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## **Uranium mineralization in the Alum Shale Formation (Sweden): Evolution of a U-rich marine black shale from sedimentation to metamorphism**

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### ► To cite this version:

Andrei Lecomte, Michel Cathelineau, Raymond Michels, Chantal Peiffert, Marc Brouand. Uranium mineralization in the Alum Shale Formation (Sweden): Evolution of a U-rich marine black shale from sedimentation to metamorphism. *Ore Geology Reviews*, 2017, 88, pp.71-98. 10.1016/j.oregeorev.2017.04.021 . hal-02376740v1

**HAL Id: hal-02376740**

**<https://hal.science/hal-02376740v1>**

Submitted on 28 Nov 2019 (v1), last revised 29 Nov 2019 (v2)

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1           Uranium mineralization in the Alum Shale Formation  
2           (Sweden): evolution of a U-rich marine black shale from  
3                            sedimentation to metamorphism

4  
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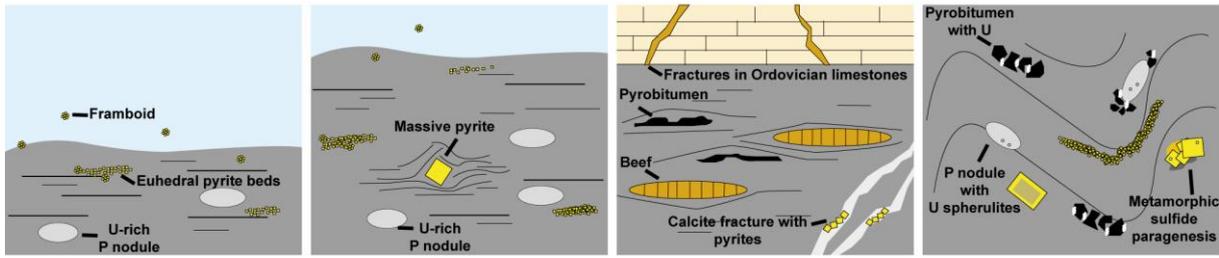
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18 Graphical abstract

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21

## 22 **Abstract**

23           The Alum Shale Formation is a metal-rich black shale, deposited on the  
24 Baltoscandian platform between Middle Cambrian and Early Ordovician. These  
25 black shales may be of particular economic interest for their relatively high uranium  
26 content (100-300 ppm) and their wide distribution from Norway to Estonia.  
27 Scandinavian Alum Shale may thus constitute a great potential resource of uranium,  
28 as a low grade ore. The Alum Shale Formation is particularly interesting to study the  
29 mineralogical expression and content of uranium in series submitted to progressive  
30 burial and metamorphism. For this purpose, the behavior of U, P, Ti and organic  
31 matter was studied on a series of representative samples from most Alum Shale  
32 prospecting zones. In southern Sweden, where Alum Shale underwent fairly shallow  
33 burial, uranium concentrations have no mineralogical expression except a rather high  
34 U content of biogenic phosphates. Calcite concretions (beefs) and fractures recorded  
35 the migration of hot overpressured hydrocarbons and brines from thermally mature  
36 areas to immature Alum Shale. However, thermal maturation and fluid migration  
37 did not allow remobilization of uranium and metals. At the opposite, in northern  
38 Sweden, where the series were folded, duplicated and submitted to low grade  
39 Greenschist metamorphism during Caledonian orogeny, phospho-silicates U-Si-Ca-P  
40 ( $\pm$ Ti  $\pm$ Zr  $\pm$ Y) and minor amounts of uraninite are identified and indicate that U, P,  
41 and Ti were mobile and precipitated as new phases. The effect of metamorphism is  
42 therefore important to consider as the leachability of U, especially during (bio)-  
43 hydrometallurgical processes, which will be by far different between the two  
44 considered areas.

45 Keywords: uranium; Alum Shale; organic matter; metamorphism; fluid inclusions;

46 hydrocarbons

47

## 48        **1. Introduction**

49            Lower Palaeozoic black shales extend over most of northern Europe, from  
50 Norway to Estonia across the Baltic Sea. These sediments were deposited on the  
51 Baltoscandian platform during an interval of great tectonic stability (Andersson *et al.*,  
52 1985). In particular, the Alum Shale Formation is an organic-rich marine sequence  
53 deposited over present Scandinavia between Middle Cambrian and Early  
54 Ordovician. The name Alum refers to the alum salt  $KAl(SO_4)_2 \cdot 12H_2O$  that formed  
55 under supergene conditions and was extracted from this black shale over 300 years  
56 ago. As many other black shales deposited in marine environments, Alum Shale  
57 contains high metal concentration compared to ordinary shales, especially Ni, Mo,  
58 Co, Cu, Zn, U, V, As, Se, Ag, Au and PGE (Vine and Tourtelot, 1970; Holland, 1979;  
59 Wignall, 1994). Nevertheless, Scandinavian Alum Shale is of particular interest  
60 because of its somewhat higher uranium content (100-300 ppm) and its wide  
61 extension. Therefore, they may constitute a potential uranium resource for the future.

62            The Alum Shale Formation is particularly interesting for the study of the  
63 mineralogical expression and content of uranium in series submitted to progressive  
64 burial and metamorphism. In order to understand the behavior of U, P, Ti and  
65 organic matter at increasing P-T conditions, a series of representative samples from  
66 most Alum Shale prospection zones were studied: i) samples from southern Sweden,  
67 where Alum Shale underwent rather shallow burial, and ii) samples from northern  
68 Sweden, where Alum Shale was folded, duplicated and submitted to low grade  
69 Greenschist metamorphism during Caledonian orogeny. The main objective was to  
70 identify the mineralogical expression of metals and uranium in these low grade ores,

71 and especially changes expected to occur during burial and metamorphism. Indeed,  
72 the nature of the U bearers is poorly known, and was almost not studied, most  
73 available data dealing with bulk U grades for evaluation of the mining potential and  
74 radioprotection purposes (Armands, 1972; Parnell, 1984; Andersson *et al.*, 1985;  
75 Buchardt *et al.*, 1997). Knowledge about the form at which U occurs in the ore is  
76 valuable information regarding ore treatment processes and recoverable reserve  
77 estimation.

78

## 79 **2. Geological setting**

80 In Sweden, the Alum Shale Formation can be subdivided into three  
81 geographical and structural provinces (Fig. 1): (a) autochthonous platform cover  
82 units (southern Sweden) lying on the Proterozoic basement, unaffected by  
83 Caledonian orogeny; (b) parallochthonous Alum Shale duplicated along the  
84 Caledonian Front with a metamorphic and hydrothermal imprint during the  
85 Caledonian orogeny (420-400 Ma); (c) allochthonous units in Sweden and Norway  
86 showing Greenschist facies metamorphic grade (Sundblad and Gee, 1984). The Alum  
87 Shale Formation is a marine sequence deposited between Middle Cambrian and  
88 Early Ordovician (Tremadoc) on Lower Cambrian sediments, the latter resting on a  
89 crystalline Palaeoproterozoic basement (Nielsen and Schovsbo, 2007). The  
90 sedimentation took place in a shallow-water epicontinental basin bordered by the  
91 Tornquist Sea to the South and the Iapetus Ocean to the North and West (Scotese and  
92 McKerrow, 1990). In the Early Cambrian, rising sea-level led to extensive flooding  
93 over the Baltoscandian sector of Baltica. A succession of transgressive and regressive

94 events occurred early to Middle Cambrian and ended with major Hawke Bay  
95 regression, terminating deposition of Lower Cambrian sediments (Nielsen and  
96 Schovsbo, 2011). During Middle Cambrian, marine transgression shifted the paleo-  
97 shoreline to the north-east (Andersson *et al.*, 1985; Buchardt *et al.*, 1997; Schovsbo,  
98 2002). From then, Baltoscandian epicontinental sea was characterized by extremely  
99 low depositional rates and dysoxic to anoxic conditions, especially in the deeper  
100 parts of the basin (Nielsen and Schovsbo, 2015). These particular conditions  
101 prevailed until Early Ordovician and favored Alum Shale deposition. During  
102 Caledonian orogeny, Alum Shale underwent Greenschist facies metamorphism.  
103 Besides, in the Caledonian foreland basin and in southern Sweden and Denmark,  
104 deep burial (up to 4 km) initiated thermal maturation of organic matter and  
105 hydrocarbon generation (Buchardt *et al.*, 1997, Schovsbo *et al.*, 2011).

106         The Alum Shale Formation is generally 15-35 meters thick but extremely  
107 variable, from 2 meters in Öland to 95 meters in Skåne. In the Caledonides, the  
108 formation is duplicated by thrust sheets and the thickness reaches up to 180 meters  
109 (Andersson *et al.*, 1985). Scandinavian Alum Shale is dominated by organic-rich (up  
110 to 20% TOC) marine black shales, with variable proportions of grey shales and silt  
111 beds, limestones and carbonate concretions. The latter generally trapped large  
112 amounts of hydrocarbons (Andersson, 1985; Thickpenny, 1984). In the Upper  
113 Cambrian, small lenses of organic matter (kolm) occur and are often highly  
114 uraniferous (up to 5000 ppm).

115

### 116         **3. Sampling and analytical procedure**

117            Sampling procedure aimed at selecting representative black shale samples of  
118 various thermal maturity, from immature or slightly mature Alum Shale to  
119 metamorphic rocks. Several locations were selected, with the least mature black  
120 shales (Västergötland, Östergötland, Närke and Öland), overmature Alum Shale in  
121 Skåne and metamorphic Alum Shale (Lövstrand, Myrviken and Tåsjö). Sampling  
122 locations are indicated on figure 1. Samples were taken on several drill cores stored  
123 in SGU's coreyards (Geological Survey of Sweden) and are listed in table 1. Most of  
124 these cores correspond to historical drilling projects. Studies were conducted on thin  
125 sections and polished sections, the latter included with Araldite in an aluminum ring  
126 of 25 mm diameter.

127            Petrographical studies were done using optical microscopes in reflected light, a  
128 SEM Hitachi S-4800 coupled to a ThermoNORAN Si(Li) detector, and a FEG SEM  
129 JEOL 7600F (hot cathode) with an Oxford Instruments SDD-type EDS spectrometer.  
130 Analyses were performed at 10 kV. Electron Probe Micro-Analysis (EPMA) analyses  
131 were performed using a CAMECA SX100, with an acceleration voltage of 20 kV and  
132 beam current of 20 nA.

133            X-Ray diffractograms were acquired using a D8 Bruker diffractometer with a  
134 non-monochromatic CoK $\alpha$  radiation (35 kV, 45 mA). Air-dried (AD), ethylene glycol  
135 (EG)-saturated and 550°C-heated XRD preparations (fractions < 2  $\mu$ m) are analyzed  
136 to determine diffracted intensities of clays over 3-40°2 $\theta$  range with a 0.02°2 $\theta$  step and  
137 3 seconds per step.

138            Multi-elements concentrations in phosphate nodules, carbonaceous residues  
139 and fluid inclusions were measured using a LA-ICP-MS system composed of a

140 GeoLas excimer laser (ArF, 193 nm, Microlas, Göttingen, Germany) associated with  
141 an Agilent 7500c quadrupole ICP-MS. Quantification of the results was achieved  
142 using the standard NIST SRM 610 (Pearce *et al.*, 1997) and subroutine data processing  
143 (Leisen, 2011). Sample density was calculated for several metamorphic and immature  
144 Alum Shale, measuring their volume by water immersion after paraffin coating.

145 Raman spectra of carbonaceous material from the Alum Shale were acquired  
146 using a LabRAM HR microspectrometer (Horiba Jobin Yvon) equipped with a  
147 600 gr/mm grating, using the 514.53 nm radiation of an Ar<sup>+</sup> laser with a final power  
148 of about 1mW (Stabilite 2017, Newport Spectra Physics). The laser was focused in the  
149 sample using a 100X objective. Acquisition time was set in such a way that the  
150 intensity reached at least 1/3 of the saturation level of the CCD (i.e. 20000 counts per  
151 second). Each measurement is the sum of 6 spectrum acquisition of 30 to 40 seconds  
152 each.

153 Sulfur isotope compositions were measured with a Cameca IMS1280 HR2  
154 (CRPG, Nancy, France) using simultaneous measurements of <sup>32</sup>S, <sup>33</sup>S, and <sup>34</sup>S in  
155 multicollection mode, with a Cs<sup>+</sup> primary beam of 1nA intensity. Data were corrected  
156 for instrumental mass fractionation using several sulfide standards: Maine (pyrite,  
157  $\delta^{34}\text{S} = -19.3\text{‰}$ ), Spain (pyrite,  $\delta^{34}\text{S} = -2.95\text{‰}$ ), NiS ( $\delta^{34}\text{S} = 19.14\text{‰}$ ). Analyses consisted  
158 of 3 minutes of presputtering followed by data acquisition in 40 cycles of 3 seconds.  
159 Sulfur isotope measurements are reported as part per thousand deviations with  
160 respect to Canyon Diablo Troilite using  $\delta$  notation.

161 Microthermometric data were acquired on a Linkam MDS 600 stage coupled  
162 with an Olympus BX-51 microscope equipped with a UV-light source (Mercury

163 lamp,  $\lambda=365$  nm) allowing the recognition of fluorescent petroleum-bearing fluid  
164 inclusions. Phase transition temperatures can be measured between  $-196^{\circ}\text{C}$  and  
165  $600^{\circ}\text{C}$ , with an accuracy of  $\pm 0.1^{\circ}\text{C}$ . In this study we measured homogenization  
166 temperature of hydrocarbon-bearing and aqueous inclusions, which correspond to  
167 the transition between a biphasic liquid-vapor inclusion and a monophasic liquid or  
168 gas inclusion.

169 Raman analyses of aqueous inclusions were performed using a LabRAM HR  
170 microspectrometer (Horiba Jobin Yvon), using the 457 nm radiation of an  $\text{Ar}^+$  laser  
171 with a final power of about 80 mW. Each measurement is the sum of 4 spectrum  
172 acquisition of 30 to 60 seconds each. Beam parameters and accumulation time were  
173 adjusted to obtain the best signal/background ratio. Chlorinities of aqueous phases  
174 were calculated using the method of Dubessy *et al.* (2002).

175 Infrared spectra of hydrocarbons in inclusions are recorded in transmission  
176 mode using a Bruker Vertex 70 Fourier transform infrared spectrometer coupled to a  
177 Hyperion 3000 microscope. The microscope is equipped with a MCT (mercury  
178 cadmium telluride) cooled at 77 K. The size of the beam can be reduced down to a  
179 diameter of  $20\mu\text{m}$  with X15 objective magnification. The IR spectra are obtained in  
180 the mid-infrared region with a  $2\text{ cm}^{-1}$  spectral resolution. Each sample is scanned  
181 about 90 seconds and the influence of atmospheric water and carbon dioxide was  
182 always subtracted.

183 Confocal laser scanning microscopy (CLSM) measurements were acquired on a  
184 Biorad rainbow system coupled to a Nikon inverted microscope following procedure  
185 described in Pironon *et al.* (1998). 3D reconstruction was used to calculate the volume

186 of gaseous filling at room temperature. Isochores and isopleths of hydrocarbon-  
187 bearing inclusions were determined with FIT-Oil software (Fluid Inclusion  
188 Thermodynamic-Oil, evolution of PIT software; Thiéry *et al.*, 2000) using  
189 homogenization temperature and previously calculated  $\alpha/\beta$  parameters.  $\alpha/\beta$   
190 parameters represent the composition of heavy alkanes ( $\geq C_{10}$ ) and light alkanes ,  
191 respectively (Montel, 1993; Thiéry *et al.*, 2000). Isochores of aqueous inclusions in the  
192  $CH_4$ - $H_2O$ -NaCl system, with various NaCl concentration and  $CH_4$  concentration  
193 below 1 molal, were calculated using the method of Zhang and Frantz (1987).

## 194 **4. Results**

### 195 **4.1. Mineralogy of the Alum Shale Formation**

196 The Alum Shale Formation is an organic-rich marine black shale showing  
197 variable facies, from dark gray calcareous mudstone to black laminated mudstone  
198 depending on the organic matter content (Fig. 2). Sulfides, especially pyrites, are  
199 disseminated throughout the shale. Metamorphic Alum Shale is often folded and  
200 present calcite precipitation as pressure shadows around massive pyrite or inside  
201 fractures with pyrobitumen. The detrital fraction is composed of quartz, feldspars  
202 (orthose and albite) and clays (Fig. 3). Clays composition is slightly variable but  
203 always remains dominated by illite and illite-smectite mixed-layer minerals. The  
204 latter are characterized by a left shoulder on illite main peak and doublets on  
205 secondary peaks. Smectite is emphasized by peak shift after glycolation and peak  
206 disappearance after heating at 550°C. Minor kaolinite and chlorite are also observed.  
207 With deep burial and metamorphism, illite peak gets thinner and shows the illite-  
208 muscovite transition.

209

## 210 **4.2. Geochemistry of the Alum Shale Formation**

211 As many other black shales deposited in marine environments, Alum Shale  
212 contains metal concentration higher than ordinary marine shales. In figure 4, whole-  
213 rock concentrations of several elements (As, Co, Cu, Cr, Mo, Ni, Pb, Th, U, V, Zn) in  
214 the Alum Shale Formation and reference metalliferous black shales are plotted and  
215 compared to the “Marine Shales” (Turekian and Wedepohl, 1961). Metalliferous  
216 black shales include Chinese Cambrian black shales from Tarim basin (Yu *et al.*,  
217 2009), Ronneburg Silurian black shales (Lippmaa *et al.*, 2011) and American Devonian  
218 black shales (Ohio shale, Lewis *et al.*, 2010). Complete dataset is in table 2 for eight  
219 metamorphic samples (Myrviken, Lövstrand and Tåsjö) and thirteen non  
220 metamorphic samples (Närke, Östergötland, Öland, Skåne and Västergötland). The  
221 Alum Shale Formation is remarkable because of a particularly higher uranium  
222 content compared to other metalliferous black shales. In Upper Cambrian Alum  
223 Shale, U content is generally higher than 100 ppm (mean  $118\pm 48$  ppm) and may reach  
224 several hundreds ppm. On the contrary in most metalliferous black shale worldwide,  
225 U content does not exceed a few tens of ppm.

226 Besides, in Scandinavian Alum Shale, organic carbon content and total sulfur  
227 content (TS) are generally high but values are scattered. Total Organic Carbon (TOC)  
228 ranges between 5 and 20 wt.% (mean  $12\pm 4$  wt.%) and total sulfur between 4.6 and 6.3  
229 wt.% (mean  $5.5\pm 0.6$  wt.%). When plotted in a TS vs TOC diagram (Fig. 5a), Alum  
230 Shale analyses display a positive correlation across “euxinic sediments” and “normal  
231 oxygenated sediments” fields. This correlation line crosscut TS-axis at around 4.9  
232 wt.%. Moreover, whole-rock V/Cr and V/(V+Ni) ratios are high, between 4.26 and

233 18.67 (mean  $9.19 \pm 4.65$ ) and between 0.68 and 0.85 (mean  $0.77 \pm 0.04$ ), respectively (Fig.  
234 5b).

235 Finally, when plotted against both organic carbon (Fig. 6a) and phosphorus  
236 (Fig. 6b) concentrations, uranium content displays a positive correlation. In  
237 particular, density-corrected uranium concentration increases along with total  
238 organic carbon following two different trends for metamorphic and immature  
239 samples. Indeed, in metamorphic Alum Shale, U concentration increases with a  
240 steeper slope than in immature samples. Thus, for equivalent percentages of organic  
241 carbon, metamorphic samples are twice as rich as immature samples.

242

### 243 **4.3. Carbon, sulfur and uranium in immature Alum Shale**

#### 244 **4.3.1. Organic matter accumulation**

245 In immature Alum Shale, organic matter is composed of fluorescent liptinite  
246 and non-fluorescent pseudo-vitrinite (Fig. 7a and 7b). In most immature samples,  
247 liptinite displays yellow-green fluorescence, whereas Västergötland's lipnite is  
248 scarcer and shows orange-brown fluorescence. Rock-Eval results are listed in table 3.  
249 Rock-Eval S1 values are between 0.45 and 1.71 mg HC/g Rock and S2 values  
250 between 13.00 and 99.94 mg HC/g Rock. Hydrogen Index (HI) values range between  
251 132 and 544 mg HC/g TOC. Tmax values range between 406 and 426°C confirming  
252 immature organic matter (Tissot and Welte, 1984). When plotted in a S2 versus TOC  
253 diagram (Fig. 8), immature Alum Shale lines up on the Type II organic matter trend  
254 (Langford and Blanc-Valleron, 1990). Västergötland's Alum Shale appears to be  
255 anomalous with lower IH values, which may be related to previously described  
256 maceral composition. In IH-Tmax (Fig. 9) and S1-S2 (Fig. 10) diagrams, organic

257 matter falls in the immature Type II area, with an excellent petroleum potential.

258

#### 259 *4.3.2. Sulfide paragenesis during sedimentation and diagenesis*

260 The Alum Shale Formation contains sulfide mineralization, in particular  
261 pyrites with various shapes and distributions (Fig. 11): (a) disseminated spherulites  
262 or framboids in shale layers and rarely in bitumen; (b) small anhedral crystals  
263 scattered in black shale; (c) beds or clusters of small euhedral crystals, mostly  
264 underlining sedimentary bedding; (d) massive anhedral to euhedral pyrites; (e)  
265 pyrite cements and overgrowths in fractures.

266 In immature Alum Shale, five pyrite generations (named Py1 to Py5 in tables  
267 and figures) have been identified over petrographic features. The first generation  
268 corresponds to disseminated framboids and small euhedral crystals following shale  
269 stratification. The second generation occurs as beds or nodules of massive pyrite and  
270 may be locally reworked and cemented framboids clusters. This recrystallization  
271 stage seems to be synchronous with partial pyrite cementation of detrital grains. The  
272 third generation is represented by large pyrite crystals which are either scattered in  
273 the shale or grow on recrystallized -mainly framboids- beds perpendicularly to the  
274 shale bedding. Massive pyrites display a homogeneous texture, sometimes with  
275 growth zones, and may deform shale lamination. The fourth generation corresponds  
276 to fracture infillings as pyrite cement or large-scale euhedral crystals. Cementation is  
277 not homogeneous and has high porosity. The fifth generation occurs as  
278 homogeneous pyrite veins and small pyrite overgrowths.

279 Trace elements content in sulfides is often helpful to distinguish different  
280 precipitation conditions. In the case of immature Alum Shale, no particular

281 enrichment was measured in pyrites, except for framboids, where Cu and As  
282 concentrations are higher than co-genetic euhedral pyrites (Fig. 12a and b).

283 Every pyrite generation was analyzed by SIMS (Secondary Ion Mass  
284 Spectrometry) to determine sulfides isotopic composition. Sulfur isotopic data are  
285 listed in table 4 and represented as a histogram (Fig. 13). First generation (clusters of  
286 framboids and euhedral crystals) shows high  $\delta^{34}\text{S}$  values between 30 and 40‰. One  
287 single framboid was analyzed and has a slightly negative  $\delta^{34}\text{S}$  (-4‰). Second pyrite  
288 generation values range between 22 and 26‰. Third generation correspond to  
289 massive pyrites. Analyses yield  $\delta^{34}\text{S}$  results between 18 and 25‰. Inside most  
290 crystals, neither chemical zoning nor isotopic composition gradient was observed.  
291 However, isotopic zoning was measured into a large pyrite with  $\delta^{34}\text{S}$  increasing from  
292 core to rim (16‰ to 23‰). Besides, a small pyrite inclusion in the center shows high  
293 sulfur isotopic composition ( $\delta^{34}\text{S} = 33\%$ ) similar to that of first generation. Fourth  
294 generation cementing massive pyrites shows homogeneous  $\delta^{34}\text{S}$  values (30-31‰).  
295 Rare subhedral pyrites on the edges of these cemented areas have the same isotopic  
296 signature. In homogeneous fracture infillings and late pyrite overgrowths (fifth  
297 generation),  $\delta^{34}\text{S}$  ranges between 19 and 23‰.

298

### 299 **4.3.3. Uranium concentration in immature shales**

300 No detectable uranium mineral was observed in immature Alum Shale.  
301 However, in the Alum Shale Formation, calcium phosphate nodules are  
302 disseminated and generally parallel to the stratification. These nodules are several  
303 hundreds of micrometers long and are composed of apatite-( $\text{CaF}[\text{OH}]$ ) (Fig. 14). REE  
304 analyses (Table 5) were carried out using LA-ICP-MS. REE spectra normalized to

305 North American Shale Composite (NASC REE concentrations after Gromet *et al.*,  
306 1984) are plotted in figure 15a. Apatite-(CaF[OH]) nodules display bell-shaped REE  
307 patterns, centered on Eu. Such patterns are similar to those measured on pre-jurassic  
308 biogenic marine phosphates. Uranium concentration in these phosphate nodules  
309 were measured with LA-ICP-MS. The results (Table 5) show between 131 and  
310 185 ppm uranium grades.

311

#### 312 **4.4. Impact of burial and thermal maturation on organic matter and uranium**

##### 313 **4.4.1. Thermal maturation of the Alum Shale Formation and oil generation**

314 Burial and thermal maturation of Alum Shale lead to oil and gas generation.  
315 Hydrocarbons are present as pyrobitumen or impregnation of phosphate nodules in  
316 the black shale, but also as fluid inclusions in calcite crystals (Fig. 16a and b), which  
317 occur as: (a) carbonate concretions composed of large fibrous calcite crystals, up to 10  
318 centimeters long. These concretions, parallel to shale bedding, may be up to 1.5  
319 meters long and 50 centimeters thick. The core is made of microcrystalline calcite and  
320 bioclasts, whereas rims are recrystallized in pure calcite with frequent cone-in-cone  
321 structures. (b) brecciated levels composed of centimetric non-oriented angular  
322 particles of pure calcite in a matrix of microcrystalline calcite and detrital grains; (c)  
323 fractures with calcite infillings in Ordovician limestones.

324 Fluid inclusions (Fig. 16c to d), in particular petroleum inclusions, are  
325 abundant in breccias and fractures, but scarce in fibrous crystals. They are mostly  
326 biphasic  $L_w$ -V (liquid water and vapor bubble) or  $L_{oil}$ -V (liquid oil and vapor bubble),  
327 although some monophasic  $L_{oil}$  or triphasic  $L_w$ - $L_{oil}$ -V inclusions have been observed.  
328 In 3-phase inclusions, oil always occurs as droplets in aqueous phase and vapor

329 phase is contained in oil (Fig. 16f). Shapes vary from rounded or ellipsoidal shapes  
330 for aqueous or small oil inclusions to irregular shapes for large petroleum inclusions.  
331 Most inclusions are small (<10  $\mu\text{m}$ ) although a few can reach several tens of microns.  
332 Distribution of fluid inclusion is not homogeneous in calcite crystals. They are  
333 generally clustered (several inclusions to tens of inclusions of various size) or  
334 distributed along calcite cleavage planes. These fluid inclusion planes are tens to  
335 hundreds of microns long and are always constrained within a single crystal. Oil is  
336 generally yellow to brown, rarely colorless. Under UV-epifluorescence, petroleum  
337 inclusions display various colors: yellow to orange-brown for most of them, white,  
338 blue, or green-blue. Isolated and clustered inclusions in concretions or fractures are  
339 considered as primary inclusions trapped during calcite growth. Short intragranular  
340 fluid inclusion planes are taken as primary when parallel to cleavage or rarely  
341 pseudo-secondary when randomly oriented. A few planes are obviously posterior to  
342 calcite crystallization and are labeled as secondary. These intergranular trails contain  
343 small oil inclusions with blue-colored UV-epifluorescence and crosscut crystal  
344 fabrics.

345 Homogenization temperatures ( $T_h$ ) were measured on 213 fluid inclusions  
346 (185 oil inclusions and 28 aqueous inclusions) from 6 concretion samples, and 207  
347 inclusions (172 oil inclusions and 35 aqueous inclusions) in 3 limestone fractures.  
348 Distinction between inclusions was made according to the parameters previously  
349 described: host rock (concretion/breccia or fractures), timing of formation (primary,  
350 pseudo-secondary or secondary), liquid phase (oil or water) and fluorescence color  
351 (yellow-orange-brown or white-blue). Microthermometry results are presented in

352 histograms (Fig. 17).

353 In calcite crystals from concretions and breccias (Fig. 17a), homogenization  
354 temperatures show a wide range of values between 60 and 200°C.  $T_h$  distribution of  
355 petroleum inclusions is bimodal with a primary mode between 70 and 100°C and a  
356 secondary mode between 120 and 150°C. Inclusions with yellow-orange-brown  
357 fluorescence have principal and secondary modes centered around 80°C and 130°C,  
358 respectively. Inclusions with white-blue fluorescence have principal and secondary  
359 mode centered around 90°C and 140°C, respectively.  $T_h$  of aqueous inclusions range  
360 between 90 and 170°C, with a unimodal distribution centered around 140°C. The  
361 distribution of oil inclusions is essentially driven by primary and pseudo-secondary  
362 inclusions.  $T_h$  of blue-fluorescing secondary inclusions range between 83 and 105°C.

363 In fractures (Fig. 17b), inclusions have a wide range of  $T_h$  between 5 and 190°C.  
364 Inclusions with yellow-orange-brown fluorescence have principal and secondary  
365 modes centered around 100°C and 150°C, respectively. Inclusions with white-blue  
366 fluorescence have unique mode centered on 100°C.  $T_h$  of aqueous inclusions range  
367 between 90 and 180°C, with a unimodal distribution centered around 150°C.

368 Determination of chlorinity in aqueous phase and gas content in fluid  
369 inclusions were performed with Raman spectroscopy. Only aqueous inclusions were  
370 analyzed due to high fluorescence of hydrocarbons disrupting Raman signal. Water  
371 chlorinity was calculated at room temperature from band area ratio of water phase. 9  
372 inclusions in concretions have salinities between 9.5 and 20.9 wt.% eq. NaCl (mean  
373  $15 \pm 3.2$  wt.% eq. NaCl). 3 inclusions in fractures have salinities between 12 and  
374 19.4 wt.% eq. NaCl (mean  $16 \pm 3.7$  wt.% eq. NaCl). Besides, composition of gaseous

375 phase was analyzed in aqueous inclusions. Methane is always detected and is  
376 sometimes associated with carbon dioxide. However, dissolved methane  
377 concentration at homogenization temperature was not detected, which indicates  
378 rather low concentration in CH<sub>4</sub>.

379 Infrared spectroscopy was used to investigate composition of petroleum  
380 inclusions (Table 6 for inclusions observed with confocal laser scanning microscopy).  
381 CH<sub>4</sub> content in concretions and fractures is variable and range between 26.2 and  
382 47.3 mol% (mean 38.3±7.8 mol%) and between 16.9 and 48.7 mol% (mean  
383 30.9±9.8 mol%), respectively. CO<sub>2</sub> was not detected in most concretion inclusions but  
384 was present at low concentration (0.3 to 2.9 mol%) in fracture inclusions. In the same  
385 way, alkane content varies greatly within samples: 52.5 to 73.8 mol% (mean  
386 61.7±6.9 mol%) in breccias and concretions; 50.7 to 80.9 mol% (mean 68±9.5 mol%) in  
387 limestone fractures. All these parameters are not correlated with host mineral,  
388 homogenization temperature or fluorescence color. Only CO<sub>2</sub> concentration seems to  
389 be slightly higher in fractures than in concretions. On the contrary, CH<sub>2</sub>/CH<sub>3</sub> ratio is  
390 clearly distinct between host minerals. In concretions and breccias, ratios vary  
391 between 1 and 3.6 (mean 2.4±0.9, a single inclusion has a ratio close to 1) whereas in  
392 fractures ratios vary between 0.6 and 1.6 (mean 1.1±0.4). In concretions, higher  
393 CH<sub>2</sub>/CH<sub>3</sub> ratios imply longer aliphatic chains and therefore lower maturity than in  
394 fractures. Besides, a correlation is observed between CH<sub>2</sub>/CH<sub>3</sub> ratios related to oil  
395 maturity and fluorescence color: inclusions with a ratio close to 1 show white-blue  
396 fluorescence, yellow fluorescence around 2 and orange-brown fluorescence above  
397 2.5. In fractures, predominance of inclusions with with-blue fluorescence over rare

398 inclusions with orange-brown fluorescence may indicate greater maturity of oil  
399 trapped in fractures, as already suggested by  $\text{CH}_2/\text{CH}_3$  ratios.

400 Confocal laser scanning microscopy was performed on several petroleum  
401 inclusions (features in table 6) to measure oil volume whereas volume of the gas  
402 bubble is determined by spherical approximation. Degree of gaseous filling ( $F_v$ ) is  
403 used with microthermometry results and thermodynamic modeling to estimate  
404 pressure-temperature trapping conditions of petroleum inclusions.  $F_v$  ranges  
405 between 3 and 27% for inclusions in concretions and between 5 and 25% for  
406 inclusions in fractures.  $F_v$  vs  $T_h$  diagram (Fig. 18) is useful to characterize petroleum  
407 composition from black oil to dry gas. Oil trapped in concretions falls in the range of  
408 heavy black oils and appears to be heavier than oil in fractures, which ranges  
409 between black oil and light oil.

410 Thermodynamic properties and P-T trapping conditions of fluids can be  
411 reconstructed with thermometric and compositional data of petroleum and aqueous  
412 inclusions. Petroleum isopleths and isochores are represented in figure 19. No  
413 aqueous inclusion was observed in the immediate vicinity of modeled oil inclusions.  
414 Therefore, aqueous isochores were calculated with contemporaneous inclusion from  
415 the same sample and are represented by a band rather than lines. Dashed lines  
416 correspond to a "standard" isochore calculated using the mode of  $T_h$  distribution and  
417 average salinity. P-T trapping conditions are determined by the intersection of oil  
418 and aqueous isochores. In concretions, primary mode hydrocarbon inclusions  
419 ( $T_h < 100^\circ\text{C}$ ) indicate trapping temperature between 170 and 190°C and trapping  
420 pressure between 650 and 750 bars. With secondary mode inclusions ( $T_h > 110^\circ\text{C}$ ),

421 trapping temperature and pressures range between 150 and 170°C and 180 and  
422 280 bars, respectively. In fractures, P-T domains appear to be much more continuous  
423 from high pressure to relatively low pressure. Low  $T_h$  inclusions indicate trapping  
424 temperature around 180-190°C and pressures between 500 and 600 bars. Most oil  
425 inclusions with  $T_h$  above 100°C correspond to trapping temperature around 170-  
426 180°C and trapping pressure between 350 and 430 bars.

427 Finally, LA-ICPMS analysis of fluid inclusions trapped in calcite did not show  
428 any significant concentration in metal or uranium (detection limit of 0.5 to 1 ppm).

429

#### 430 ***4.4.2. Impact of burial diagenesis on uranium content: experimental input***

431 The TOC richest immature sample (from Närke), was heated in gold cells  
432 during 24 hours at 350°C and 700 bars to simulate thermal maturation and  
433 hydrocarbon generation. Pyrolyzed matter was then solvent-extracted. Hydrocarbon  
434 extracts and pyrolysis residues were both analyzed and uranium content measured.  
435 LA-ICPMS analysis did not allow us to detect any particular uranium content in the  
436 solvent extracts (within detection limit). However, residues contain similar, but  
437 slightly higher, uranium concentrations, compared to unheated shale (139.9 and  
438 132.4 ppm versus 124.5 ppm). TOC values decreased by more than 20% with  
439 hydrocarbon generation, from 18.48 wt.% to 14.41 and 14.24 wt.%. Density-corrected  
440 values are plotted in figure 6a. Alum Shale samples display a U-constant evolution  
441 during thermal maturation.

442

### 443 **4.5. Impact of metamorphism on carbon, sulfur and uranium mineralization**

#### 444 ***4.5.1. Organic matter behavior with metamorphism: geothermometer***

445 *application*

446 The Raman spectrum of carbonaceous matter is composed of several peaks  
447 situated in first order (1100–1800  $\text{cm}^{-1}$ ) and second-order (2500–3100  $\text{cm}^{-1}$ ) regions  
448 (Tuinstra and Koenig, 1970; Nemanich and Solin, 1979). The number, position, width  
449 and intensity of peaks depend on the degree of structural organization of  
450 carbonaceous material, from very disordered carbonaceous matter to graphite and it  
451 can be used as a geothermometer (e.g. Beyssac *et al.*, 2002, 2003(a), 2003(b); Beyssac  
452 and Lazzeri, 2012; Lahfid *et al.*, 2010).

453 In metamorphic Alum Shale samples, organic matter is composed of  
454 disseminated pseudo-vitrinite particles and bitumen veinlets in the schist. Bitumen  
455 with conchoidal fractures can also be found in veins, trapped in calcite (Fig. 7c to f).  
456 Raman spectroscopy of carbonaceous material (RSCM) was applied on different  
457 metamorphic samples from the Caledonian front (Tåsjö and Myrviken), in order to  
458 characterize the degree of organization of organic matter and estimate metamorphic  
459 temperature. Both pseudo-vitrinite and bitumen have been studied and Raman data  
460 are provided in table 7. Organic material in the Alum Shale shows first-order and  
461 second-order regions corresponding to very disordered carbonaceous matter (Fig.  
462 20a). We thus applied a fitting procedure using five bands with Lorentzian profiles  
463 (Lahfid *et al.*, 2010; Lecomte *et al.*, 2014). The decomposed first-order region of  
464 carbonaceous matter spectrum (Fig. 20b) is composed of a predominant graphite  
465 peak including a graphite band s.s. (G) at  $1595\pm 3 \text{ cm}^{-1}$  and a defect band (D2) at  
466  $1608\pm 3 \text{ cm}^{-1}$ , and a secondary composite (D) peak with major defect band (D1) at  
467  $1332\pm 2 \text{ cm}^{-1}$  and a left shoulder (defect band (D4) at  $1218\pm 9 \text{ cm}^{-1}$ ). In disordered CM,  
468 intensity of the valley between (D1) and (G) is high and indicates the existence of

469 another band (D3) at  $1513\pm 8\text{ cm}^{-1}$ .

470 Following procedure described by Lahfid *et al.* (2010), using two area ratios  
471  $RA1 = (D1 + D4) / (D1 + D2 + D3 + D4 + G)$  and  $RA2 = (D1 + D4) / (D2 + D3 + G)$ ,  
472 yield an estimate of the maximal temperature that underwent the organic matter:  
473  $RA1 = 0.0008T + 0.3758$  and  $RA2 = 0.0045T + 0.27$  (Table 7). In metamorphic Alum  
474 Shale, calculated temperatures are slightly higher at Tåsjö ( $305\pm 11^\circ\text{C}$  with RA1 and  
475  $302\pm 14^\circ\text{C}$  with RA2) than at Myrviken ( $285\pm 11^\circ\text{C}$  with RA1 and  $279\pm 13^\circ\text{C}$  with RA2).  
476 In such low-grade metamorphic systems, temperature is considered to be the key  
477 parameter for carbonaceous matter evolution at geological time scales even if other  
478 parameters (pressure, time or deformation) are less well constrained (Beysac *et al.*,  
479 2003(a); Lahfid *et al.*, 2010).

480

#### 481 **4.5.2. Modification of sulfide paragenesis**

482 In metamorphic Alum Shale from the Caledonian front, all pyrites generations  
483 described in immature shales (Py1 to Py5) have been affected by metamorphism  
484 during Caledonian orogeny. Several particular modifications can be identified,  
485 namely: (a) intense fracturing throughout the Alum Shale, with pyrite and calcite  
486 fillings, and numerous pyrite overgrowths (Fig. 21a and b). In particular, these  
487 overgrowths are much more frequent in metamorphic samples than in immature  
488 ones, and occur not only in fractures but also around previous pyrite generations,  
489 often completely cataclased by deformation. These secondary crystals can reach  
490 several tens of microns and calcite precipitates in pressure shadows around massive  
491 pyrites; (b) plastic deformation of pyrite beds (framboids and small euhedral  
492 crystals), initially parallel to stratification (Fig. 21c); (c) pressure-solution features on

493 small euhedral pyrites, with interpenetrating grain boundaries (Fig. 21d); (d)  
494 precipitation of new sulfides (chalcopyrite and sphalerite) coexisting with late pyrite  
495 after fracturing stage. Chalcopyrite and sphalerite generally occurs as cements  
496 around euhedral pyrites or as fracture fillings (Fig. 21e to h).

497 In metamorphic Alum Shale, the latest pyrite generation (named Py6), which  
498 is sub-synchronous with chalcopyrite and sphalerite, is enriched in Ni, As, Se and Cd  
499 compared to syngenetic pyrites (Fig. 12c and d). Besides, early pyrites, and in  
500 particular framboids, preserved their trace elements signature, which is emphasized  
501 by (Cu,As,Ni)-rich clusters in massive pyrites. Isotopic analyses on late metamorphic  
502 pyrites yield  $\delta^{34}\text{S}$  values between 9 and 15‰ (Fig. 13).

503

#### 504 **4.5.3. Uranium mineralogical expression and metamorphism**

505 Apatite-(CaF[OH]) nodules can also be found in metamorphic Alum Shale,  
506 but they are more porous than in non metamorphic samples (Fig. 14e). Bell-shaped  
507 REE spectra are flattened with a preferential enrichment in light and heavy REE (La,  
508 Ce, Tm, Yb, Lu) compared to middle REE (Fig. 15b). Some of them display a negative  
509 anomaly in Eu. Besides, whereas uranium concentration in non metamorphic shales  
510 does not exceed a few hundreds ppm, it can reach several thousands ppm uranium  
511 in metamorphic black schists (between 322 and 2655 ppm uranium).

512 As previously mentioned, no detectable uranium mineral was observed in  
513 immature Alum Shale. On the contrary, in metamorphic Alum Shale, two types of  
514 uranium bearing-minerals were detected: (a) uraninite and uranium titanate micro-  
515 inclusions in synmetamorphic pyrites (Fig. 22a and b); (b) complex assemblages of U,  
516 Ti, and Y phospho-silicates (Fig. 22c to f). In details, preserved uraninites and

517 uranium titanates are rare and can only be found in euhedral pyrites and  
518 overgrowths associated with retrograde metamorphism. These pyrites are the latest  
519 to crystallize around preexisting sulfides and pyrobitumens (Lecomte *et al.*, 2013). On  
520 the contrary, uranium phospho-silicates are frequently found disseminated in the  
521 organo-mineral matrix or in patches around pyrobitumen veins, pseudo-vitrinite  
522 particles or pyrite. Uranium phospho-silicates seem to crystallize essentially at the  
523 periphery of carbonaceous particles and on pyrite framboids. Rare occurrences show  
524 particular textures with uraninite or urano-titanates cores rimmed by U-Ti phospho-  
525 silicates. Corrosion gulfs around these U-Ti oxides are also filled with U-Ti phospho-  
526 silicates. Spherulites of uranium phospho-silicates were also found in apatite-  
527 (CaF[OH]) nodules. In metamorphic Alum Shale, these porous phosphates nodules  
528 are often surrounded by pyrobitumen. Uranium minerals have been analyzed with  
529 electronic microprobe and standard-calibrated SEM (Table 8). All these  
530 phosphosilicate clusters correspond to phosphocoffinites with variable Ti, Y, Zr  
531 content.

532 Uranium phospho-silicates have variable analytical totals between 70 and 98.33 wt.%.  
533 Low analytical totals in (phospho)-coffinite are probably related to micro-porosity or  
534 hydration (Deditius *et al.*, 2008). Atoms per formula units (APFU) of Si, P, Ca, Pb,  
535 Ti, U, Y and Zr in uranium minerals were calculated on the basis of two oxygens and  
536 one cation (Table 8). Three groups can be separated based on Y and Ti concentration:  
537 (a) Y-poor/Ti-rich phospho-silicates ("Brannerite" group); (b) Y-poor/Ti-poor  
538 phospho-silicates ("Uraninite" group); (c) Y-rich/Ti-poor phospho-silicates  
539 ("Xenotime" group), including micro-spherulites apatite-(CaF[OH]) nodules. In

540 figure 23, Ti and U+Pb+Zr concentrations are plotted against Si and P content,  
541 respectively. Uraninite ( $\text{UO}_2$ ), brannerite ( $\text{U}_{0,33}\text{Ti}_{0,66}\text{O}_2$ ), coffinite ( $\text{U}_{0,5}\text{Si}_{0,5}\text{O}_2$ ) and  
542 xenotime ( $\text{Y}_{0,5}\text{P}_{0,5}\text{O}_2$ ) are also indicated. Pb and Zr content is low and these two  
543 elements are substituted for U in phospho-silicates. Pb and Zr will thus be  
544 considered with U concentration in successive graphs. Y-poor/Ti-rich phospho-  
545 silicates are aligned between “brannerite” and “coffinite” end-members, the former  
546 corresponding to well-preserved U-Ti oxides micro-inclusions in pyrite. Y-poor/Ti-  
547 poor phospho-silicates are aligned between “uraninite” and “coffinite” end-  
548 members, the former corresponding to well-preserved U oxides micro-inclusions in  
549 pyrite; the gap between analyses and theoretical evolution is caused by the presence  
550 of calcium in U phospho-silicates. Y-rich/Ti-poor phospho-silicates are aligned  
551 between “brannerite” and “coffinite” end-members, the former corresponding to rare  
552  $\text{YPO}_4$  crystals. Ca content is generally constant, whatever the concentration in Si, but  
553 increases along with P, only in the case of Y-poor/Ti-poor phospho-silicates  
554 (“uraninite”).

555

## 556 **5. Discussion**

### 557 **5.1. Sedimentation and uranium preconcentration**

558 Sulfur, mainly present as sulfide, and organic carbon contents (Fig. 5a)  
559 provide different information on conditions of sedimentation for the Alum Shale of  
560 Sweden. In Carbon-Sulfur plots, marine sediments deposited in oxygenated waters  
561 display a positive correlation fitting the origin of the diagram. Indeed, pyrite  
562 precipitation occurs below the sediment-water interface and is limited by the

563 concentration of organic carbon (Berner and Raiswell, 1983). On the contrary,  
564 sediments deposited in euxinic conditions would not display any correlation or  
565 would have a positive intercept with the total sulfur axis (Raiswell and Berner, 1985).  
566 This positive intercept represents the formation of pyrite in the water column and at  
567 the sediment-water interface, regardless of the organic carbon content. The slightly  
568 positive correlation line and the presence of data points in the “normal marine  
569 sediments” field can be explained by euxinic conditions, but where pyrite  
570 precipitation is limited by the concentration of available iron (Lyons and Berner,  
571 1992; Leventhal, 1995). Besides, the evolution of the V/Cr ratio as a function of V/(V  
572 +Ni) allows characterizing the level of oxygenation during sedimentation (Jones and  
573 Manning, 1994; Hatch and Leventhal, 1992). For the Alum Shale Formation (Fig. 5b),  
574 V/Cr and V/(V+Ni) ratios indicate sedimentation in suboxic to anoxic conditions.

575         During sedimentation, organic matter was accumulated as fluorescent liptinite  
576 macerals and non-fluorescent pseudo-vitrinite macerals. However, vitrinite derived  
577 from humification of vascular plants cannot exist in pre-silurian sediments. In fact,  
578 pseudo-vitrinite is frequently observed in Cambrian Scandinavian shales (Kisch,  
579 1980, Buchardt *et al.*, 1990) or in Tarim basin sediments (China) and may originate  
580 from multicellular benthic algae (Wang, 2000). In the Alum Shale Formation, pseudo-  
581 vitrinite and graptolites display identical reflectance, which suggests that vitrinite-  
582 like particles may in fact be fragments of graptolites (Petersen *et al.*, 2013). Therefore,  
583 petrographic observations are consistent with Rock-Eval analyses and support  
584 organic matter accumulation in marine settings (Type II kerogens, Figures 8 and 9).

585         In the Alum Shale Formation, five successive pyrite generations (Py1 to Py5,

586 Fig. 13) precipitated during sedimentation and diagenesis. No particular trace-  
587 element enrichment was measured in pyrites, which may indicate similar  
588 geochemical conditions or low availability in interstitial fluids during sulfide  
589 precipitation. High Cu and As content in framboids may be linked to specific affinity  
590 of some trace elements (Mo, As, Cu), due to fast nucleation and high specific surface  
591 of framboids.

592 The wide spread of  $\delta^{34}\text{S}$  values in syn-sedimentary to syn-diagenetic pyrites  
593 (-10 to +40‰; data from Dahl, 1990 and this study in Fig. 13) together with the  
594 existence of negative values suggest the implication of bacterial processes resulting in  
595 sulfate reduction and sulfide precipitation (Fig. 24).

596 When looked in details, disseminated framboids display negative  $\delta^{34}\text{S}$  (-4‰  
597 measured in this study). Negative values measured by Dahl (1990) on whole-rock  
598 pyrites may thus be explained by the predominance of framboids over other pyrites  
599 generations. Bacterial sulfate reduction (BSR) is known to produce  $^{32}\text{S}$ -rich sulfides  
600 compared to initial sulfate (Goldhaber *et al.*, 1978). Indeed, while inorganic sulfate  
601 reduction yield a 22‰ sulfate-sulfide isotope fractionation (Harrison and Thode,  
602 1958), bacterial pathway is responsible for higher fractionation, up to 46‰ on  
603 bacterial cultures (Kaplan and Rittenberg, 1964) and 40‰ in sediments (Habicht and  
604 Canfield, 2001 ; Canfield, 2001). Considering a  $\delta^{34}\text{S}$  value of about 30‰ for initial  
605 sulfate [ $\delta^{34}\text{S}$  of  $\text{SO}_4^{2-}$  in marine Cambrian waters (Claypool *et al.*, 1980; Strauss, 1997),  
606 the most likely sulfate source for early pyrites], such fractionation brings in  $\delta^{34}\text{S}$   
607 down to -15‰. Unlike disseminated framboids, cogenetic euhedral pyrites and  
608 cemented framboids clusters form beds parallel to shale stratification and show

609 highly positive  $\delta^{34}\text{S}$ , above  $\delta^{34}\text{S}$  of sulfate in marine Cambrian waters. Theoretically,  
610 sulfate supply and availability are the main processes affecting isotope variability in  
611 sedimentary sulfides. Indeed, considering an open system in which sulfate reservoir  
612 is permanently replenished, isotope fractionation remains constant and yield to  
613 negative  $\delta^{34}\text{S}$  in the case of predominant bacterial sulfate reduction. On the contrary,  
614 in a closed system, reduction of sulfate pool to sulfides preferentially removes  $^{32}\text{S}$   
615 and thus enriches residual sulfate in  $^{34}\text{S}$ . Sulfides show higher and higher  $\delta^{34}\text{S}$  which  
616 tend towards value of starting sulfate. However, even in an ideally closed system,  
617 sulfide  $\delta^{34}\text{S}$  cannot exceed  $\delta^{34}\text{S}$  of initial sulfate, due to mass conservation between  
618  $^{32}\text{S}$  and  $^{34}\text{S}$  once sulfate is depleted. Jørgensen (2004) even considers that such a  
619 distinction between open and closed systems cannot be applied to marine sediments  
620 because: (a) it passes over vertical diffusion processes of  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$  in the  
621 sediment, and particularly the fact that isotope ratios of these fluxes differ from those  
622 of  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$  reservoirs at different depths; (b) most present-day sediments used  
623 as analogues, including in anoxic closed basins such as Black Sea, cannot be  
624 considered as truly closed systems because they are never completely isolated from  
625 seawater sulfate reservoir. Moreover, in the case of the Alum Shale Formation,  
626 precipitation of disseminated framboids or micro-pyrites, beds of euhedral pyrites  
627 and framboids clusters is probably very early, in the water column, at water-  
628 sediment interface or within first centimeters of the sediment. Therefore, isotope  
629 composition of sulfides precipitated in sediment and in particular progressive  $\delta^{34}\text{S}$   
630 enrichment do not seem to be related to the development of a closed system, but  
631 rather to fractionation and vertical diffusion of  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$  with a  $\delta^{34}\text{S}$  enrichment

632 of interstitial water sulfates. This model is based on isotopic measurement of sulfides  
633 from the Black Sea, in which pyrites that precipitated in the water column have  
634 positive  $\delta^{34}\text{S}$ , sometimes close to  $\delta^{34}\text{S}$  of initial sulfate pool (Lyons and Berner, 1992;  
635 Wilkin and Arthur, 2001). Jørgensen (2004) thus demonstrated important  $\delta^{34}\text{S}$   
636 enrichment of  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$  toward sediment depth. This is not related to the  
637 development of a closed system s.s. but to a steeper gradient for  $^{32}\text{S}$  than for  $^{34}\text{S}$ ,  
638 which yields larger  $^{32}\text{S}$  depletion and thus  $^{34}\text{S}$ -rich remaining sulfate at depth. Such a  
639 process may generate sulfates with extreme  $\delta^{34}\text{S}$ , up to +135‰ 40 meters below  
640 sediment-water interface (Rudnicki *et al.*, 2001). Moreover, elevated gradients can  
641 yield  $\delta^{34}\text{S}$  increase of 40‰ within 2-3 meters and 70‰ within 15-20 meters in the  
642 sediment. On the contrary,  $\text{H}_2\text{S}$  gradient is steeper for  $^{34}\text{S}$  than for  $^{32}\text{S}$ . These  
643 gradients have important consequences for sulfate and sulfide diffusion in the  
644 sediment (Jørgensen, 1979; Goldhaber and Kaplan, 1980; Chanton *et al.*, 1987).  
645 Indeed, compared with interstitial waters at the same depth, downward  $\text{SO}_4^{2-}$  flux is  
646 enriched in  $^{32}\text{S}$  and upward  $\text{H}_2\text{S}$  flux is enriched in  $^{34}\text{S}$ . This differential diffusion,  
647 although limited in comparison with sulfate and sulfide concentrations in modern  
648 sediments (Jørgensen, 2004) implies: (1)  $^{32}\text{S}$  transfer toward depth and therefore  
649 limitation of  $\delta^{34}\text{S}$  increase in deep sulfates; (2) light sulfide conservation at depth and  
650 heavy  $\text{H}_2\text{S}$  flux toward surface. The behavior and evolution of isotopic ratios sulfates  
651 and sulfides in sediments is a complex system that cannot be reduced to the  
652 differentiation between an open system and closed system.

653 In the Alum Shale Formation, with an increase in the first meters of the  
654 sediment as previously described,  $\delta^{34}\text{S}$  values of interstitial water sulfates may reach

655 70 to 80‰, and lead to high  $\delta^{34}\text{S}$  in sedimentary pyrites through bacterial sulfate  
656 reduction (30-40‰ in pyrite clusters and beds of first generation). In that case,  
657 framboids with negative  $\delta^{34}\text{S}$  should be considered as the earliest pyrites precipitated  
658 through BSR in the water column or at the sediment-water interface, from a primary  
659 sulfate pool (seawater sulfate). Second and third pyrite generations have close  $\delta^{34}\text{S}$   
660 values between 18 and 26‰, lower than early pyrites. Petrographically, some of  
661 these pyrites correspond to recrystallization of cemented early pyrites, and their  
662 signature may therefore be a mixing between negative  $\delta^{34}\text{S}$  of framboids and high  
663  $\delta^{34}\text{S}$  of euhedral pyrites. The large pyrite crystals, which remain disseminated in the  
664 shale or grow perpendicular to some pyrite band and form centimeter-scale beds and  
665 nodules, have very similar  $\delta^{34}\text{S}$  around 24-25 ‰. Besides, no differences in isotope  
666 ratio were measured between the base (or core) and the top (or edge) of the crystals,  
667 which would indicate a homogeneous growth phase. However, a massive pyrite  
668 with an early pyrite inclusion display a  $\delta^{34}\text{S}$  increase from core to rim (16 to 23‰).  
669 Therefore, after crystallization of high- $\delta^{34}\text{S}$  primary pyrites ( $\delta^{34}\text{S} = 30\text{-}40\text{‰}$ ), a phase  
670 of cementation and crystal growth occurred, with  $\delta^{34}\text{S}$  around 15-16‰. This phase is  
671 followed by progressive  $^{34}\text{S}$  enrichment of residual sulfate, either locally through  
672 closed system Rayleigh fractionation or with sulfate  $\delta^{34}\text{S}$  increase with depth. The  
673 fourth pyrite generation, which correspond to massive pyrite cementation, may be  
674 the end of  $^{34}\text{S}$  enrichment process with  $\delta^{34}\text{S}$  around 30-31‰, close to that of sulfates  
675 in Cambrian marine waters.

676         Although  $\delta^{34}\text{S}$  evolution of pyrite generation can be explained by progressive  
677 enrichment of sulfates in  $^{34}\text{S}$ , the 15-25‰ drop of  $\delta^{34}\text{S}$  between early pyrites

678 precipitated in the sediment and the second generation of pyrite, which cements  
679 detrital grains and early pyrites, remains unclear. Considering similar isotope  
680 fractionation for the first four generations precipitated in non-indurated sediment,  
681 the best explanation implies supply of light sulfate from overlying seawater during  
682 reworking of superficial sediment, which would have brought a 20‰ decrease of the  
683  $\delta^{34}\text{S}$  of interstitial water sulfate. In the same way, the fifth generation of pyrite is  
684 characterized by a 10‰ drop of the  $\delta^{34}\text{S}$ , although being the latest generation in a  
685 general trend of increasing  $\delta^{34}\text{S}$ . These pyrites, which correspond to fracture fillings  
686 in the shale and overgrowths in fractures within massive pyrites, precipitated during  
687 late diagenesis at temperatures between 50 and 100-120°C (maximum temperature  
688 indicated by fluorescence colors of macerals). One possible explanation involves light  
689  $\text{H}_2\text{S}$  generated by kerogen thermal maturation in the most mature Alum Shale  
690 (Amrani *et al.*, 2005). Besides, bacterial activity and bacterial sulfate reduction is  
691 generally possible at temperatures below 80°C (Machel, 2001), and rarely up to 110°C  
692 (Jørgensen, 1992). Considering, maximum temperatures suggested by kerogens, it is  
693 thus necessary to take into account potential influence of thermochemical sulfate  
694 reduction (TSR) occurring at temperatures above 100°C (Machel, 2001; Basuki *et al.*,  
695 2008). TSR can theoretically yield isotope fractionation between 0 and -20‰ (Machel,  
696 1995). Indeed, whereas TSR experimental reproduction brings fractionation between  
697 10 and 20‰ (Harrison and Thode, 1957; Kiyosu and Krouse, 1990), in most  
698 sedimentary deposits no fractionation is measured (Krouse, 1977; Orr, 1977; Worden  
699 and Smalley, 1996; Cai *et al.*, 2001). Therefore, the last generation of pyrite may also  
700 precipitate through TSR of sulfates showing a  $\delta^{34}\text{S}$  around 20-30‰.

701 In immature Alum Shale, uranium mineralization has no expression as even  
702 discrete mineral phases. However, uranium concentration is positively correlated  
703 with organic carbon content (Fig. 6a) and phosphorus concentration (Fig. 6b),  
704 indicating a specific association where uranium shows a dissemination and/or a  
705 complexation with organic matter or phosphates. Such a close relationship was  
706 previously suggested by several studies on *kolm*, organic matter lenses containing up  
707 to several thousands ppm uranium, in particular in cerium-bearing minerals (Cobb  
708 and Kulp, 1961; Armands, 1972; Parnell, 1984).

709 The correlation between phosphorus and uranium contents in Alum Shale is  
710 linked to the existence of a major uranium-bearing phase as calcium phosphate  
711 nodules. These apatite-(CaF[OH]) nodules are disseminated in the black shale and  
712 show typical bell-shaped REE patterns, with a strong enrichment in middle REE.  
713 This type of pattern is common in marine sediments, particularly in pre-Jurassic  
714 biogenic phosphates, and can be explained by two successive processes: an  
715 adsorption mechanism during early diagenesis and a substitution mechanism  
716 associated with recrystallization during late diagenesis (Reynard *et al.*, 1999). These  
717 apatite-(CaF[OH]) nodules contain 100 to 3000 ppm uranium and therefore constitute  
718 an important part of uranium mineralization (Fig. 25). However, the projection of  
719 whole-rock U concentration to the 18% phosphorus content typical of apatite,  
720 indicates that apatite in the Alum Shale could contain up to 1500  $\mu\text{g}\cdot\text{cm}^{-3}$  uranium  
721 (i.e. around 600 ppm U). This result suggests that only uranium content below  
722 600 ppm in phosphate nodules corresponds to the primary homogeneous  
723 preconcentration associated with sedimentation and diagenesis, whereas higher

724 values may indicate local reconcentration as phosphosilicate spherulites (Fig. 25).

725

## 726 **5.2. Burial and thermal maturation**

727 During burial and thermal maturation, Alum Shale generated hydrocarbons  
728 that were trapped as fluid inclusions in carbonate levels within the black shale and in  
729 fractured Ordovician limestones. Petroleum and aqueous isochores indicate high  
730 trapping temperature ( $>150^{\circ}\text{C}$ ) and extremely variable trapping pressure, from  
731 700 bars for low- $T_h$  inclusions to 200 bars for high- $T_h$  inclusion (Fig. 26). Besides, P-T  
732 domains seem to be aligned in a rather similar temperature range, which may  
733 suggest isothermal decompression during calcite crystallization. Several theoretical  
734 pathways are indicated on figure 26. First hypothesis considers an underestimated  
735 burial with low geothermal gradient ( $<20^{\circ}\text{C}/\text{km}$ ), consistent with present-day  
736 foreland basin gradients and suggested by Huigen and Andriessen (2004) for the  
737 Caledonian foreland basin. In that case, high pressures could be reached but at  
738 temperatures below  $100^{\circ}\text{C}$ . Second hypothesis uses a normal geothermal gradient to  
739 obtain high pressure/high temperature conditions. Finally, a third hypothesis  
740 considers a low burial to explain low trapping pressure of most inclusions in  
741 concretions, but precludes high pressure conditions.

742 Alum Shale in central Sweden (Västergötland, Östergötland, Närke) is  
743 immature and did not encountered temperatures above  $90\text{-}100^{\circ}\text{C}$ . Besides, Alum  
744 Shale burial is mainly related to the development of a Silurian-Devonian foreland  
745 basin during Caledonian orogeny (Ziegler, 1988; Middleton *et al.*, 1996). Basin  
746 modeling (Samuelson and Middleton, 1998, 1999) indicates a 2 kilometers deep  
747 maximum burial in central Sweden (Västergötland, Närke). Since the Caledonian

748 foreland basin gets thinner eastward, maximum burial during the Devonian ranges  
749 between 1 and 2 kilometers at Åland (Cederbom, 1997 and Larson *et al.*, 1998, cited in  
750 Larson *et al.*, 1999). The initial uplift, probably starting in the Devonian, is faster in  
751 the western part of the basin. This implies lateral redistribution of the sediments  
752 which leads to a rather uniform 2 kilometers deep basin infill around 250 Ma (Larson  
753 *et al.*, 1999). Therefore, Alum Shale burial in central Sweden never exceeded 2  
754 kilometers in the Devonian, and probably less in the Ordovician, because most post-  
755 Cambrian accumulated sediments correspond to foreland basin filling during the  
756 Silurian-Devonian period. U-Pb dating of cone-in-cone calcite indicates that  
757 formation of late concretions in the Upper Cambrian Alum Shale took place during  
758 Early Ordovician (Israelson *et al.*, 1996) at relatively limited depth. By analogy with  
759 present-day geothermal gradients in hypothermal foreland basins and considering  
760 the thermal age of basement rocks (Huigen and Andriessen, 2004), a low paleo-  
761 geothermal gradient of 20°C/km seems to be realistic and implies that temperature  
762 reached by most immature Alum Shale may not have exceeded a few tens of degrees.  
763 Since concretions and fractures are pre-Permian, local thermal maturation related to  
764 Permian dolerite intrusions cannot be considered as a major process of hydrocarbon  
765 generation. Moreover, thermal influence of intrusions on Alum Shale is limited to a  
766 few tens of meters (30 meters at Kinnekulle according to Samuelsson and Middleton,  
767 1999), which excludes any significant influence of Permian intrusions on regional  
768 heating at the end of the Palaeozoic (Tullborg *et al.*, 1996; Larson *et al.*, 1998).

769         Although it is not possible to completely rule out either overestimation of P-T  
770 trapping conditions because of inclusion volume modification or underestimation of

771 maximum burial in particular considering extremely low thermal gradient, it seems  
772 to be clear that theoretical pathways are unachievable with foreland basin evolution  
773 and that formation of calcite concretions and fractures is related to the circulation of  
774 overpressured and overheated fluids. Such concretions, described as bedding-  
775 parallel veins or beefs, are indeed widespread in low-permeability strata in  
776 sedimentary basins and generally contain solid or liquid hydrocarbons. Beefs may be  
777 the result of fluid overpressure linked to petroleum generation (Cobbold *et al.*, 2013;  
778 Rodrigues *et al.*, 2009). To explain the existence of beefs, concretions, breccias and  
779 fractures containing hydrocarbons in immature areas, it is necessary to consider  
780 contemporaneous migration of hydrocarbons and brines from mature and  
781 overmature Alum Shale to immature Alum Shale. In that model, overpressure allows  
782 fracture opening and calcite precipitation, which in turn induce fluid pressure drop.  
783 These regional migrations are already active in the Ordovician and lead to primary  
784 beef formation. First inclusions contain black oils with orange-brown fluorescence  
785 and formed at high pressure (>500 bars) and high temperature (>150°C). Second  
786 assemblage is characterized by a higher proportion of mature oils with white-blue  
787 fluorescence. These inclusions are associated with numerous brine inclusions and  
788 have been trapped around 150-170°C and 200 bars. This pressure drop is interpreted  
789 as a decompression after fracture opening. Beefs have been locally dislocated and  
790 reworked as breccias. Angular calcite particles preclude long-distance transport and  
791 may suggest insitu reworking. Such breccias have only been observed at Öland, in a  
792 more proximal environment than Västergötland or Närke. Fracture fillings in  
793 Ordovician limestones are later. The presence of monophasic oil inclusions at room

794 temperature indicates high pressure trapping. Low- $T_h$  inclusions have been trapped  
795 at high pressure between 600 and 700 bars and temperatures around 200°C, whereas  
796 high- $T_h$  inclusions have been trapped around 400 bars and 170-180°C. Therefore,  
797 fluid inclusions have recorded a major pressure drop of several hundreds of bars  
798 between first opening of fractures by overpressured hydrocarbons and brines and  
799 the final sealing. Temperature decrease is probably related to fluid cooling during  
800 calcite precipitation within a rather cold host rock.

801         However, these fluids do not contain significant uranium concentration (see  
802 section 4.4.1). Thermal maturation simulation (Dahl, 1990; this study) shows that  
803 uranium remains immobile during maturation. In the meantime, carbon loss reaches  
804 up to 10% or more (22% in this study) with the formation of 10% residual carbon  
805 (Horsfield *et al.*, 1992). Thus, carbon loss during thermal maturation of Alum Shale  
806 leads to a relative enrichment in uranium due to rock density changes in response to  
807 the carbon loss, which may partly explain the steeper slope of the correlation line in  
808 metamorphic samples compared to immature samples.

809

### 810         **5.3. Uranium remobilization during metamorphism**

811         During Caledonian orogeny, Alum Shale has been heated up to 305±11°C, as  
812 recorded by organic material. This temperature corresponds to sub-greenschist  
813 metamorphic facies, as previously suggested by Kisch (1980).

814         During metamorphism, uranium preconcentration is remobilized and  
815 crystallized as uraninite or uranotitanate. Some micro-crystals remain preserved from  
816 alteration as inclusions in metamorphic pyrites. Outside pyrites, uraninites and  
817 urano-titanates are now replaced by U-Ti phospho-silicates clusters or rims around

818 U-Ti oxides primary cores. These phospho-silicates contain U, Ti, Y, Zr, Pb with  
819 highly variable concentrations and can be gathered in three chemical groups: a) Y-  
820 poor/Ti-rich phospho-silicates (“Brannerite” group); (b) Y-poor/Ti-poor phospho-  
821 silicates (“Uraninite” group); (c) Y-rich/Ti-poor phospho-silicates (“Xenotime”  
822 group). These distinct U-Ti phospho-silicate series result from silicification and/or  
823 phosphorization of different mineral precursors, which can rarely be found  
824 preserved throughout the Alum Shale. Y-poor/Ti-rich phospho-silicates result from  
825 the silicification of brannerite. Silicification comes along a drop in Ti content,  
826 associated with TiO<sub>2</sub> crystallization, whereas U concentration remains constant. Y-  
827 poor/Ti-poor phospho-silicates result from the silicification of uraninite, with  
828 U ↔ Ca and Si ↔ P substitutions. In this series, Y concentration remains low. Finally,  
829 Y-rich/Ti-poor phospho-silicates result from the silicification of Y-phosphate, with  
830 Y ↔ U and P ↔ Si substitutions. During Greenschist facies metamorphism, uranium  
831 can also be redistributed in sedimentary apatite-(CaF[OH]) nodules. U  
832 concentrations above 600 ppm thus correspond to reconcentration areas with local  
833 crystallization of phosphosilicate micro-spherulites.

834

## 835 **6. Conclusions**

836 Scandinavian Alum Shale is among the most uraniferous black shale units  
837 throughout Earth history and extends over most of northern Europe. As in many  
838 other black shales, uranium was preconcentrated during sedimentation. In the Alum  
839 Shale Formation, uranium primary accumulation occurred in organic matter and  
840 biogenic marine phosphate nodules. Besides, it is clear that primary concentration

841 has not been affected by early burial, thermal maturation of organic matter and  
842 petroleum generation. Migrating fluids in the Alum Shale Formation did not carry  
843 any particular uranium content. However, uranium was remobilized during  
844 Greenschist facies metamorphism of Caledonian orogeny and crystallized as  
845 uraninite and brannerite minerals. Rare remnants of this crystallization stage are  
846 found as micro-inclusions in syn-metamorphic pyrites. Most of mineralization  
847 actually evolved to complex U-Ti phospho-silicates, as clusters associated with  
848 carbonaceous matter or spherulites inside biogenic phosphate nodules.

849 This work shows that, despite its relatively high syndimentary  
850 preconcentration, uranium remains immobile through the stages of diagenesis, burial  
851 and thermal maturation. However, pressure-temperature conditions reached during  
852 Caledonian orogeny are high enough to favor new uranium speciation as U-Ti oxides  
853 and phospho-silicates. The knowledge of uranium mineralogy and its particular  
854 association with phosphates is crucial to assess potential extraction feasibility and  
855 adjust recovery processes. This result is also of great interest for the oil and gas  
856 companies prospecting hydrocarbons in southern Sweden Alum Shale. Thus,  
857 uranium could be considered to have a potential penalizing effect on the quality of  
858 released waters during the gas recovery by hydrofracturing. But, as it occurs up to  
859 the oil window as poorly soluble phosphates, the risks of potential water  
860 contamination by radionuclides are probably minimized.

861

## 862 **Acknowledgments**

863 The authors would like to thank M. Hudson (Mawson Resources) and C.

864 Caillat (AREVA) for helping us during this study and for their assistance during the  
865 field trip in Sweden. We are grateful to the Geological Survey of Sweden (SGU),  
866 especially L. Hildebrand and L. Wickström, for welcoming us in Malå and Uppsala  
867 and for their technical assistance in the sampling process. We acknowledge Niels H.  
868 Schovsbo for his useful comments and suggestions.

869 This work was supported by Institut Carnot Énergie et Environnement en Lorraine  
870 (ICEEL), Labex Ressources 21 (supported by the French National Research Agency  
871 through the national program “Investissements d’avenir”, reference ANR-10-LABX-  
872 21-LABEX RESSOURCES 21) and AREVA.

873

874

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1116 **Table caption**

1117 **Table 1** List of samples with corresponding wells and depths

1118 **Table 2** Selected metals, carbon, sulfur and phosphorus whole rock concentrations in  
1119 several Alum Shale samples (Total Organic Carbon TOC, Total Sulfur TS and Total  
1120 Phosphorus TP are in wt.%. Other elements are in ppm)

1121 **Table 3** Rock Eval analyses on several Alum Shale samples. S1 and S2 are in  
1122 mg HC/g Rock, S3 in mg CO<sub>2</sub>/g Rock, T<sub>max</sub> in °C, TOC in wt.%, HI in mg HC/g TOC  
1123 and OI mg CO<sub>2</sub>/g TOC

1124 **Table 4** δ<sup>34</sup>S values (in ‰) for different pyrite generations in the Alum Shale  
1125 Formation

1126 **Table 5** Uranium and Rare Earth Element concentrations in apatite-(CaF[OH])  
1127 nodules (ppm) from LA-ICP-MS analysis

1128 **Table 6** Main features of selected hydrocarbon-bearing inclusions in concretions and  
1129 fractures. Homogenization temperatures Th are in °C, vapor volume fractions Fv in  
1130 %, CH<sub>4</sub>, CO<sub>2</sub> and alkane content in mol/kg

1131 **Table 7** Peak area and calculated temperatures for Raman spectra on carbonaceous  
1132 nodules. RA1 and RA2 are two area ratios used to estimate temperature.  
1133 Carbonaceous matter types (CM) are indicated as PB Cal (Pyrobitumen under  
1134 calcite), PB (Pyrobitumen) and PV (Pseudo-vitrinite)

1135 **Table 8** Composition of U-Ti bearing minerals in Alum Shale determined by EPMA  
1136 in weight percents of major oxides

1137

1138

1139 **Figure captions**

1140 **Fig. 1** Geological map of the Fennoscandian Shield with main Alum Shale  
1141 occurrences (modified from Thickpenny, 1984). For a more comprehensive map of  
1142 Lower Palaeozoic strata in Baltoscandia see Nielsen and Schovsbo, 2015

1143 **Fig. 2 a.** Metamorphic Alum Shale (Tåsjö) with fractured massive pyrites and calcite  
1144 in pressure shadows; **b.** Metamorphic Alum Shale (Tåsjö) with fractured pyrite beds  
1145 and calcite-pyrobitumen fracture fillings (left); **c.** Immature Alum Shale  
1146 (Västergötland)

1147 **Fig. 3** X-Ray diffractograms of immature Alum Shale (Närke) and metamorphic  
1148 Alum Shale (Tåsjö)

1149 **Fig. 4** Average concentrations (As, Co, Cr, Cu, Mo, Ni, Pb, Th, U, V, Zn) in Alum  
1150 Shale occurrences analyzed for this study (dots for metamorphic samples from  
1151 Myrviken, Lövstrand and Tåsjö, squares for non metamorphic samples from Närke,  
1152 Östergötland, Öland, Skåne, Västergötland), compared with reference shales (Marine  
1153 shales from Turekian and Wedepohl, 1961; Tarim basin black shales from Yu *et al.*,  
1154 2009; Ronneburg black shales from Lippmaa *et al.*, 2011; Ohio shale from Lewis *et al.*,  
1155 2010)

1156 **Fig. 5 a.** Carbon-sulfur plot for the Alum Shale Formation. Oxic marine depositional  
1157 settings and euxinic (anoxic-sulfidic) water column are indicated. Euxinic but Fe-  
1158 limited sediments would plot along a sub-horizontal trend with an extrapolated  
1159 positive intercept on the S-axis (Raiswell and Berner, 1985; Leventhal, 1995). **b.** V/(V  
1160 + Ni) vs. V/Cr crossplot for the Alum Shale Formation. Depositional settings ranges  
1161 for V/Cr and V/(V + Ni) are from Jones and Manning (1994) and from Hatch and

1162 Leventhal (1992), respectively

1163 **Fig. 6** Uranium-carbon plot (a) and uranium-phosphorus plot (b) for several Alum  
1164 Shale occurrences. All values are density-corrected. Artificial maturation residues are  
1165 indicated in Fig. 6a

1166 **Fig. 7** Petrographic features of organic matter in the Alum Shale Formation. **a.** UV-  
1167 Fluorescent macerals (liptinite) in immature Alum Shale (Östergötland); **b.** UV-  
1168 Fluorescent macerals (liptinite) in immature Alum Shale (Närke); **c.** Pseudo-vitrinite  
1169 in immature Alum Shale (Närke); **d.** Pyrobitumen in metamorphic Alum Shale  
1170 (Myrviken); **e.** Pyrobitumen vein in metamorphic Alum Shale (Tåsjö); **f.** Pyrobitumen  
1171 vein (with calcite) in metamorphic Alum Shale (Tåsjö). Bit: pyrobitumen, Cal: calcite,  
1172 PV: pseudo-vitrinite, Pyr: pyrite, Qtz:quartz

1173 **Fig. 8** S<sub>2</sub> vs. TOC diagram for immature and metamorphic Alum Shale

1174 **Fig. 9** IH vs. T<sub>max</sub> diagram for immature and metamorphic Alum Shale

1175 **Fig. 10** S<sub>1</sub> vs. S<sub>2</sub> diagram for immature and metamorphic Alum Shale

1176 **Fig. 11** Petrographic features of sedimentary and diagenetic sulfides. **a.** Framboids  
1177 and euhedral pyrites in immature Alum Shale (Östergötland); **b.** Detailed view of an  
1178 isolated framboid (Västergötland); **c.** Beds of (sub)euhedral pyrites underlining  
1179 sedimentary (Tåsjö); **d.** Beds of (sub)euhedral pyrites (Tåsjö); **e.** Massive pyrite with  
1180 core of coalescent syn-sedimentary pyrites and large pyrite crystals growing  
1181 perpendicularly (Närke); **f.** Large isolated pyrite and deformation of sedimentary  
1182 bedding (Närke); **g.** Massive pyrites in heterogeneous porous cement (Östergötland);  
1183 **h.** Homogeneous pyrite veins and fracture fillings of euhedral pyrites (Östergötland)

1184 **Fig. 12** As, Cu and Ni content in sulfides from immature and metamorphic Alum

1185 Shale. **a.** Diagenetic pyrite with no particular enrichment in As, Cu and Ni; **b.**  
1186 Framboids with high Cu concentration compared to syngenetic euhedral pyrites; **c.**  
1187 Synmetamorphic pyrite overgrowth with Ni enrichment and framboids remnants  
1188 with high Cu concentration; **d.** Massive diagenetic pyrite with no particular  
1189 enrichment and metamorphic overgrowths with Ni-rich pyrite and chalcopyrite  
1190 (Ccp)

1191 **Fig. 13** Histogram of  $\delta^{34}\text{S}$  values of pyrite in the Alum Shale Formation

1192 **Fig. 14 a.** Apatite-(CaF[OH]) nodule surrounded by pyrites in immature Alum Shale  
1193 (Östergötland); **b.** Carbonaceous matter veinlet (black) with uranium phospho-  
1194 silicates (white) and syn-sedimentary pyrites (light grey) in metamorphic Alum Shale  
1195 (Tåsjö); **c.** Porous apatite-(CaF[OH]) nodule surrounded by uranium phospho-  
1196 silicates clusters (white) in metamorphic Alum Shale (Tåsjö); **d.** Porous apatite-  
1197 (CaF[OH]) nodule surrounded by carbonaceous matter and uranium phospho-  
1198 silicates clusters (white) in metamorphic Alum Shale (Tåsjö); **e.** Uranium phospho-  
1199 silicates spherulites inside apatite-(CaF[OH]) nodule (Tåsjö); **f.** Apatite-(CaF[OH])  
1200 anhedral crystals associated with uranium phospho-silicates and carbonaceous  
1201 matter on the edge of a porous apatite-(CaF[OH]) nodule (Tåsjö). Ap: apatite-  
1202 (CaF[OH]), C: carbonaceous matter, P-cof: uranium phospho-silicates of various  
1203 composition (see text for details), Py: pyrite. Red circles and green circles correspond  
1204 to uranium minerals chemical analyses and phosphate nodules LA-ICP/MS  
1205 analyses, respectively

1206 **Fig. 15** REE patterns in apatite-(CaF[OH]) nodules from immature and metamorphic  
1207 Alum Shale. All spectra are normalized to North American Shale Composite (NASC

1208 REE concentrations after Gromet *et al.*, 1984) and metamorphic shales values are  
1209 multiplied by 10 to improve readability

1210 **Fig. 16 a.** Breccia with angular calcite crystals (Öland); **b.** Top view of calcite  
1211 concretion (beef) with centimetric crystals (Västergötland); **c.** Hydrocarbon-bearing  
1212 inclusions in calcite (Öland); **d.** Aqueous inclusion in calcite (Öland); **e.** UV-  
1213 fluorescent oil inclusions (Västergötland); **f.** 3-phase (oil-water-gas) inclusion (Öland)

1214 **Fig. 17** Histograms of homogenization temperatures for fluid inclusions in  
1215 concretions (a) and fracture fillings in Ordovician limestones (b)

1216 **Fig. 18** Evolution of vapor volume fraction with homogenization temperature for  
1217 various hydrocarbon-bearing inclusions in concretions (blue circles) and fractures  
1218 (red squares)

1219 **Fig. 19** Pressure-Temperature diagrams for inclusions in concretions (a) and fractures  
1220 (b). Black lines represent isochores and isopleths of petroleum inclusions. Gray bands  
1221 represent domain of isochores for aqueous inclusions. Dotted line is determined with  
1222 the mode of homogenization temperatures and the mean salinity of aqueous  
1223 inclusions. Trapping conditions correspond to intersection of intersection domains in  
1224 blue for concretions (A', A, B) and in red for fractures (C, D, and E)

1225 **Fig. 20 a.** Example of Raman spectra obtained on carbonaceous matter in Alum Shale;  
1226 **b.** Peak fitting on first order region of Raman spectra using Lorentzian profiles.  
1227 Complete dataset in table 3

1228 **Fig. 21** Sulfide modifications in metamorphic Alum Shale. **a.** Cataclased massive  
1229 pyrite (Myrviken); **b.** Fractured massive pyrite with pyrite overgrowths and late  
1230 calcite fillings (Tåsjö); **c.** Folded bed of framboids and (sub)euhedral pyrites (Tåsjö);

1231 **d.** Interpenetrative boundaries on euhedral pyrites (Tåsjö); **e.** Framboids in  
1232 synmetamorphic pyrite overgrowths (Myrviken); **f.** Fractures in pyrites filled with  
1233 chalcopyrite and sphalerite (Myrviken); **g.** Massive pyrite with chalcopyrite and  
1234 sphalerite inclusions (Myrviken); **h.** Pyrite-chalcopyrite-sphalerite paragenesis  
1235 (Myrviken). Ccp: chalcopyrite, Pyr: pyrite, Sph: sphalerite

1236 **Fig. 22 a.** Brannerite (white) in syn-metamorphic pyrites (Myrviken); **b.** Uraninite  
1237 (white dots) in syn-metamorphic pyrites surrounded by barite (Tåsjö); **c.** Uranium  
1238 phospho-silicates in metamorphic Alum Shale (Myrviken); **d.** Altered uraninite core  
1239 (white) rimmed by uranium phospho-silicates (Tåsjö); **e.** Pyrite rimmed by U-Ti  
1240 phospho-silicates (Tåsjö); **f.** Brannerite rimmed by U-Ti phospho-silicates (Tåsjö).  
1241 Brn: brannerite, Brt: barite, Gn: galena, P-cof: uranium phospho-silicates of various  
1242 composition (see text for details), Py: pyrite, Urn: uraninite. Red circles correspond to  
1243 uranium mineral chemical analyses

1244 **Fig. 23** Ti-Si (a), U-P (b), U+Ca+Y-Si+P (c) and Ca+Y+P-U+Si (d) diagrams for U-Ti-Y  
1245 minerals in Alum Shale (APFU Atoms Per Formula Unit). Theoretical uraninite, (P-  
1246 )coffinite, brannerite and xenotime are indicated by large black dots. Circles  
1247 represent Y-poor/Ti-rich minerals (Brannerite group), squares represent Y-poor/Ti-  
1248 poor minerals (Uraninite group) and diamonds represent Y-rich/Ti-poor minerals  
1249 (Xenotime group)

1250 **Fig. 24** Evolution of  $\delta^{34}\text{S}$  values in pyrites from sedimentation to metamorphism.  
1251 Pyrite generations are indicated as Py1 to Py6 in the figure and described in the text

1252 **Fig. 25** Uranium-phosphorus plot for the Alum Shale Formation for whole rock  
1253 (same data as Fig. 6b) and discrete uranium concentrations in phosphate nodules

1254 (frequency of occurrence histogram on the right). The shaded line illustrates the  
1255 extrapolation at  $60 \text{ mg.cm}^{-3}$  of phosphorus (average phosphorus content in apatite-  
1256  $(\text{CaF}[\text{OH}])$ )

1257 **Fig. 26** Pressure-Temperature diagram with trapping condition of fluid inclusions  
1258 and possible evolution pathways: 1) low geothermal gradient pathway ( $<20^\circ\text{C}/\text{km}$ );  
1259 2)  $20\text{-}30^\circ\text{C}/\text{km}$  geothermal pathway; 3) low burial

1260 **Fig. 27** Schematic scenario proposed to describe the evolution of organic matter,  
1261 sulfides and uranium in the Alum Shale Formation, from sedimentation to  
1262 Greenschist metamorphism

1263

1264