

Cadmium sulfide in a Mesoproterozoic terrestrial environment

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ABSTRACT

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

KEYWORDS: cadmium, greenockite, Mesoproterozoic, Torridonian, oxygenation, Scotland.

Introduction

WE report Cd sulfide mineralization in the Mesoproterozoic of Scotland. The occurrence of Cd sulfides in rocks deposited in a terrestrial environment is unusual, and we discuss this in the context of the limited oxygenation of the Mesoproterozoic atmosphere.

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

Cadmium is a highly redox-sensitive element (van Geen *et al.*, 1995; Rosenthal *et al.*, 1995;

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

The Cd sulfide documented here is in the late Mesoproterozoic Stoer Group, Torridonian Supergroup, northwest Scotland. The Stoer Group was deposited in a continental setting including alluvial fan, fluvial and lacustrine environments (Stewart, 2002). The succession includes a distinctive unit of grey-black shale in the Poll a' Mhuilte Member of the Bay of Stoer

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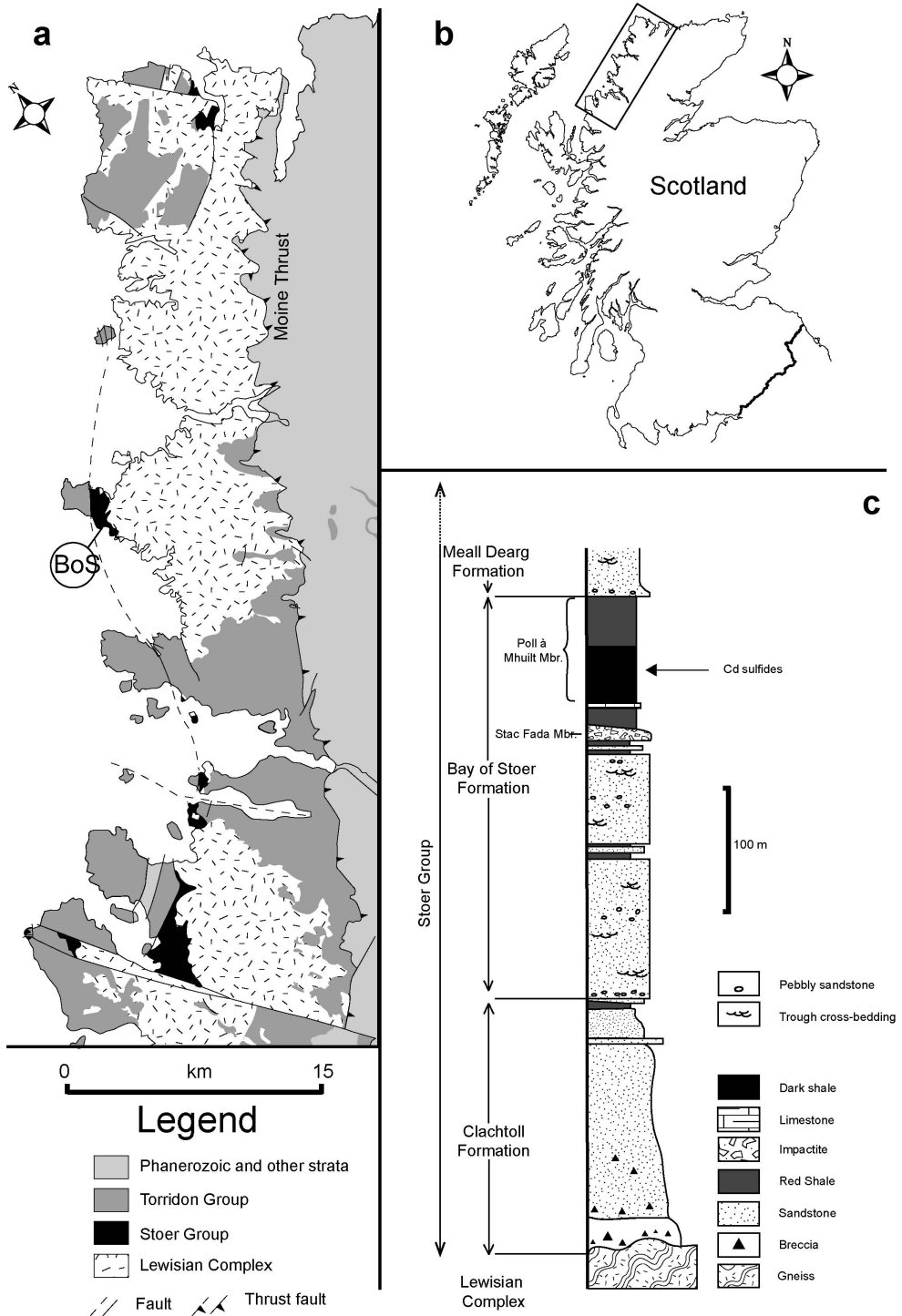


FIG. 1. Location maps for Bay of Stoer (BoS) locality, and summary geological succession for Bay of Stoer showing the horizon yielding Cd sulfide.

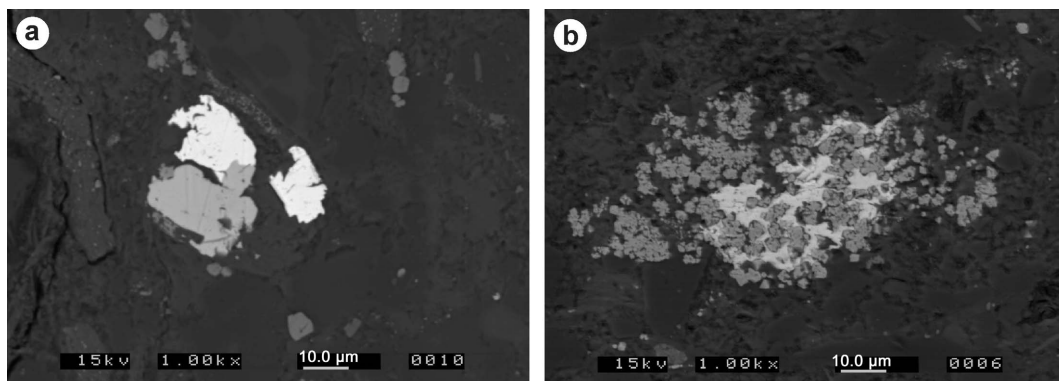


FIG. 2. Backscattered electron micrographs of sulfides in grey-black shale, Bay of Stoer: (a) crystal cluster of greenockite (light grey) and galena (bright); (b) rhomboid pseudomorph after gypsum, mineralized by pyrite (dull grey), then subsequently by baryte (bright).

Formation (Fig. 1), interpreted as lacustrine (Stewart, 2002; Andrews *et al.*, 2010). The lake waters and groundwaters were carbonate-rich, as shown by calcite in the matrix of the black shale, a discrete limestone bed at the base of the black shale (Fig. 1) and calcite cements in the subjacent/superjacent shales. This unit closely follows a meteorite impact deposit dated at 1.18 Ga (Parnell *et al.*, 2011). Palaeomagnetic studies suggest a low latitude in the northern hemisphere (Darabi and Piper, 2004). The rocks have experienced low-grade regional metamorphism, but their sedimentary characteristics are perfectly preserved.

Methodology

Samples of the shale were collected from the north side of the Bay of Stoer (section described

by Stewart, 2002, National Grid Reference NC 032285). The samples were prepared as polished thin sections and examined using an ISI ABT-55 scanning electron microscope with Link Analytical 10/55S EDAX facility. Measurements were made using elemental Zn, Se and Fe standards, and a pyrite (53.41% S) standard. The carbon content of the shale was measured using a LECO CS225 elemental analyser.

Results

Disseminated sulfides occur in a grey-black shale, whose mean organic carbon content is 0.22% ($n = 69$). The shale is composed predominantly of quartz grains with a clay mineral matrix. Most sulfide crystals are in the size range 10–100 μm , but some pyrite nodules are on a millimetre-scale. The sulfides occur as clusters of sub-micron

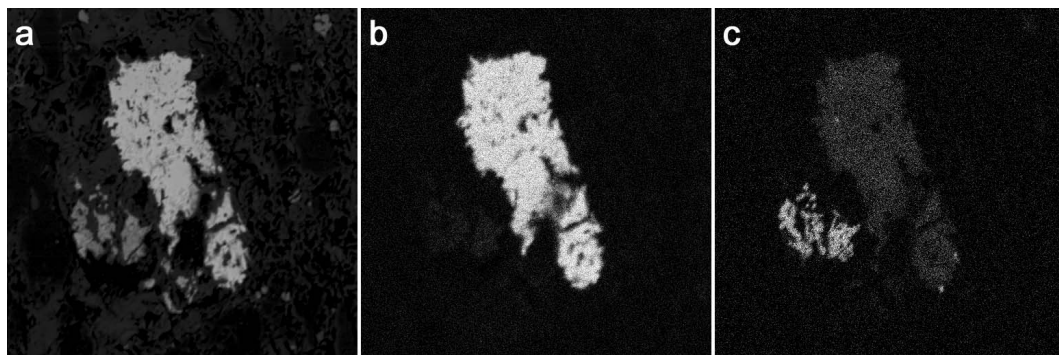


FIG. 3. Backscattered electron micrograph and X-ray maps for a Cd sulfide crystal, Bay of Stoer: (a) crystal cluster of greenockite and adjacent smaller cluster of sphalerite; (b) X-ray map for Cd; (c) X-ray map for Zn, showing traces of Zn in greenockite, and the Zn-rich nature of the smaller crystal cluster. Image field width 100 μm .

crystals and as single crystals (Figs 2, 3). The sulfate mineral baryte also occurs in the same rock. The most common phase is an Fe sulfide, the stoichiometry and cubic habit of which indicate is pyrite. Three other sulfides occur: Zn sulfide, Pb sulfide and Cd sulfide, which are assumed to be sphalerite, galena and greenockite, respectively. The Fe sulfide also contains variable traces of Cu. The sphalerite and pyrite both show micron-scale intergrowths with baryte, which appears to be paragenetically later than the sulfides (Fig. 2). Paragenesis between the sulfides is not normally evident, but in some cases the Cd sulfide appears to be earlier than the sphalerite (Fig. 2).

Examination of ten crystal clusters showed that the Cd sulfide has a consistent composition. Quantitative analyses from crystals larger than 10 μm (Table 1) record trace levels of Zn (1.74 to 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.% Fe and 21.6 wt.% S. Sphalerite crystals also contain trace levels of Cd up to 0.5 wt.%. A whole-rock analysis of grey-black shale measured 14.3 ppm Cd and 132 ppm Zn. The traces of Zn in the Cd sulfide are also evident in X-ray maps (Fig. 3).

The timing of sulfide mineralization cannot be determined with absolute certainty. However, the larger pyrite nodules have a pre-compaction morphology (Parnell *et al.*, 2010) and the sulfides mineralize uncompacted pseudomorphs after gypsum (Fig. 2), suggesting that they were precipitated during early diagenesis, i.e. during the Mesoproterozoic. The Stoer Group sulfide crystal clusters are closely comparable in size and morphology to those forming in modern sulfide-rich wetlands, where anaerobic conditions have been deliberately engineered (Gammons and Frandsen, 2001), further consistent with an early origin for them. The Pb-Zn-Cd sulfide assemblage

has not been detected in the unconformably overlying Diabaig Formation of the early Neoproterozoic (~1.0 Ga) Torridon Group, which contains grey shales with limited organic carbon contents comparable to those of the Stoer Group.

Discussion

Mineralogy

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

Oxygenation in the Stoer Group environment

The section in which the Cd sulfide occurs is one in which the degree of oxidation requires careful judgement. The small organic carbon contents for the grey-black shale probably represent only ~30% of the organic carbon content before thermal maturation to their current state of mild regional metamorphism (Cornford, 1998), suggesting initial values of ~0.7%. The initial value could have been even greater, if some carbon had been utilized during anaerobic degradation. However, even these corrected values are not high for shales, and not comparable to anoxic seafloor sediments which typically would be several times richer in carbon. Bearing in mind that the oxygen content in the late

TABLE 1. Compositions (wt.%) of Cd sulfide crystals in the 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

MESOPROTEROZOIC CADMIUM SULFIDE

TABLE 2. Mean compositions (wt.%) of Cd sulfide from the Stoer Group (present study) and of greenockite in the literature (see text).

Wt.%	Argentina (<i>n</i> = 8) (Mogessie <i>et al.</i> , 2009)	Australia (<i>n</i> = 6) Patterson, 1985)	Indonesia (<i>n</i> = 20) (Marcoux <i>et al.</i> , 1993)	Scotland (<i>n</i> = 10) (Present study)
Cd	71.89	71.3	72.95	74.74
Fe	<0.28	n.q.	n.q.	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

n.q. = not quantified, *n* = number of grains analysed

Mesoproterozoic atmosphere was ~10% of the present level (Canfield, 2005), and bioturbation had not evolved, oxygen exposure times for organic matter (Hartnett *et al.*, 1998) would have been much lower than today. Hence organic carbon was not oxidized so readily as in younger rocks (Canfield and Farquhar, 2009), and the carbon content of the Stoer Group sediments is modest in those circumstances. There was clearly a contrast in depositional conditions between the shales which are grey-black and the overlying and underlying sandstones and shales which are red. However the contrast may have been limited: The grey-black shales contain numerous pseudomorphs after gypsum (Stewart, 2002), indicating that sulfur was in the oxidized sulfate form during deposition. The Stoer Group sulfides were precipitated during early diagenesis, but sulfur isotope compositions indicate a contribution from both sulfide reducers and sulfide oxidizers (Parnell *et al.*, 2010), and the petrographic observations of post-sulfide baryte also show that sulfides were re-oxidized back to sulfates. The evidence indicates that the redox conditions were fluctuating close to the boundary between reducing and oxidizing. The occurrence of metalliferous reduction spheroids in red shales lower down in the Bay of Stoer Formation (Fig. 1) also reflects this fine balance of redox conditions (Spinks *et al.*, 2010).

Metal sources

The measured 14.3 ppm Cd in a Stoer Group sample is more than an order of magnitude greater than a mean value of 0.8 ppm for shales (Fergusson, 1990). The level of oxygenation was high enough by the Mesoproterozoic to allow weathering of sulfides on the continents (Reinhard

et al., 2009). Anomalous sources of Zn, and hence Cd, in the hinterland of the Stoer Group include Palaeoproterozoic pegmatites in the Lewisian metamorphic basement (von Knorring and Dearnley, 1960; Institute of Geological Sciences, 1982) and exhalative sulfide deposits in the Palaeoproterozoic Loch Maree Group (Jones *et al.*, 1987). Both the Lewisian basement and the Loch Maree Group are unconformably overlain by, and could have contributed detritus to, the Stoer Group (Stewart, 2002). The meteorite impact event that created the Stac Fada Member below could have been a source of metal, but metallic phases have not been detected in samples of the Stac Fada Member, so this is unlikely.

Cd sulfide precipitation

The crustal abundance of Zn is ~500 times that of Cd, so the occurrence of Cd sulfide, rather than Cd-bearing sphalerite, calls for comment. Sphalerite is present in the rocks, so it was available to host the Cd. The ratio of Zn to Cd in natural waters varies widely, suggesting that major fractionation occurs in weathering and transport pathways and during subsequent burial in sediments (Nolting *et al.*, 1999; Gerringa *et al.*, 2001). This fractionation will reflect different responses to fluctuating redox and ionic strength values in ambient waters. Zinc and Cd can both cycle between precipitation as sulfides and dissolution back into pore waters during seasonal fluctuations in water oxygenation (Holmes *et al.*, 1974; Framson and Leckle, 1978). The stability constants of greenockite are greater than those of sphalerite (Dyrssen, 1988). Consequently, Zn will redissolve from sediment back into pore waters at lower oxygen concentrations than Cd (Gerringa *et al.*, 2001), resulting in higher Zn/Cd ratios in the

pore waters than in the original depositional waters. At the limited and fluctuating oxygen levels in the Stoer Group sediments, there was potential for substantial fractionation of the two metals by repeated cycles of precipitation and dissolution, and selective concentration of Cd in the relatively organic-rich grey-black shale facies, but not in the red facies. Modelling of ground-water geochemistry is restricted by our limited knowledge of the content of oxygen and other volatile species. However, we can assume that with depth the sediment was increasingly anoxic, and the ratio of sulfide to bicarbonate would increase. A phase diagram for the Cd–Zn–O–H–S–C system (Fig. 4, after Schwartz, 2000) shows that the stability field for Cd sulfide is greater than that for Zn sulfide, so they are likely to become fractionated under conditions of fluctuating sulfide/bicarbonate ratio, as is observed in the Stoer Group. Another example of fractionation of Cd from Zn and consequent precipitation of Cd sulfide in conditions of limited oxygenation, in Zn–Pb sulfide ore deposits, is given by Young *et al.* (1987).

Occurrences of Cd enrichment in Phanerozoic sedimentary rocks are almost exclusively in

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

We cannot exclude a biological role in the Cd sulfide precipitation, especially given its occurrence in terrestrial sediments containing organic carbon. Lacustrine algae, the assumed progenitor of the Stoer Group organic matter, are today concentrating Cd in the Great Lakes (Intwala *et al.*, 2008), and microbial activity is known to immobilize Cd in soils (Kurek and Bollag, 2004). Further insight into the possibilities of a genetic relationship to biological activity may be gained in the future through Cd isotope measurements (Ripperger *et al.*, 2007).

Conclusions

The occurrence of Cd sulfide in the Mesoproterozoic sediments of the Stoer Group is unusual because Cd normally occurs as a trace component of sphalerite. However it can be understood in the context of low oxygenation of the atmosphere during the Mesoproterozoic. In those circumstances, even near-surface sediments were periodically anoxic, when Cd sulfide could precipitate. This may have been a time when the oxygen content was high enough to cause sulfide weathering on the continents, and subsequent transport of metals and sulfate, but sufficiently limited to cause their ready fixation as sulfides in terrestrial sediments.

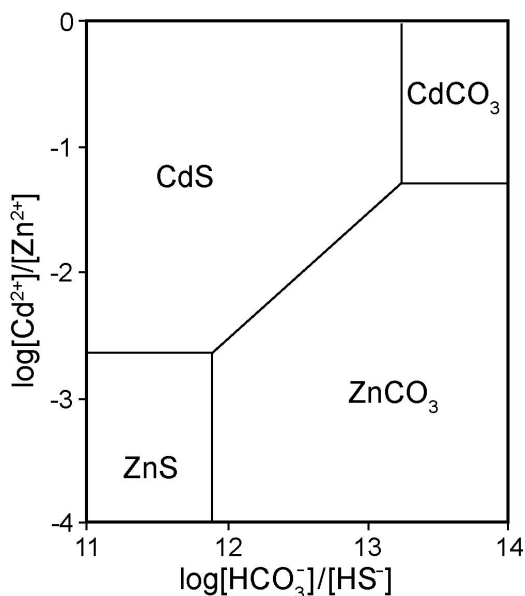


FIG. 4. Phase diagram for the Zn–Cd–O–H–S–C system at 25°C (after Schwartz, 2000). The larger stability field for Cd sulfide than Zn sulfide would enhance fractionation between the metals as bicarbonate/sulfide ratios fluctuated.

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