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## Speciation of trace elements in the Bowland Shale

--Manuscript Draft--

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<b>Abstract:</b>	Samples of Bowland Shale and equivalents in Ireland, representing a range of thermal maturities from oil window to gas window, contain trace elements distributed through multiple residences. The trace element distribution reflects the depositional environment, and influences subsequent element release. Measurements of Se, Cu, As, U and Mo indicate variable retention in loosely-bound and strongly-bound forms. The trace elements are especially associated with diagenetic pyrite. Shales from Ireland, at higher thermal maturity, have relatively high proportions of loosely-bound Se, Cu and As, which may reflect expulsion from the pyrite during recrystallization. The shale samples consistently contain high contents of organic matter, reflecting deposition in an anoxic environment. The Se, Mo and U in particular may be bound to organic matter, which may have adverse environmental impacts upon weathering of the shale.
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**Speciation of trace elements in the Bowland Shale**

**Parnell, J., Nwoko, K., Feldmann, J., Armstrong, J.**

**GSLSpecPub2020-195R1**

Response to Editors comments on R1 (by line number on track change version)

9. Abstract is lengthened a little bit, including a clause on trace elements. An introduction to trace elements has been added to the Introduction, which is the correct place for it.

45. Reference inserted.

66. Reference inserted.

73. Two references inserted.

92. Acronym now explained here.

96. Reworded more elegantly.

109 (x2). Words deleted and tense made consistent.

110. Explanation for acronym moved earlier

121, 166. (This reflects contributions by two different chemists). I have ensured these two bits of writing are now consistent.

177. Reference to syngensis inserted.

243. Reworded.

257. 'High temperature' deleted.

271. Clumsy sentence simplified to flow properly.

314. New sentences added on Pendle Hill, and future studies.

## 1 Speciation of trace elements in the Bowland Shale

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8

### 9 Abstract

10 Samples of Bowland Shale and equivalents in Ireland, representing a range of thermal maturities  
11 from oil window to gas window, contain trace elements distributed through multiple residences.

12 **The trace element distribution reflects the depositional environment, and influences subsequent**  
13 **element release.** Measurements of Se, Cu, As, U and Mo indicate variable retention in loosely-  
14 bound and strongly-bound forms. **The trace elements are especially associated with diagenetic**  
15 **pyrite.** Shales from Ireland, at higher thermal maturity, have relatively high proportions of loosely-  
16 bound Se, Cu and As, which may reflect expulsion from **the** pyrite during recrystallization. The  
17 shale samples consistently contain high contents of organic matter, **reflecting deposition in an**  
18 **anoxic environment.** ~~to which~~**The** Se,- Mo and U in particular may be bound **to organic matter,** and  
19 which may have adverse environmental impacts **upon weathering of the shale.**

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21 **Introduction**

22 Data for trace element contents in shales contribute to our understanding of shale deposition and  
23 subsequent behaviour. Concentrations and ratios of trace elements reflect depositional  
24 environments, including provenance and redox state, and also the availability of nutrients to the  
25 ambient biota. Once deposited, the contents influence mineralogy and diagenetic processes, and in  
26 some cases could constitute resources of rare elements.

27 Black shales, such as the Bowland Shale, may be rich in trace elements for a variety of reasons,  
28 relating to depositional environment, diagenesis and metamorphism. These aspects of geological  
29 history are manifested in variations in content of organic matter, sulphide (pyrite) and clay minerals,  
30 all of which could influence the concentration of trace elements. For example, many elements are  
31 co-precipitated with pyrite, both in the depositional environment and during diagenesis (Large et al.  
32 2009, Gregory et al. 2015).

33 The speciation of trace elements relates to their residence within the host rock. Data for speciation  
34 helps to understand:

- 35 (i) The mineral residence of trace elements in the depositional environment, particularly  
36 reflecting variations in oxidation (e.g. Alagarsamy et al. 2005, Peltier et al. 2005).
- 37 (ii) Changes to the residence of trace elements during burial diagenesis, which affects their  
38 availability for reactions and liberation into solution (e.g. Abanda & Hannigan 2006).
- 39 (iii) Consequent extraction efficiency of trace elements that are resources for future  
40 technologies, such as rare earth elements (e.g. Josso et al. 2018).
- 41 (iv) Potential release of trace elements during weathering, for example the surface  
42 alteration of the sulphide fraction can release large volumes of trace elements (e.g.  
43 Courtin-Nomade et al. 2009, Fairgray et al. 2020).

44 This study focusses on the Bowland Shale and time-equivalents in Ireland including the Clare Shale,  
45 which were deposited in a series of sub-basins within an epicontinental sea on the Laurasian  
46 continent, during late Viséan-early Namurian time (Waters & Condon 2012, Könitzer et al. 2014,  
47 Gross et al. 2015, Newport et al. 2018). Earlier Viséan carbonate sediments were followed by deep  
48 water siliciclastic sediments at the end-Viséan, and progradation of deltas from the north in the  
49 Namurian. The Bowland Shales consist of hemipelagic mudrocks and interbedded turbiditic/deltaic  
50 sandstones. These rocks were variably buried up to several kilometers depth, with maximum burial  
51 achieved at end-Carboniferous and end-Cretaceous, with intervening Permian uplift (Andrews 2013).

52 In Ireland, the thermal history reflects a combination of burial and a heat pulse during the Permo-  
53 Carboniferous Variscan Orogeny (Hitzman et al. 1998).

54 The Bowland Shale, and equivalent rocks in Ireland (Fig. 1), is suitable for a study of speciation, as it  
55 has anomalously high contents of several trace elements (Parnell et al. 2016, [Emmings et al. 2020](#)). It  
56 is of interest for its potential release of trace elements into the agricultural environment and water  
57 supply (Armstrong et al. 2019, Parnell et al. 2018), and it can be sampled at a range of thermal  
58 maturities and thus degrees of diagenesis, which could influence mineralogy and hence speciation.  
59 Thermal maturity has also been found to influence the ratios of trace elements in shales (Akinlua et  
60 al. 2010, Abarghani et al. 2020), although only to a limited degree and not in a consistent,  
61 predictable manner. As far as possible, the samples are all organic-rich mudrocks, to minimize  
62 variations that reflect the depositional environment.

63 Five elements were chosen for study of speciation. Selenium (Se) is known to be anomalously rich in  
64 the Bowland Shale and equivalents and consequently to be a cause of concern for agriculture (Webb  
65 & Atkinson 1965, Webb et al. 1966, Rogers et al. 1990). It is therefore the subject of more detailed  
66 study here. Molybdenum (Mo) has also been identified as a possible problem for agriculture in  
67 Ireland (Webb & Atkinson 1965). Copper (Cu) is of interest as it forms secondary minerals on the  
68 Bowland Shale equivalent in Ireland (Francis & Ryback 1987, Moreton et al. 1995), suggesting that it  
69 is abundant and mobile. Arsenic (As) is incorporated into sulphides in high concentrations, and it can  
70 help the incorporation of other trace elements by creating vacancies for cation residence (Deditius  
71 et al. 2008, Berner et al. 2013). Each of these elements is strongly incorporated in pyrite (Gregory et  
72 al. 2015). Uranium (U) is associated with Carboniferous organic matter in several sites around the  
73 Irish Sea (Parnell 1988, Parnell et al. 2016), and is concentrated in the Bowland Shale around Edale  
74 (Ball et al. 1992, Bottrell 1993, Hyslop 1993) and in soils above Bowland Shale equivalents in Ireland  
75 (Williams & Brown 1971), but is unlike the other four elements in not being strongly incorporated  
76 into pyrite ([Tribovillard et al. 2006](#)).

77

## 78 **Methodology**

79 Samples of black shale from nine localities in the Bowland Shale and equivalents in Britain and  
80 Ireland (Fig. 1) were studied for elemental composition, thermal maturity and speciation. All samples  
81 were collected from natural exposures, avoiding any fractured or weathered material might contain  
82 disproportionately high contents of elements in loosely bound form, and possibly may be partly  
83 leached ([Emmings et al. 2017](#), [Armstrong et al. 2019](#)).

84 The total organic carbon (TOC) and total sulphur (TS) contents of powdered samples were  
85 determined using a LECO CS744 at the University of Aberdeen. Total carbon (TC) and TS  
86 concentrations were measured (Fig. 2) by combustion analysis of 0.1 mg powdered sample, using an  
87 excess of tungsten and iron chip combustion accelerators. To determine TOC, inorganic carbon was  
88 removed by dissolving 0.2 mg of sample in an excess of 20% hydrochloric acid (HCl), producing a  
89 decarbonated sample fraction. Decarbonated samples were subsequently analysed for TOC using  
90 LECO combustion analysis. Certified LECO standards were used to produce a multi-point calibration  
91 daily before sample analysis. Each sample was analysed in duplicate and an average calculated to  
92 account for any analytical variability.

93 Thermal maturity is characterized by vitrinite reflectance, measured in rocks at/near the sampled  
94 localities, in Ireland (Clayton et al. 1989), Isle of Man (Shelton et al. 2011) and England (Andrews  
95 2013).

96 High-resolution image analysis was performed at the University of Aberdeen ACEMAC Facility using a  
97 Zeiss Gemini field emission gun scanning electron microscope (FEG-SEM) on polished blocks of black  
98 shale. Samples were carbon coated and analysed at 20 Kv, with a working distance of 10.5 mm.  
99 Samples were analysed using Oxford Instruments EDS x-ray analysis. Laser Ablation-Inductively  
100 Coupled Plasma-Mass Spectrometry (LA-ICP-MS) was used to map trace elements in pyrite (Fig. 3),  
101 as detailed by Armstrong et al. (2019).

102 The analysis by high performance liquid chromatography-inductively coupled plasma-mass  
103 spectrometry (HPLC-ICP-MS) analysis allows comparison with standards for a range of Se species,  
104 following the approach of Qin et al. (2017). In the Bowland Shale samples, selenite (Se<sup>IV</sup>) and  
105 selenate (Se<sup>VI</sup>) species are evident in 0.1 M KH<sub>2</sub>PO<sub>4</sub> extracts using 50 ppb mixed Se<sup>IV</sup>/Se<sup>VI</sup> standards,  
106 and selenite is evident in 0.1 M NaOH extracts. Elemental selenium (Se<sup>0</sup>) was identified in 1 M  
107 Na<sub>2</sub>SO<sub>3</sub> extracts.

108 For the determination of ~~the total concentration of elements~~ whole rock element concentrations in  
109 ~~the whole sample~~, 50 mg of each sample was pre-digested overnight in 5 ml concentrated HCl/ HNO<sub>3</sub>  
110 (3:1 v/v) and digested in a microwave for 25 minutes. For speciation measurements, 4 g sample was  
111 extracted with 10 ml milli Q water, filtrate obtained and analysed with ICP-MS. 50 mg sample was  
112 sequentially extracted with 10 ml 0.1 M KH<sub>2</sub>PO<sub>4</sub>, 1 M NaOH and 1 M Na<sub>2</sub>SO<sub>3</sub>. The dry residue was  
113 digested as above. The apportioning of fractions is presented as percentage distributions (Figs. 4, 5),  
114 as conventional for speciation studies (Jacks & Nystrand 2019, Jew et al. 2020). Sequential analysis  
115 for Se follows the approach of Kulp & Pratt (2004). All fractions were analysed using HPLC-ICP-MS,  
116 using 50 ppb mixed Se<sup>IV/VI</sup> and 5 ppm elemental Se standards. Certified reference materials (marine

117 sediments NRCC PACS-2, MESS-2 and BCSS-1) were digested as above and analysed using ICP-MS.  
118 ICP-MS was undertaken using a Agilent ICP-MS 7900 instrument (single quadrupole, helium gas  
119 mode (collision gas)). For additional quality control, a mass balance approach was used to compare  
120 the sum of the fractions to the total element analysis.

121 Separately, ~~a whole suite of~~ major and minor elements in shale samples ~~was/were~~ determined at  
122 ALS, Co. Galway, Republic of Ireland, measured using ~~inductively coupled plasma mass spectrometry~~  
123 ~~(ICP-MS)~~. Samples of ~30 g rock were milled and homogenised, and 0.25 g digested with perchloric,  
124 nitric, hydrofluoric and hydrochloric acids to near dryness. The residue was topped up with dilute  
125 hydrochloric acid, and it was analysed using a Varian 725 instrument. Samples with high  
126 concentrations were diluted with hydrochloric acid to make a solution of 12.5 mL, homogenized,  
127 then analysed by ICP-MS. Results were corrected for spectral inter-element interferences. The limits  
128 of detection/resolution are 0.05 and 10,000 ppm. A cross-plot of Re and Mo contents (ppm) for  
129 shale samples is used to characterize the degree of oxygenation in the depositional environment,  
130 within the framework of Ross & Bustin (2009).

131 Principles for interpretation

132 For the elemental concentrations of Se and its associated elements (Cu, As, Mo, U) , the 0.1 M  
133  $\text{KH}_2\text{PO}_4$  extracts represent the ligand exchangeable fractions ~~and some organic species~~, the NaOH  
134 extracts ~~also~~ represent ~~the~~ organic matter associated fractions,  $\text{Na}_2\text{SO}_3$  fractions represent the  
135 elemental species in the case of Se; and the  $\text{HNO}_3/\text{HCl}$  digested residual fraction (total acid fraction,  
136 TAF) are associated with recalcitrant kerogen and silicates. Analyte recoveries of 3 marine sediment  
137 reference materials (PACS-2, MESS-2, and BCSS-2) were in the range 72% - 98% and were considered  
138 satisfactory. While sediment reference material samples are not completely representative of  
139 geological materials like the analysed black shales, they enable an assessment of the accuracy of the  
140 sample preparation method to extract analytes in a given phase, in this case the  $\text{HNO}_3/\text{HCl}$  acid  
141 fractions.

142

## 143 Results

144 All nine sample contain organic carbon above 2 %, and all except one (Altmush) have sulphur  
145 contents above 1 wt. % (Fig. 2, Table 1). The C/S ratios range from 0.60 to 5.80.

146 The proportions of each element in each fraction in the speciation study is given in Figures 4 and 5,  
147 and Table 2. The samples with highest carbon and sulphur contents are from southwest Ireland, and

148 they have high proportions of trace elements in the more mobile fraction. The sum of the fractions  
149 to the total element analysis was consistently in the range 1.0 to 1.5, which is satisfactory.

150 The data set for major and minor elements in the whole rock shale samples is given in Table 3. The  
151 data set highlighted several variations related to mineralogy:

- 152 (i) Samples (T, H, P) with higher than average contents of K, Al and Rb, suggesting more  
153 clay/mica/feldspar. This is consistent with higher contents of trace elements Ba (in  
154 feldspar) and Cr (in heavy minerals).
- 155 (ii) Samples (T, H, P) with higher than average contents of Ca, Mg, Mn and Sr, suggesting  
156 more carbonate minerals. Associated apatite is indicated by higher contents of P, Ce, La,  
157 Y and U.
- 158 (iii) Samples (L, B, W) with higher than average contents of Fe, S and As, suggesting more  
159 pyrite. This is consistent with higher contents of Cu, Co, Sb, Se and W.

160 Notably, groups (i) and (ii) include the same samples, i.e. they are both calcareous and clay-rich.

161 Despite the variations, all eight samples plot within the field characteristic for an anoxic environment  
162 of deposition, in an Re/Mo cross-plot as framed by Ross & Bustin (2009).

163 The vitrinite reflectance values vary from ~ 0.9 % in central England to ~4.5 % in south west Ireland  
164 (Clayton et al. 1989, Shelton et al. 2011, Andrew 2013). The reflectance in the vicinity of Altmush is  
165 variable, with marked lateral change, associated with very high palaeogeothermal gradients  
166 (Corcoran & Clayton 2001), and for the purposes of interpretation it is grouped with other samples  
167 in Ireland which have relatively high reflectance values due to Variscan metamorphism. The  
168 relatively high reflectance of 2.5 % at Poyllvaish, Isle of Man is attributed to localised igneous  
169 intrusions (Dickson et al. 1987) rather than regional metamorphism, so is grouped with the low  
170 maturity samples from England.

171 The mapping of Se and As in pyrite-bearing shale by LA-ICP-MS (Fig. 3) shows that the Se and As are  
172 strongly co-located with Fe, i.e. the trace elements are resident in pyrite. Electron microscopy shows  
173 that the samples consistently contain pyrite framboids. In addition, samples from Whiddy Island and  
174 Ballyunion contain a second generation of pyrite, consisting of blocky euhedral crystals that  
175 envelop the earlier framboids (Fig. 7). The pyrite is associated with micron-scale blebs of zinc and  
176 copper sulphides (Armstrong et al. 2019).

177 The selenium speciation data obtained from HPLC-ICP-MS analysis enabled the identification of  
178 various extracted species (Fig. 8). The water-soluble fraction (WSF) contains water soluble Se<sup>VI</sup>, Se<sup>IV</sup>  
179 and organic Se species, while the 0.1 M KH<sub>2</sub>PO<sub>4</sub> extracts represent the adsorbed and exchangeable



180 Se<sup>IV</sup> and some organic Se species. Fractions extracted with 0.1 M NaOH represent the tightly bound  
181 Se<sup>IV</sup> and base-soluble organic selenide species while the 1 M Na<sub>2</sub>SO<sub>3</sub> extract accounted for the Se<sup>0</sup>  
182 species (Qin et al. 2017).

## 183 Discussion

### 184 Sample compositions

185 The samples are all of similar bulk composition, i.e. they are mudrocks rich in organic matter and  
186 pyrite. Additionally, the samples from Trough of Bowland, Pendle Hill and Poyllvaish contain seams  
187 with calcareous cement, and clay/mica. All samples have total organic carbon (TOC) contents  
188 exceeding 2 %, and they would classify as hydrocarbon source rocks (Demaison & Moore 1980). The  
189 C/S ratios lower than the mean marine composition (Fig. 2) are consistent with SEM observations of  
190 widespread pyrite framboids that formed during syngensis or diagenesis. Trace elements could be  
191 associated with organic carbon and sulphide in each of them. As the samples from southwest Ireland  
192 have high proportions of trace elements in the more mobile fraction, the trace elements are not simply  
193 distributed according to pyrite content, as the pyrite-bound component would not be the most highly  
194 mobile (e.g. Fougerouse et al. 2019).

195 The localities sampled exhibit vitrinite reflectance values from 0.9 to ~4.5 %, representing a range  
196 from oil window to gas window thermal maturities (Clayton et al. 1989, Shelton et al. 2011, Andrew  
197 2013). A comparison (Fig. 4) between 5 samples from England and the Isle of Man in the oil window  
198 (England reflectance <1.5 %) and 4 samples from Ireland in the gas window (reflectance >1.5 %)   
199 distinguishes rocks which have experienced sample burial diagenesis, and those which have  
200 experienced deformation and low-grade metamorphism related to the Variscan Orogeny.

### 201 Interpretation of Bowland Shale data

202 Trace elements reside in shales in several different sites, including bound to organic matter, bound to  
203 clays, bound to iron oxides, substitution in sulphides, incorporation in carbonates and in resistant  
204 (heavy) mineral phases (e.g. Jones & Manning 1984, Morse & Luther 1999, Rimstidt et al. 1998, Algeo  
205 & Lyons 2006, Sipos et al. 2014, Gregory et al. 2015). The speciation of trace elements is partly related  
206 to the mineral residence, but not in an absolute numerical equivalence. Thus for example, the loosely  
207 bound fraction could include contributions from clays, organic matter and soluble secondary minerals,  
208 while the resistant fraction might include contributions from sulphides, silicates and oxides. Therefore,  
209 data are best used to make broad comparisons within the data set of Bowland Shale samples.

210 The measurements show that each of the elements is distributed through multiple residences, but  
211 that the relative proportions attributable to the different fractions vary between elements. The

212 predominant residence for the trace elements is consistently in the residue fraction, which includes  
213 sulphides and silicates (Figs. 4, 5). This is consistent with the assumptions that As, Cu, Se, and to some  
214 extent Mo, are resident in the pyrite (Morse & Luther 1999, Deditius et al. 2011, Gregory et al. 2015).  
215 Uranium is more variably a trace element within relatively insoluble zircon, monazite and titanite, and  
216 also adsorbed on apatite, organic matter and iron oxide (Smedley et al. 2006). The residence of  
217 elements in pyrite is shown also by LA-ICP-MS maps (Fig. 3), in which Se and As are strongly co-located  
218 with the iron (Fe) in pyrite.

219 Inspection of the data indicates that it is useful to discriminate two groups of samples (Fig. 5); the 4  
220 samples in Ireland that reached higher thermal maturity, and the other 5 samples in England and the  
221 Isle of Man that reached lower thermal maturity. In interpreting the total data, we simplify it by  
222 combining the two loosely bound fractions ( $K_2HPO_4$ , NaOH extracts). The two groups of samples  
223 exhibit a clear difference in their distribution of elements through the fractions. The contents in the  
224 high maturity group are higher in the combined loosely-bound fraction than in the low maturity group,  
225 for Cu (32 % vs. 4 %), As (51 % vs. 15 %), Se (49 % vs. 28 %) and U (25 % vs. 12 %), and correspondingly  
226 the contents for the high maturity group are lower in the residue. The values for Mo are similar for  
227 both groups. The whole rock data confirm that some trace elements, including Cu, As and Se, are  
228 resident in sulphides. The data for U and Mo do not correlate specifically with the speciation data. The  
229 difference in U speciation between high and low maturity samples is regardless of whether the U is in  
230 a carbonate-bearing sample.

231 Sulphides, organic matter

232 If the trace element load is predominantly in sulphides, the lower contents in the high maturity group  
233 of samples imply that some of the load was expelled during increase in temperature, which in this  
234 sample set was related to Variscan metamorphism and deformation. This is consistent with evidence  
235 for sulphide mobility and precipitation in the British Isles and elsewhere during the Variscan Orogeny  
236 (e.g. Marignac et al. 2003, Walter et al. 2019, Lang et al. 2020). Studies of mineralization elsewhere  
237 show that trace elements including As and Mo can be mobilised and expelled during low grade  
238 metamorphism of pyrite (Pitcairn et al. 2010, Large et al. 2012, Majumdar et al. 2019), and hence their  
239 contents become ~~reduced~~ diminished. Pyrite in youngest, Cenozoic, black shales has much higher Mo  
240 contents than pyrite in older black shales (Gregory et al. 2015), reflecting the ready loss of Mo from  
241 pyrite during recrystallization (Chappaz et al. 2014). Pyrite *can* be formed late in the history of the  
242 host shale, but it typically has a lower trace element content (Gregory et al. 2015). Electron  
243 micrographs of shales in the high maturity group show that they contain two generations of pyrite. An  
244 early generation of framboidal pyrite is coated with a later generation of euhedral pyrite (Fig. 7),

245 evidencing the recrystallization that is commonly accompanied by a reduction in trace element load  
246 (Large et al. 2009).

247 The distinct distribution of Mo, which has the highest mean fraction associated with organic matter  
248 (Figs. 4, 5), and is richest in the Altmush sample which has the highest C/S ratio (lowest S content),  
249 indicates a relatively strong organic affinity. Previous studies report a similar positive relationship of  
250 Mo with organic matter in other black shales (Algeo & Lyons 2006, Chappaz et al. 2014), although it  
251 can be resident in pyrite (Vorlicek et al. 2004). Changes between affinity with organic matter and pyrite  
252 with changing maturity are possible due to loss of substrate mass to increase the Mo/TOC ratio  
253 (Dickson et al. 2020), ~~high temperature~~ thermal sulphate reduction to form new sulphides (Ardakani  
254 et al. 2016) and enrichment in Mo introduced by migrating hydrocarbons (Ardakani et al. 2020).  
255 However, there is no clear difference in Mo contents between the low and high maturity groups that  
256 would point to one of these processes. None of the high maturity Irish localities show evidence of  
257 migrated hydrocarbons as bitumens in vein-fillings or porosity in associated sandstones. A marked link  
258 with organic matter is similarly evident in the Se data, especially in the high maturity samples where  
259 the association with sulphides is reduced. The association of Se with organic matter is also shown in  
260 black shales elsewhere (Mitchell et al. 2012). The distribution of U is less clear, but speciation studies  
261 in other rocks similarly indicate an important affinity of U in organic matter (Cumberland et al. 2016,  
262 Jew et al. 2020).

263 Correlations ( $R^2$  values) between carbon and sulphur with the five elements in Table 1, using whole  
264 rock contents in Table 3, emphasize that Se, Cu and to some extent As, increase with both C and S  
265 contents. Mo also shows some correlation with S, and U shows no positive correlation with either C  
266 or S.

267 ~~The limited evidence elsewhere for a role for~~ During thermal ~~maturity maturation, suggests that~~ the  
268 breakdown of organic matter could release trace elements directly, or release sulphur that then  
269 reacted with and fixed trace elements (Abarghani et al. 2020), within the oil window that the Bowland  
270 Shale samples experienced. The observation of two generations of pyrite in the most mature samples  
271 could be consistent with such a scenario, but if much of the trace element load was resident in the  
272 first generation of pyrite rather than organic matter then enrichment would not be expected in the  
273 second generation. On the contrary, where trace elements are associated with organic matter in the  
274 Bowland Shale samples, that association seems to survive maturation.

275 Weathering

276 The broad trends in distribution can be linked to observations of weathering and aqueous transport  
277 of weathering products in the natural environment. The entry of anomalous concentrations of trace  
278 elements into the surface environment is important where it impacts upon agricultural land, and  
279 where it impacts the water supply. The formation of ochreous precipitates can concentrate mobile  
280 fractions (e.g. Parnell et al. 2018), which could be mobilized in quantity during periods of high rainfall  
281 and flooding onto soils which are otherwise not accessed (Giles & Griffiths 2020). The ready formation  
282 of secondary Cu and As minerals, recognized for almost 200 years (Kane 1844, Francis & Ryback 1987,  
283 Moreton et al. 1995), and evidence of U concentration in the secondary minerals (Armstrong et al.  
284 2019) on the black shale of Ballybunion, may reflect the high proportion of loosely bound elements in  
285 the more mature samples found in Ireland. Geochemical mapping shows that Se and Mo are released  
286 into the agricultural environment from underlying black shale bedrock in southwest and central  
287 Ireland (Webb & Atkinson 1965, McGrath & Fleming 2007, Fellowes et al. 2013). Uranium anomalies  
288 also occur in Irish soils above Bowland Shale equivalents (Williams & Brown 1971). The release of  
289 these elements probably reflects a mixture of the weathering breakdown of sulphides and the loose  
290 affinity of the organically-bound fractions.

291 Weathering of sulphides is also evident in sections at lower thermal maturity. For example, the  
292 oxidation of pyrite in Bowland Shale in the Edale district has released ochreous, iron(hydr)oxide  
293 precipitates (Steward & Cripps 1983, Adams et al. 2007, Parnell et al. 2018). These precipitates contain  
294 anomalous levels of Se and As, but they are only on a local scale (Parnell et al. 2018).

295 There is a limit to how much can be implied about the behaviour of other elements, but the whole  
296 rock data shows that several elements, including Co and Sb have a particular affinity for sulphides, and  
297 therefore may be released during the recrystallization and weathering of the sulphides.

298 Selenium

299 Speciation of Se was assessed in more detail because the Bowland Shale is consistently rich in Se  
300 relative to mean shale compositions (Parnell et al. 2016), and other Se-rich shales have caused  
301 ecological problems (Mast et al. 2014, Carsella et al. 2017). This study, and other studies of  
302 speciation of shales (Matamoros-Velozá et al. 2014, Kulp & Pratt 2004, Stillings & Amacher 2010)  
303 emphasize the importance of Se in pyrite, which can enter the environment as iron (hydr)oxides.

304 Elemental selenium is unstable and is rapidly oxidised to  $\text{Se}^{\text{IV}}$ , as observed in the Bowland Shale  
305 samples. However, it has been identified in other shales containing organic carbon (Kulp & Pratt  
306 2004, Zhu et al. 2004, Grauch et al. 2004). Selenite and selenate are most toxic, while elemental  
307 selenium has very low solubility and thus low toxicity (Gupta & Gupta 2016, Eswayah et al. 2017).

308 The relatively soluble selenite and selenate fractions contribute to selenium in the water supply,  
309 which can be high enough to exceed safety limits and shut water wells (Bassil et al. 2014). Mobile  
310 selenium can be concentrated in iron (oxy)hydroxides, to form ochreous precipitates, which can be  
311 ecologically damaging (e.g. Prange 2007, Rahman & Bastola 2014). Although the Se-rich Bowland  
312 Shales have a past record of causing toxicity (Crinion 1980, Rogers et al. 1990), we are not aware  
313 that this is a current problem in Britain and Ireland.

314 The selenite and selenite species were most easy to identify (i.e. most relatively abundant) in the  
315 samples of lower thermal maturity, i.e. those in England, and particularly from Pendle Hill (Fig. 8).  
316 Further work in this region should examine spoil heaps from old quarries on Pendle Hill (Earp et al.  
317 1961), where water is draining through broken shale and there are crusts of iron oxide which may  
318 reflect migration and re-deposition of trace elements. Detailed sampling will show the proportions  
319 of Se species which enter groundwater or are remineralized.

320 These data for the Bowland Shale show that speciation studies have the potential to inform us about  
321 element release from shales into the environment. Such studies are, however, relatively few. The  
322 value of speciation studies will become clearer through further studies of how data vary with (i)  
323 thermal maturity of shales, (ii) degree of surface weathering, (iii) initial trace element concentration,  
324 and (iv) hydrogeology.

## 325 **Conclusions**

326 The data from the sequential speciation study of Bowland Shale samples show that each of the  
327 measured elements is distributed through multiple residences in the shales. Comparison of the  
328 variations within the sample set shows:

- 329 (i) The high proportions of the residue fraction reflect the predominance of trace element  
330 residence in pyrite.
- 331 (ii) A higher proportion of loosely-bound fractions in the high maturity samples suggests the  
332 expulsion of trace elements from pyrite. This could have occurred during  
333 recrystallization of pyrite associated with Variscan metamorphism, assuming that the  
334 pyrite originally contained a consistent trace element content.
- 335 (iii) Each element is partially present in loosely-bound form; most consistently (low and high  
336 maturity samples) Se and Mo, and also U, which are probably associated with organic  
337 matter.
- 338 (iv) Detailed analysis of the Se fractions identified elemental Se, reflecting the reducing  
339 environment of organic-rich shales.

340

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570

571 **Figure Captions**

572 Fig. 1. Map of Britain and Ireland showing locations of samples of Bowland Shale and equivalents  
573 used for speciation study.

574 Fig. 2. Cross-plot of sulphur and organic carbon contents in samples used for speciation study. Most  
575 samples are more sulphur-rich than the modern marine sediment composition (defined by dashed  
576 line on plot) determined by Berner & Raiswell (1983).

577 Fig. 3. Maps of Fe, Se and As distribution in pyrite-bearing black shale from A, Ballybunion and B,  
578 Whiddy Island, measured by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry. Trace  
579 elements Se and As are much richer in pyrite (distribution defined by Fe) than in surrounding matrix.  
580 Colour indicates element quantity (% or ppm).

581 Fig. 4. Percentage distributions of four fractions obtained by sequential analysis for Se, Cu, As, U and  
582 Mo in nine samples of Bowland Shale and equivalents.

583 Fig. 5. Mean percentage distributions of four fractions obtained by sequential analysis for Se, Cu, As,  
584 U and Mo in nine samples of Bowland Shale and equivalents, and in groups of relatively low thermal  
585 maturity (T, H, P, L, E) and relatively high thermal maturity (A, D, B, W).

586 Fig. 6. Cross-plot of Re and Mo contents (ppm) for shale samples, within framework of Ross & Bustin  
587 (2009), which shows all plot within the field characteristic for an anoxic environment of deposition.

588 Fig. 7. Scanning electron micrograph of shale rich in pyrite (bright), Whiddy Island. An early  
589 generation of framboidal pyrite is coated with a later generation of euhedral pyrite, showing  
590 recrystallization which could involve expulsion of trace elements from the sulphide fraction.

591 Figure 8. Identification of selenium species by HPLC. A, Identification of selenite ( $\text{Se}^{\text{IV}}$ ) and selenate  
592 ( $\text{Se}^{\text{VI}}$ ) species in 0.1 M  $\text{KH}_2\text{PO}_4$  extracts with HPLC-ICP-MS using 50 ppb mixed  $\text{Se}^{\text{IV}}/\text{Se}^{\text{VI}}$  standards. B,  
593 Identification of selenite ( $\text{Se}^{\text{IV}}$ ) species in 0.1 M NaOH extracts with HPLC-ICP-MS. C, Identification of  
594 elemental selenium ( $\text{Se}^0$ ) species in 1 M  $\text{Na}_2\text{SO}_3$  extracts with HPLC-ICP-MS using a 5 ppm elemental  
595 selenium standard. Elemental selenium is unstable and is rapidly oxidised to  $\text{Se}^{\text{IV}}$ . Localities D,  
596 Dunshaughlin; E, Edale; H, Pendle Hill; L, Wiswell Lane; W, Whiddy Island.

597

Table 1. Composition of nine samples used for speciation study.

Locality	Local Stratigraphy	Lab. No.	Carbon (C%)	Sulphur (S%)	C/S	Vitrinite Reflectance (%)	Se Total ppm	Cu Total ppm	As Total ppm	U Total ppm	Mo Total ppm
Trough of Bowland (T)	Bowland Shale	ST19	3.58	2.13	1.68	0.9	1.87	77.8	1.76	16.8	66.4
Pendle Hill (H)	Bowland Shale	ST23	4.19	1.70	2.46	~1	3.55	68.0	1.74	11.0	30.8
Wiswell Lane (L)	Bowland Shale	ST41	2.22	3.73	0.60	~1	3.52	87.5	4.99	10.9	45.1
Edale (E)	Edale Shales	ST53	3.51	3.87	0.91	1.1	0.70	29.1	1.16	6.47	29.4
Poyllvaish (P)	Bowland Shale	ST33	5.48	1.02	5.37	2.5	2.00	68.0	1.06	34.1	36.9
Altmush (A)	Ardagh Shale Fm.	ST36	4.00	0.69	5.80	1-3	1.86	79.5	0.98	10.4	22.4
Dunshaughlin (D)	Loughshinny Fm.- Donore Fm.	ST38	5.27	1.75	3.01	3.5	3.91	20.6	1.22	7.04	56.5
Ballybunion (B)	Clare Shale	ST46	6.21	5.60	1.11	4.4	3.20	158.0	2.10	11.3	107.0
Whiddy Island (W)	East Point Fm.	ST32 4	8.72	8.52	1.02	~4.5	6.57	202.0	4.25	5.90	66.7
Correlation with C (R <sup>2</sup> )			--	0.39			0.68	0.71	0.36	0.36 Inv.	0.11

Correlation with S (R <sup>2</sup> )			0.39	--				0.52	0.84	0.34	0.02	0.31
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Table 2. Percentage distributions of speciation fractions for nine samples.

Locality	Trough of Bowland (T)	Pendle Hill (H)	Wiswell Lane (L)	Edale (E)	Poyllvaish (P)	Altmush (A)	Dunshaughlin (D)	Ballybunion (B)	Whiddy Island (W)	Mean (low)	Mean (high)
<b>Se (%)</b>											
KH <sub>2</sub> PO <sub>4</sub>	8	8	9	8	10	13	10	7	6	9	9
NaOH	21	15	23	16	19	42	56	43	20	19	40
Na <sub>2</sub> SO <sub>3</sub>	7	4	8	7	7	6	7	14	17	7	11
Residue	64	73	60	68	65	38	27	36	57	66	39
<b>Cu (%)</b>											
KH <sub>2</sub> PO <sub>4</sub>	1	3	2	2	3	20	27	44	14	2	27
NaOH	3	2	2	2	2	7	12	1	1	2	5
Na <sub>2</sub> SO <sub>3</sub>	2	2	3	3	3	9	9	4	4	2	6
Residue	94	93	93	93	92	64	52	51	81	93	62
<b>As (%)</b>											
KH <sub>2</sub> PO <sub>4</sub>	4	3	2	2	4	7	21	36	18	3	20
NaOH	12	10	15	14	11	33	39	31	22	12	31



Na <sub>2</sub> SO <sub>3</sub>	9	5	3	4	8	5	4	3	4	6	4
Residue	75	82	80	80	77	55	36	30	57	79	44
<b>U (%)</b>											
KH <sub>2</sub> PO <sub>4</sub>	5	4	7	6	2	9	9	9	7	5	9
NaOH	8	4	9	12	2	20	15	16	12	7	16
Na <sub>2</sub> SO <sub>3</sub>	10	5	9	9	4	12	9	12	9	7	11
Residue	78	87	75	73	92	59	68	63	72	81	65
<b>Mo (%)</b>											
KH <sub>2</sub> PO <sub>4</sub>	18	9	4	8	6	3	4	2	4	9	3
NaOH	33	31	38	38	38	57	42	23	31	36	38
Na <sub>2</sub> SO <sub>3</sub>	5	4	5	5	9	4	3	3	5	6	4
Residue	44	56	53	49	47	36	51	72	60	50	55

Table 3. Whole rock analyses for samples of Bowland Shale, determined by ICP-MS

Locality	Tr. of Bowland	Pendle Hill	Poynlvaish	Altmush	Dunshaughlin	Wiswell Lane	Ballybunion	Edale	Whiddy Island	
Element	Lab code	ST19	ST23	ST33	ST36	ST38	ST41	ST46	ST53	ST324
Ag	ppm	0.24	0.27	0.53	0.22	0.66	0.29	0.59	0.25	1.06
Al	%	0.52	0.70	0.97	0.30	0.25	0.40	0.30	0.55	0.47
As	ppm	16.4	17.5	10.6	9.0	10.9	51.8	26.6	38.0	53.1
Ba	ppm	140	230	40	140	40	40	30	30	50
Ca	%	9.52	3.94	20.60	0.12	0.07	1.35	0.03	1.59	0.13
Cd	ppm	8.50	16.30	7.71	2.33	0.65	16.55	0.56	2.47	1.27
Ce	ppm	24.70	18.35	76.70	3.32	2.28	6.55	12.30	9.51	8.72
Co	ppm	16.7	10.9	9.9	6.7	4.5	31.5	182.0	31.2	531.0
Cr	ppm	24	51	26	5	5	15	7	9	15
Cu	ppm	73.5	69.2	77.3	90.9	15.0	86.8	169.5	83.0	248.0
Fe	%	2.15	1.62	0.97	1.22	0.93	4.13	4.31	3.91	7.36
Hg	ppm	0.07	0.06	0.03	0.06	0.13	0.09	0.45	0.11	0.38
K	%	0.22	0.23	0.18	0.15	0.10	0.14	0.08	0.17	0.17
La	ppm	11.3	8.4	42.8	1.5	1.0	2.6	4.8	3.4	4.4
Li	ppm	4.5	3.8	13.6	1.3	0.5	2.4	2.1	10.0	2.3
Mg	%	0.30	0.18	1.42	0.02	0.02	0.13	0.03	0.34	0.08
Mn	ppm	231	177	98	15	18	63	27	402	84
Mo	ppm	66.8	28.8	40.5	20.0	55.6	38.5	118.5	50.4	66.6
Na	%	0.08	0.03	0.04	0.01	0.01	0.02	0.01	0.02	0.07
Ni	ppm	111.0	109.0	69.4	29.7	19.3	100.5	42.7	102.5	95.2
P	ppm	600	310	5840	460	40	170	320	380	670
Pb	ppm	43.8	39.3	10.6	33.2	7.4	15.7	29.0	43.9	35.6
Rb	ppm	15.2	16.9	9.4	7.3	9.6	9.0	4.3	12.0	8.2
Re	ppm	0.177	0.169	0.128	0.117	0.138	0.073	0.256	0.123	0.245
S	%	2.24	1.66	1.01	0.65	1.64	4.19	5.24	4.29	9.26
Sb	ppm	3.07	3.07	2.47	0.97	0.82	6.03	3.36	4.40	9.28
Sc	ppm	6.3	4.6	6.2	4.0	1.1	4.8	1.0	6.1	1.9
Se	ppm	16.8	33.0	18.2	16.0	36.0	32.6	36.3	20.9	80.4
Sr	ppm	520.0	171.5	662.0	21.9	5.6	64.3	181.5	51.0	12.2
U	ppm	12.65	6.95	46.00	6.82	2.82	5.06	6.49	20.90	7.02
V	ppm	55	161	185	45	48	39	35	26	40
W	ppm	2.57	3.64	3.09	10.45	13.50	13.50	55.10	27.10	126.50
Y	ppm	20.30	12.10	54.20	3.45	5.17	11.55	10.15	16.05	6.16
Zn	ppm	207	152	103	49	27	163	18	70	29
Zr	ppm	6.6	7.4	8.9	3.9	3.4	7.1	11.2	15.5	19.4
Re/Mo		2.6x10 <sup>-3</sup>	5.9x10 <sup>-3</sup>	3.2x10 <sup>-3</sup>	5.9x10 <sup>-3</sup>	2.5x10 <sup>-3</sup>	1.9x10 <sup>-3</sup>	2.2x10 <sup>-3</sup>	2.4x10 <sup>-3</sup>	3.7x10 <sup>-3</sup>



figure 1

















