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.

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   fluviatile and lacustrine environments (Stewart 2002). The succession includes a distinctive unit of grey-

39   black shale in the Poll a' Mhuilt 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 uncompacted 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.

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

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

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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)
Cd	71.89	71.3	72.95	74.74
Fe	<0.28	NQ	NQ	0.40
Zn	4.78	6.65	4.76	4.65
S	22.68	22.5	21.95	21.60
Total	99.34	100.45	99.66	101.39

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

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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.

313

A — Geological map showing distribution of Phanerozoic & Other Strata, Torridon Group, Stoer Group, and Lewisian Complex, with faults and thrust faults. Moine Thrust labelled at right. BoS circled. Scale bar: 0 to 15 km.

Legend

Symbol	Description
	Phanerozoic & Other Strata
	Torridon Group
	Stoer Group
	Lewisian Complex
//	Fault
⊥⊥	Thrust Fault

B — Map of Scotland with study area outlined.

C — Stratigraphic column. Stoer Group comprising Meall Dearg Formation, Bay of Stoer Formation (including Poll à Mhuilt Mbr. and Stac Fada Mbr.), and Clachtoll Formation, overlying Lewisian Complex. Cadmium sulphides arrowed in the Poll à Mhuilt Mbr. Scale bar: 100 m.

Symbol	Description
o	Pebbly Sandstone
∿	Trough cross-bedding
	Dark Shale
	Limestone
	Impactite
	Red Shale
	Sandstone
▲	Breccia
	Gneiss