 2002, Pufahl & Hiatt 2012). It precipitates in sediments as the  
29 sulphide greenockite (CdS) in anoxic conditions, and is liberated into solution in oxidizing conditions. The  
30 sensitivity of Cd to oxygen levels is so marked that seasonal fluctuations in the chemistry of modern  
31 near-surface waters may be enough to alternate between sulphide deposition and solution (Holmes et  
32 al. 1974). Cd is therefore a valuable element in assessing ancient levels of oxygenation, and is one of  
33 several bio-essential metals whose limited availability during the low-oxygen conditions of the early  
34 Proterozoic could have inhibited the evolution of complex life (Anbar & Knoll 2002, Saito et al. 2003,  
35 Morel 2008).

36 The Cd sulphide documented here is in the late Mesoproterozoic Stoer Group, Torridonian Supergroup,  
37 North West Scotland. The Stoer Group was deposited in a continental setting including alluvial fan,  
38 fluvial and lacustrine environments (Stewart 2002). The succession includes a distinctive unit of grey-  
39 black shale in the Poll a' Mhuil Member of the Bay of Stoer Formation (Fig. 1), interpreted as lacustrine  
40 (Stewart 2002, Andrews et al. 2010). The lake waters and groundwaters were carbonate-rich, evidenced  
41 by calcite in the matrix of the black shale, a discrete limestone bed at the base of the black shale (Fig. 1)  
42 and calcite cements in the subjacent/superjacent shales. This unit closely follows a meteorite impact  
43 deposit dated at 1.18 Ga (Parnell et al. 2011). Palaeomagnetic studies suggest a low latitude in the

44 northern hemisphere (Darabi & Piper 2004). The rocks have experienced low-grade regional  
45 metamorphism, but their sedimentary characteristics are perfectly preserved.

## 46 **Methodology**

47 Samples of the shale were collected from the north side of the Bay of Stoer (section described by  
48 Stewart 2002, National Grid Reference NC 032285). The samples were prepared as polished thin  
49 sections and examined using an ISI ABT-55 scanning electron microscope with Link Analytical 10/55S  
50 EDAX facility. Measurements were made using elemental Zn, Se and Fe standards, and a pyrite (53.41 %  
51 S) standard. The carbon content of the shale was measured using a LECO CS225 elemental analyzer.

## 52 **Results**

53 Disseminated sulphides occur in a grey-black shale, whose mean organic carbon content is 0.22% (n=69).  
54 The shale is composed predominantly of quartz grains with a clay mineral matrix. Most sulphide crystals  
55 are in the size range 10 to 100 microns, but some pyrite nodules are on a millimeter-scale. The sulphides  
56 occur as clusters of sub-micron crystals and as single crystals (Figs. 2, 3). The sulphate mineral barite also  
57 occurs in the same rock. The most common phase is an iron sulphide, whose stoichiometry and cubic  
58 habit indicates is pyrite. Three other sulphides occur: Zn sulphide, Pb sulphide and Cd sulphide, which  
59 are assumed to be sphalerite, galena and greenockite. The Fe sulphide also contains variable traces of  
60 Cu. The sphalerite and pyrite both show micron-scale intergrowths with barite, which appears to be  
61 paragenetically later than the sulphides (Fig. 2). Paragenesis between the sulphides is not normally  
62 evident, but in some cases the Cd sulphide appears to be earlier than the sphalerite (Fig. 2).

63 Examination of ten crystal clusters showed that the Cd sulphide has a consistent composition.  
64 Quantitative analyses from crystals larger than 10 microns (Table 1) record trace levels of Zn (1.74 to  
65 5.90 wt.%) and Fe (0.14 to 1.00 wt.%). The mean composition is 74.7 wt. % Cd, 4.65 wt. % Zn, 0.40 wt. %

66 Fe and 21.6 wt. % S. Sphalerite crystals also contain trace levels of Cd up to 0.5 wt. %. A whole rock  
67 analysis of grey-black shale measured 14.3 ppm Cd and 132 ppm Zn. The traces of Zn in the Cd sulphide  
68 are also evident in X-ray maps (Fig. 3).

69 The timing of sulphide mineralization cannot be determined with absolute certainty. However, the  
70 larger pyrite nodules have a pre-compaction morphology (Parnell et al. 2010) and the sulphides  
71 mineralize uncompact pseudomorphs after gypsum (Fig. 2), suggesting that they were precipitated  
72 during early diagenesis, i.e. during the Mesoproterozoic. The Stoer Group sulphide crystal clusters are  
73 closely comparable in size and morphology to those forming in modern sulphide-rich wetlands, where  
74 anaerobic conditions have been deliberately engineered (Gammons & Frandsen 2001), further  
75 consistent with an early origin for them. The Pb-Zn-Cd sulphide assemblage has not been detected in the  
76 unconformably overlying Diabaig Formation of the early Neoproterozoic (~1.0 Ga) Torridon Group,  
77 which contains grey shales with limited organic carbon contents comparable to those of the Stoer  
78 Group.

## 79 **Discussion**

### 80 *Mineralogy*

81 The Cd sulphide is most likely to be the mineral greenockite, which occurs in comparable carbonaceous  
82 sediments elsewhere (Ripley et al. 1990, Lesven et al. 2010, Fleurance et al. 2013). Cadmium forms  
83 mixed sulphides with Zn and Fe, and other published analyses for greenockite show levels of Zn and Fe  
84 very similar to those of the Stoer Group Cd sulphide (Table 2; Patterson 1985, Marcoux et al. 1993,  
85 Mogessie et al. 2009). Another Cd sulphide, hawleyite, a cubic dimorph of the greenockite, also occurs  
86 (Traill & Boyle 1955), but is much less widely reported. However, the significance of the occurrence lies  
87 in the redox control of Cd sulphide precipitation.

88 *Oxygenation in the Stoer Group environment*

89 The section in which the Cd sulphide occurs is one in which the degree of oxidation requires careful  
90 judgment. The low organic carbon contents for the grey-black shale probably represent only about 30%  
91 of the organic carbon content before thermal maturation to their current state of mild regional  
92 metamorphism (Cornford 1998), suggesting initial values of about 0.7%. The initial value could have  
93 been even greater, if some carbon had been utilized during anaerobic degradation. However, even these  
94 corrected values are not high for shales, and not comparable to anoxic seafloor sediments which  
95 typically would be several times richer in carbon. Bearing in mind that the oxygen content in the late  
96 Mesoproterozoic atmosphere was about 10% of the present level (Canfield 2005), and bioturbation had  
97 not evolved, oxygen exposure times for organic matter (Hartnett et al. 1998) would have been much  
98 lower than today. Hence organic carbon was not oxidized so readily as in younger rocks (Canfield &  
99 Farquhar 2009), and the carbon content of the Stoer Group sediments is modest in those circumstances.  
100 There was clearly a contrast in depositional conditions between the shales which are grey-black and the  
101 overlying and underlying sandstones and shales which are red. However the contrast may have been  
102 limited: The grey-black shales contain numerous pseudomorphs after gypsum (Stewart 2002), indicating  
103 that sulphur was in the oxidized sulphate form during deposition. The Stoer Group sulphides were  
104 precipitated during early diagenesis, but sulphur isotope compositions indicate a contribution from both  
105 sulphide reducers and sulphide oxidizers (Parnell et al. 2010), and the petrographic observations of post-  
106 sulphide barite also show that sulphides were re-oxidized back to sulphates. The evidence indicates that  
107 the redox conditions were fluctuating close to the boundary between reducing and oxidizing. The  
108 occurrence of metalliferous reduction spheroids in red shales lower down in the Bay of Stoer Formation  
109 (Fig. 1) also reflects this fine balance of redox conditions (Spinks et al. 2010).

110 *Metal sources*

111 The measured 14.3 ppm Cd in a Stoer Group sample is more than an order of magnitude greater than a  
112 mean value of 0.8 ppm for shales (Fergusson 1990). The level of oxygenation was high enough by the  
113 Mesoproterozoic to allow weathering of sulphides on the continents (Reinhard et al. 2009). Anomalous  
114 sources of Zn, and hence Cd, in the hinterland of the Stoer Group include Palaeoproterozoic pegmatites  
115 in the Lewisian metamorphic basement (von Knorring & Dearnley 1960, Institute of Geological Sciences  
116 1982) and exhalative sulphide deposits in the Palaeoproterozoic Loch Maree Group (Jones et al. 1987).  
117 Both the Lewisian basement and the Loch Maree Group are unconformably overlain by, and could have  
118 contributed detritus to, the Stoer Group (Stewart 2002). The meteorite impact event that created the  
119 Stac Fada Member below could have been a source of metal, but metallic phases have not been  
120 detected in samples of the Stac Fada Member, so this is unlikely.

#### 121 *Cadmium sulphide precipitation*

122 The crustal abundance of Zn is about 500 times that of Cd, so the occurrence of Cd sulphide, rather than  
123 Cd-bearing sphalerite, calls for comment. Sphalerite is present in the rocks, so it was available to host  
124 the Cd. The ratio of Zn to Cd in natural waters varies widely, suggesting that major fractionation occurs  
125 in weathering and transport pathways and during subsequent burial in sediments (Nolting et al. 1999,  
126 Gerringa et al. 2001). This fractionation will reflect different responses to fluctuating redox and ionic  
127 strength values in ambient waters. Zinc and cadmium can both cycle between precipitation as sulphides  
128 and dissolution back into pore waters during seasonal fluctuations in water oxygenation (Holmes et al.  
129 1974, Framson & Leckle 1978). The stability constants of greenockite are greater than those of  
130 sphalerite (Dyrssen 1988). Consequently, Zn will redissolve from sediment back into pore waters at  
131 lower oxygen concentrations than Cd (Gerringa et al. 2001), resulting in higher Zn/Cd ratios in the pore  
132 waters than in the original depositional waters. At the limited and fluctuating oxygen levels in the Stoer  
133 Group sediments, there was potential for substantial fractionation of the two metals by repeated cycles

134 of precipitation and dissolution, and selective concentration of Cd in the relatively organic-rich grey-  
135 black shale facies, but not in the red facies. Modelling of groundwater geochemistry is restricted by our  
136 limited knowledge of the content of oxygen and other volatile species. However, we can assume that  
137 with depth the sediment was increasingly anoxic, and the ratio of sulphide to bicarbonate would  
138 increase. A phase diagram for the Cd-Zn-O-H-S-C system (Fig. 4, after Schwartz 2000) shows that the  
139 stability field for cadmium sulphide is greater than that for zinc sulphide, so they are likely to become  
140 fractionated under conditions of fluctuating sulphide/bicarbonate ratio, as is observed in the Stoer  
141 Group. Another example of fractionation of Cd from Zn and consequent precipitation of Cd sulphide in  
142 conditions of limited oxygenation, in Zn-Pb sulphide ore deposits, is given by Young et al. (1987).

143 Occurrences of Cd enrichment in Phanerozoic sedimentary rocks are almost exclusively in marine anoxic  
144 rocks or Mississippi Valley-type mineralization which typically include organic matter. The terrestrial  
145 occurrence of Cd sulphide in the Mesoproterozoic Stoer Group is therefore distinctive. The  
146 Mesoproterozoic non-marine Nonesuch Shale, USA, which is almost coeval with, and commonly  
147 compared with, the Stoer Group (Stewart 2002, Parnell et al. 2012, Strother 2012), also contains Cd  
148 sulphide mineralization. The Nonesuch Shale is organic-rich, like the Stoer Group (Smith 1990): the  
149 mean carbon content is greater in the Nonesuch Shale, but both represent anoxic environments. The  
150 Nonesuch Shale Cd sulphide has been alternatively interpreted as syngenetic or epigenetic (Brown 1971,  
151 1974). Additionally, near-coeval black shale in Arctic Canada, interpreted as a rift deposit not fully linked  
152 to the open ocean, also contains a Cd enrichment (Turner & Kamber 2012). The occurrence of at least  
153 two examples in Mesoproterozoic terrestrial rocks is striking and suggests an environment distinct from  
154 that in younger rocks. The most distinct aspect of the environment was the lower level of oxygenation.

155 We cannot exclude a biological role in the Cd sulphide precipitation, especially given its occurrence in  
156 terrestrial sediments containing organic carbon. Lacustrine algae, the assumed progenitor of the Stoer

157 Group organic matter, are today concentrating Cd in the Great Lakes (Intwala et al. 2008), and microbial  
158 activity is known to immobilize Cd in soils (Kurek & Bollag 2004). Further insight onto the possibilities of  
159 a genetic relationship to biological activity may be gained in the future through Cd isotope  
160 measurements (Ripperger et al. 2007).

## 161 **Conclusions**

162 The occurrence of Cd sulphide in the Mesoproterozoic sediments of the Stoer Group is unusual because  
163 Cd normally occurs as a trace component of sphalerite. However it can be understood in the context of  
164 low oxygenation of the atmosphere during the Mesoproterozoic. In those circumstances, even near-  
165 surface sediments with only limited organic carbon concentrations were periodically anoxic, when Cd  
166 sulphide could precipitate. This may have been a time when the oxygen content was high enough to  
167 cause sulphide weathering on the continents, and subsequent transport of metals and sulphate, but  
168 sufficiently limited to cause their ready fixation as sulphides in terrestrial sediments.

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## 170 **References**

171 Anbar, A.D. and Knoll, A.H. (2002) Proterozoic ocean chemistry and evolution: A bioinorganic bridge?  
172 *Science*, **297**, 1137-1142.

173 Andrews, S.D., Trewin, N.H., Hartley, A.J. and Weedon, G.P. (2010) Solar variance recorded in lacustrine  
174 deposits from the Devonian and Proterozoic of Scotland. *Journal of the Geological Society*, **167**, 847-856.

175 Brown, A.C. (1971) Zoning in the White Pine copper deposit, Ontonagon County, Michigan. *Economic*  
176 *Geology*, **66**, 543-573.



- 177 Brown, A.C. (1974) An epigenetic origin for stratiform Cd-Pb-Zn sulfides in the Lower Nonesuch Shale,  
178 White Pine, Michigan. *Economic Geology*, **69**, 271-274.
- 179 Canfield, D.E. 2005. The early history of atmospheric oxygen: Homage to Robert M. Garrels. *Annual*  
180 *Review of Earth and Planetary Sciences*, **33**, 1-36.
- 181 Canfield, D.E. and Farquhar, J. (2009) Animal evolution, bioturbation, and the sulfate concentration of  
182 the oceans. *Proceedings of the National Academy of Sciences*, **106**, 8123-8127.
- 183 Chaillou, G., Anschutz, P., Lavaux, G., Schäfer, J. and Blanc, G. (2002) The distribution of Mo, U and Cd in  
184 relation to major redox species in muddy sediments of the Bay of Biscay. *Marine Chemistry*, **80**, 41-59.
- 185 Cornford, C. (1998) Source rocks and hydrocarbons of the North Sea, in Glennie, K.W., ed., *Petroleum*  
186 *Geology of the North Sea* (4<sup>th</sup> ed.): Oxford, Blackwell, p.376-462.
- 187 Darabi, M.H. and Piper, J.D.A. (2004) Palaeomagnetism of the (Late Mesoproterozoic) Stoer Group,  
188 Northwest Scotland: implications for diagenesis, age and relationship to the Grenville Orogeny.  
189 *Geological Magazine*, **141**, 15-39.
- 190 Dyrssen, D. (1988) Sulfide complexation in surface seawater. *Marine Chemistry*, **24**, 143-153.
- 191 Falk, H., Lavergren, U. and Bergbäck, B. (2006) Metal mobility in alum shales from Öland, Sweden.  
192 *Journal of Geochemical Exploration*, **90**, 157-165.
- 193 Fergusson, J.E. (1990) *The Heavy Elements: Chemistry, Environmental Impact and Health Effects*.  
194 Pergamon Press, Oxford.
- 195 Fleurance, S., Cuney, M., Malartre, F. and Reyx, J. (2013) Origin of the extreme polymetallic enrichment  
196 (Cd, Cr, Mo, Ni, U, V, Zn) of the Late Cretaceous-Early Tertiary Belqa Group, central Jordan.  
197 *Palaeogeography, Palaeoclimatology, Palaeoecology*, **369**, 201-219.

198 Framson, P.E. and Leckle, J.O. (1978) Limits of coprecipitation of cadmium and ferrous sulfides.  
199 *Environmental Science and Technology*, **12**, 465-469.

200 Gammons, C.H. and Frandsen, A.K. (2001) Fate and transport of metals in H<sub>2</sub>S-rich waters at a treatment  
201 wetland. *Geochemical Transactions*, **1**, doi:10.1039/b0082341

202 Gerringa, L.J.A., de Baar, H.J.W., Nolting, R.F. and Paucot, H. (2001) The influence of salinity on the  
203 solubility of Zn and Cd sulphides in the Scheldt estuary. *Journal of Sea Research*, **46**, 201-211.

204 Hartnett, H.E., Keil, R.G., Hedges, J.I. and Devol, A.H. (1998) Influence of oxygen exposure time on  
205 organic carbon preservation in continental margin sediments. *Nature*, **391**, 572-574.

206 Holmes, C.W., Slade, E.A. and McLerran, C.J. (1974) Migration and redistribution of zinc and cadmium in  
207 marine estuarine system. *Environmental Science and Technology*, **8**, 255-259.

208 Institute of Geological Sciences (1982) Regional Geochemical Atlas: Sutherland. London, Institute of  
209 Geological Sciences.

210 Intwala, A., Patey, T.D., Polet, D.M. and Twiss, M.R. (2008) Nutritive substitution of zinc by cadmium and  
211 cobalt in phytoplankton isolated from the Lower Great Lakes. *Journal of Great Lakes Research*, **34**, 1-11.

212 Jones, E.M., Rice, C.M. and Tweedie, J.R. (1987) Lower Proterozoic stratiform sulphide deposits in Loch  
213 Maree Group, Gairloch, northwest Scotland. *Transactions of the Institution of Mining and Metallurgy*,  
214 **96**, B128-B140.

215 Kurek, E. and Bollag, J-M. (2004) Microbial immobilization of cadmium released from CdO in the soil.  
216 *Biogeochemistry*, **69**, 227-239.

217 Lesven, L., Lourino-Cabana, B., Billon, G., Recourt, P., Ouddane, B., Mikkelsen, O. and Boughriet, A.  
218 (2010) On metal diagenesis in contaminated sediments of the Deûle river (northern France). *Applied*  
219 *Geochemistry*, **25**, 1361-1373.

220 Marcoux, E., Milesi, J., Sohearto, S. and Rinawan, R. (1993) Noteworthy Mineralogy of the Au-Ag-Sn-  
221 W(Bi) Epithermal Ore Deposit of Cirotan, West Java, Indonesia, *Canadian Mineralogist*, **31**, 727-744.

222 Mogessie, A., Gallien, F., Bernhard, F., Bauer, C., Castro De Machuca, B., Meissl, E., Bjerg, E. and  
223 Delpino, S. (2009) Greenockite and Associated Sulfide Mineralization from the Caledonia Group Mines,  
224 Blanca Creek, LA Huerta Range, San Juan Province, Argentina, *Canadian Mineralogist*, **47**, 129-141.

225 Morel, F.M.M. (2008) The co-evolution of phytoplankton and trace element cycles in the oceans.  
226 *Geobiology*, **6**, 318-324.

227 Nolting, R.F., de Baar, H.J.W., Timmermans, K.R. and Bakker, K. (1999) Chemical fractionation of zinc  
228 versus cadmium among other metals nickel, copper and lead in the northern North Sea. *Marine*  
229 *Chemistry*, **67**, 267-287.

230 Paillet, D., Bard, E., Rostek, F., Mortlock, R. and van Geen, A. (2002) Burial of redox-sensitive metals and  
231 organic matter in the equatorial Indian Ocean linked to precession. *Geochimica et Cosmochimica Acta*,  
232 **66**, 849-865.

233 Parnell, J., Boyce, A.J., Mark, D., Bowden, S. and Spinks, S. (2010) Early oxygenation of the terrestrial  
234 environment during the Mesoproterozoic. *Nature*, **468**, 290-293.

235 Parnell, J., Hole, M., Boyce, A.J., Spinks, S. and Bowden, S. (2012) Heavy metal, sex and granites: Crustal  
236 differentiation and bioavailability in the mid-Proterozoic. *Geology*, **40**, 751-754.

237 Parnell, J., Mark, D., Fallick, A.E., Boyce, A. and Thackrey, S. (2011) The age of the Mesoproterozoic Stoer  
238 Group sedimentary and impact deposits, NW Scotland. *Journal of the Geological Society, London*, **168**,  
239 349-358.

240 Patterson, D.J. (1985) Zincian Greenockite in Stratiform Lead-Zinc-Silver Mineralization at Lady Loretta,  
241 Northwest Queensland, *Canadian Mineralogist*, **23**, 89-94.

242 Perkins, R.B. and Foster, A.L. (2004) Mineral affinities and distribution of selenium and other trace  
243 elements in black shale and phosphorite of the Phosphoria Formation. *Handbook of Exploration and*  
244 *Environmental Geochemistry*, **8**, 251-295.

245 Pufahl, P.K. and Hiatt, E.E. (2012) Oxygenation of the Earth's atmosphere-ocean system: A review of  
246 physical and chemical sedimentologic responses. *Marine and Petroleum Geology*, **32**, 1-20.

247 Reinhard, C.T., Raiswell, R., Scott, C., Anbar, A.D. and Lyons, T.W. (2009) A late Archean sulfidic sea  
248 stimulated by early oxidative weathering of the continents. *Science*, **326**, 713-716.

249 Ripley, E.M., Shaffer, N.R. and Gilstrap, M.S. (1990) Distribution and geochemical characteristics of metal  
250 enrichment in the New Albany Shale (Devonian-Mississippian), Indiana. *Economic Geology*, **85**, 1790-  
251 1807.

252 Ripperger, S., Rehkämper, M., Porcelli, D. and Halliday, A.N. (2007) Cadmium isotope fractionation in  
253 seawater – A signature of biological activity. *Earth and Planetary Science Letters*, **261**, 670-684.

254 Rosenthal, Y., Lam, P., Boyle, E.A. and Thomson, J. (1995) Authigenic cadmium enrichments in suboxic  
255 sediments: Precipitation and postdepositional mobility. *Earth and Planetary Science Letters*, **132**, 99-  
256 111.

257 Saito, M.A., Sigman, D.M. and Morel, F.M.M. (2003) The bioinorganic chemistry of the ancient ocean:  
258 the co-evolution of cyanobacterial metal requirements and biogeochemical cycles at the Archean-  
259 Proterozoic boundary? *Inorganica Chimica Acta*, **356**, 308-318.

260 Schwartz, M.O. (2000) Cadmium in zinc deposits: economic geology of a polluting element. *International*  
261 *Geology Review*, **42**, 445-469.

262 Smith, M.A. (1990) Lacustrine oil shale in the Geologic Record. *American Association of Petroleum*  
263 *Geologists Memoir*, **50**, 43-60.

264 Spinks, S.C., Parnell, J. and Bowden, S.A. (2010) Reduction spots in the Mesoproterozoic age:  
265 implications for life in the early terrestrial record. *International Journal of Astrobiology*, **9**, 209-216.

266 Stewart, A.D. (2002) The later Proterozoic Torridonian rocks of Scotland: their sedimentology,  
267 geochemistry and origin. *Geological Society, London, Memoir* **24**.

268 Strother, P.K. (2012) Paleobiology of earliest Neoproterozoic lakes. *Geological Society of America*  
269 *Abstracts with Programs*, vol. **44**, no. 7, 315.

270 Thomson, J., Nixon, S., Croudace, I.W., Pedersen, T.F., Brown, L., Cook, G.T. and MacKenzie, A.B. (2001)  
271 Redox-sensitive element uptake in north-east Atlantic Ocean sediments (Benthic Boundary Layer  
272 Experiment sites). *Earth and Planetary Science Letters*, **184**, 535-547.

273 Traill, R.J. and Boyle, R.W. (1955) Hawleyite, isometric cadmium sulphide, a new mineral. *American*  
274 *Mineralogist*, **40**, 555-559.

275 Turner, E.C. and Kamber, B.S. (2012) Arctic Bay Formation, Borden Basin, Nunavut (Canada): Basin  
276 evolution, black shale, and dissolved metal systematics in the Mesoproterozoic ocean. *Precambrian*  
277 *Research*, **208-211**, 1-18.

278 Van Geen, A., McCorkle, D.C. and Klinkhammer, G.P. (1995) Sensitivity of the phosphate-cadmium-  
279 carbon isotope relation in the ocean to cadmium removal by suboxic sediments. *Paleoceanography*, **10**,  
280 159-169.

281 Von Knorring, O. and Dearnley, R. (1960) The Lewisian pegmatites of south Harris, Outer Hebrides.  
282 *Mineralogical Magazine*, **32**, 366-378.

283 Ye, L., Cook, N.J., Liu, T., Ciobanu, C.L., Gao, W. and Yang, Y. (2012) The Niujaotang Cd-rich zinc deposit,  
284 Duyun, Guizhou province, southwest China: ore genesis and mechanisms of cadmium concentration.  
285 *Mineralium Deposita*, **47**, 683-700.

286 Young, B., Bridges, T.F. and Ineson, P.R. (1987) Supergene cadmium mineralization in the Northern  
287 Pennine Orefield. *Proceedings of the Yorkshire Geological Society*, **46**, 275-278.

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291 Table 1. Compositions (wt. %) of Cadmium Sulphide Crystals in Stoer Group

wt%	1	2	3	4	5	6	7	8	9	10
<b>Cd</b>	72.69	74.75	73.12	76.94	77.59	73.88	72.19	76.69	73.55	75.98
<b>Fe</b>	0.21	0.28	0.34	0.14	0.38	0.62	0.10	0.30	0.42	0.30
<b>Zn</b>	5.06	4.03	5.90	1.94	2.12	3.21	4.86	1.74	3.75	2.65
<b>S</b>	21.67	21.61	22.13	21.66	21.50	21.29	22.37	21.02	21.62	21.08
<b>Total</b>	99.62	100.67	101.50	100.68	101.59	99.01	100.41	99.75	99.34	100.01

292

293 Table 2. Mean Compositions (wt. %) of Cadmium Sulphide from Stoer Group (this paper) and

294 Greenockite in Literature (see text)

wt%	Argentina (n = 8)	Australia (n = 6)	Indonesia (n = 20)	Scotland (n = 10)
<b>Cd</b>	71.89	71.3	72.95	74.74
<b>Fe</b>	<0.28	NQ	NQ	0.40
<b>Zn</b>	4.78	6.65	4.76	4.65
<b>S</b>	22.68	22.5	21.95	21.60
<b>Total</b>	99.34	100.45	99.66	101.39

295

296 NQ = Not Quantified, n = Number of grains analysed

297

298

299 **Figure Captions**

300

301 Fig. 1. Location maps for Bay of Stoer (BoS) locality, and summary geological succession for Bay of Stoer  
302 showing horizon yielding Cd sulphide.

303 Fig. 2. Backscattered electron micrographs of sulphides in grey-black shale, Bay of Stoer. A, crystal  
304 cluster of greenockite (light grey) and galena (bright); B, rhomboid pseudomorph after gypsum,  
305 mineralized by pyrite (dull grey), then subsequently by barite (bright).

306 Fig. 3. Backscattered electron micrograph and X-ray maps for cadmium sulphide crystal, Bay of Stoer. A,  
307 crystal cluster of greenockite and adjacent smaller cluster of sphalerite; B, X-ray map for cadmium; D. X-  
308 ray map for zinc, showing traces of zinc in greenockite, and zinc-rich nature of smaller crystal cluster.  
309 Image field width 100 microns.

310 Fig. 4. Phase diagram for the Zn-Cd-O-H-S-C system at 25 °C (after Schwartz 2000). Greater stability field  
311 for Cd sulphide than Zn sulphide would enhance fractionation between the metals as  
312 bicarbonate/sulphide ratios fluctuated.

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