

1 Mineralogical and geochemical changes in subsurface shales straddling the
2 Ordovician–Silurian boundary in the eastern Kufra Basin, Libya

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25 **Abstract**

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27 This paper reports on the elemental geochemistry of 47 shale samples from the uppermost
28 Hirnantian–lowermost Rhuddanian Tanezzuft Formation, collected from drill core (depth
29 interval 20.8–73.2 m) from borehole JA-2 at the eastern Kufra Basin, SE Libya. Eighteen of
30 these samples were also analysed by X-ray diffraction. This study was carried out (i) to search
31 for shales with high total organic carbon (TOC >3 wt%) and associated high uranium (U >30
32 ppm) concentrations, commonly referred to as ‘hot’ shales, (ii) to test whether TOC and U
33 correlate, (iii) to study the effects of surface weathering on the behaviour and mobility of
34 major oxides, trace elements and rare earth elements (REE), and (iv) to examine the
35 relationship of the elemental composition obtained in this study and Rock-Eval pyrolysis and
36 kerogen data obtained in previous studies on the same core samples. The studied core can be
37 divided into three intervals: upper weathered section (20.8–46.5 m, influenced by Quaternary
38 weathering), unweathered section (46.5–68.5 m), and lower weathered section (68.5–73.9 m,
39 influenced by latest Ordovician weathering). Overall, the shales have low TOC values (<1 wt
40 %) and low U concentrations (<12 ppm). TOC and U do not show any correlation likely due
41 to their low values. Hence, ‘hot’ shale has not yet been proven in this part of the Kufra Basin.
42 Trace elements such as Mn and Sc show significant changes from the weathered into the
43 unweathered core section. In contrast, the majority of the major oxides, trace elements and
44 REE seem to be unaffected or at least largely unaffected by weathering processes. The
45 exception is the transition from the unweathered section into the lower weathered section of
46 the core. Here, most of the major oxides, trace elements and REE show either abrupt or
47 gradual shifts towards lower or higher element concentrations. The observed whole-rock
48 geochemical (e.g., K₂O, Rb, Sr, Th/K) and mineralogical (e.g., kaolinite/illite,

49 K-feldspar/quartz) changes suggest either a switch from one source area to another or, more
50 likely, climatic influence. The deepest part of the core may have been influenced by a more
51 humid and warm climate that has led to intensive chemical weathering and dissolution of K-
52 feldspar. During the latest Hirnantian–earliest Rhuddanian a temporary emersion event may
53 have occurred due to post-glacial rebound, which has led to the weathering of older strata.

54

55 **Keywords:**

56 Whole-rock geochemistry; X-ray diffraction analysis; Late Ordovician; Early Silurian; Kufra
57 Basin; Libya

58

59 **1. Introduction**

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61 During the Late Ordovician Epoch, large parts of West Gondwana were covered by massive
62 glaciers (e.g., Sutcliffe et al., 2000; Le Heron et al., 2009). Upon melting of the ice sheets in
63 the latest Hirnantian (ca. 444 Ma ago), huge volumes of meltwater and sediment were
64 released and shed to the periphery of Gondwana (e.g., Sutcliffe et al., 2000; Le Heron et al.,
65 2009). In Libya, these sediments are predominantly made up of compositional mature
66 sandstones (Mamuniyat Formation), forming good-quality hydrocarbon reservoirs. Polished
67 and striated surfaces are common features in these sandstones that point to their glaciogenic
68 origin (e.g., Le Heron et al., 2009, 2010, 2015). The Late Ordovician deglaciation was
69 followed by the deposition of black shales in the early Silurian (Tanezzuft Formation), with
70 some of the shales having high total organic carbon (TOC) contents (Lüning et al., 2003;
71 Vecoli et al., 2009; Abohajar et al., 2015; El Diasty et al., 2017a, b, c). These shales are often
72 called ‘hot’ shales because of their associated high uranium (U) concentration. They are the

73 most important source rock for Early Palaeozoic-sourced hydrocarbons across North Africa
74 (e.g., Lüning et al., 2000). Consequently, both the Upper Ordovician glaciogenic sediments
75 and the lower Silurian ‘hot’ shales have been the focus of geological investigations in Libya
76 (e.g., Lüning et al., 2000, 2003; Lüning and Fello, 2008; Loydell et al., 2013; Meinhold et al.,
77 2016; El Diasty et al., 2017a, b, c; Stockey et al., 2020).

78 The Murzuq and Kufra basins are large Palaeozoic basins in southern Libya (Fig. 1).
79 In the Murzuq Basin, a large number of boreholes have been drilled during the last 60 years,
80 seismic data has been acquired, and hydrocarbon reserves are proven. This is in contrast to the
81 Kufra Basin where only a handful of wells have been drilled and a hydrocarbon system is
82 unproven. Fieldwork has confirmed the presence of Late Ordovician glaciogenic sandstones
83 (Mamuniyat Formation) in the Kufra Basin (Fig. 2); equivalent sandstones are a major
84 reservoir for hydrocarbons in the Murzuq Basin. However, the existence of a potential source
85 rock (i.e., lower Silurian ‘hot’ shales) has not yet been proven in the Kufra Basin.

86 The Tanezzuft Formation ‘hot’ shales are seldom exposed and the few outcrops are
87 often strongly weathered. Surface shale samples have commonly lost all organic matter
88 through oxidation and become green and red in colouration (e.g., Lüning and Kolonic, 2003;
89 Lüning et al., 2003; Meinhold et al., 2013a). This makes them unsuitable for source rock and
90 biostratigraphic investigation. Following the retrieval of fresh material from drill core from
91 borehole (CDEG-2a) at the eastern Murzuq Basin (Meinhold et al., 2013a; Paris et al., 2012),
92 using a small portable drilling rig with the ability to obtain a core of about 3 cm in diameter, a
93 borehole more than 70 m deep was drilled through the Tanezzuft Formation at the eastern
94 Kufra Basin in April–May 2009 (Figs. 1 and 3; see Meinhold et al., 2013b for details). In this
95 borehole, unweathered shale was encountered at 46.5 m depth (Fig. 4). The recovered
96 material was used for a Rock-Eval pyrolysis study (Meinhold et al., 2013b) and for

97 palynological analyses (Thusu et al., 2013). Based on biostratigraphic correlations with
98 chitinozoan-bearing successions straddling the Ordovician–Silurian boundary in Arabia,
99 North Africa and the USA led to the conclusion that the studied samples from borehole JA-2
100 are post-glacial deposits and are of either latest Hirnantian age, or at least no younger than
101 earliest Rhuddanian (Thusu et al., 2013).

102 The present study focuses on whole-rock geochemical analysis of drill core material
103 from borehole JA-2. Major oxide, trace element and REE abundances were obtained on 47
104 shale samples from the Tanezzuft Formation from the 20.80–73.21 m interval. A
105 representative subset of 18 samples was also analysed by X-ray diffraction (XRD) to identify
106 their mineralogy. The upper section of the core from the surface down to about 46.5 m depth
107 displays signs of oxidative weathering (i.e. beige colour of the shale, and oxidation of the
108 organic matter) (for details see Meinhold et al., 2013b). This weathering corresponds likely to
109 the deep sub-Recent weathering profiles found in many places across the Sahara (Thusu et al.,
110 2013). From 46.60 m to 67.82 m depths, the core is unweathered (Fig. 4) as evidenced by its
111 organic matter content (Thusu et al., 2013; Meinhold et al., 2013b). The lithology is relatively
112 constant and ranges from greenish and grey shale to grey siltstone with micas. A lithological
113 change occurs at 67.59–67.82 m depth with the occurrence of very fine sandstone. From
114 67.97 m to 69.12 m depths, there is a sign of weathering as indicated by the oxidation of
115 pyrite and the brownish colouration of micas, in very fine, light coloured sandstone and the
116 whitish colouration of shale. Moreover, starting at 67.97 m depth, evidence of weathering is
117 indicated by a dramatic decrease in the abundance of chitinozoans (Thusu et al., 2013). The
118 lowermost section between 68.42 m and 73.90 m is weathered and includes a minor fault
119 zone. The palynomorph assemblages recovered from the JA-2 drill core material support a
120 marginal marine depositional environment (Thusu et al., 2013).

121 The geochemical data of the JA-2 core have been used (i) to study variations in major
122 oxides, trace elements and REE as amounts of weathering increase, (ii) to study the
123 relationship between other elements and Rock-Eval analysis data, and compare with data
124 obtained in a previous study by Meinhold et al. (2013a), and (iii) to study the relationship
125 between TOC and uranium (U) content. The latter is of special importance because U values
126 between 10 and 30 ppm are considered to be typical for ‘warm’ shales while values >30 ppm
127 are commonly considered to represent ‘hot’ shales, meaning shales with TOC content >3 wt%
128 (e.g., Lüning et al., 2000, 2003; Lüning and Fello, 2008).

129 Portable gamma-ray spectrometry (PGRS) is widely used to measure the U content of
130 the Tanezzuft Formation shales at outcrop to search for ‘warm’ shales and ‘hot’ shales in
131 southern Libya (e.g., Lüning et al., 2003; Lüning and Fello, 2008; Meinhold et al., 2016).
132 However, a whole-rock geochemical study on core material from the Tanezzuft Formation in
133 Dor el Gussa (Meinhold et al., 2013a) has shown that TOC contents do not correlate with U
134 abundances, at least in the range of low TOC. Therefore, total U contents obtained with PGRS
135 on outcrop samples may not always reflect the true TOC content in the rock. Samples
136 between 0.5 and 1.5 wt% TOC can still have moderate–good source potential of >3.5
137 kg/tonne, and are not associated with high U values (Meinhold et al., 2013a). Hence, absence
138 of high U values is not necessarily evidence of a lack of source potential, only of reduced
139 source potential (Meinhold et al., 2013a). The present study will provide further insight on
140 this subject and the applicability of PGRS for ‘hot’ shales search in southern Libya and in
141 other deeply weathered sections.

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143 **2. Analytical techniques**

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145 *2.1. ICP-MS analysis*

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147 The drill core material was disintegrated into small pieces with a hammer and then powdered
148 using an agate ball mill. Finely ground rock powder was dissolved by acid digestion with HF–
149 HNO₃ using an Evapoclean® system and later analysed using a PerkinElmer SCIEX Elan
150 DRC II inductively coupled plasma–mass spectrometer (ICP–MS) at the Department of Earth
151 Sciences, University of Cambridge, following the methodology as outlined in Meinhold et al.
152 (2013b). International rock standards were measured as unknown in this study for quality
153 control. Values for the BCR-2 and BHVO-2 standards measured in this study and reported
154 values from the literature for comparison are given in Supplementary Table S1 and Table S2,
155 respectively, in Appendix A.

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157 *2.2. XRD analysis*

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159 To obtain information about the mineralogical composition of drill core from borehole JA-2,
160 X-ray diffraction (XRD) analysis was carried out on 18 representative samples. Randomly
161 oriented powder samples were analysed with a Panalytical X'Pert Pro diffractometer at the
162 School of Ocean and Earth Science, University of Southampton, following the methodology
163 as outlined in Meinhold et al. (2016).

164

165 **3. Results**

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167 *3.1. Whole-rock geochemistry*

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169 Geochemical results of 47 shale samples (20.80–73.21 m depth) are presented in
170 Supplementary Table S3 (see Appendix A). Major oxides, trace elements and rare earth
171 elements (REE) obtained in this study, calculated key parameters (e.g. $U_{\text{authigenic}}$, Ce-anomaly)
172 and in addition TOC and hydrogen index (HI) (data from Meinhold et al., 2013b) have been
173 plotted against depth in Figures 4 to 8. Selected elements and element ratios are additionally
174 shown on cross plots in Figures 9 to 13. Following common practise, the REE data are shown
175 on both chondrite- and post-Archaean Australian Shale (PAAS)-normalised diagrams (Fig.
176 14). Normalisation values for chondrite (CI) and PAAS were taken from Taylor and
177 McLennan (1985) and McLennan (1989), respectively.

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179 *3.1.1. Element relationships with depth*

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181 In general, most elements show a homogenous distribution in the weathered section between
182 depths of 20.80 m and about 46.50 m (except one sample at the depth of 27.27 m) and in the
183 unweathered section between depths of about 46.50 m and 68.50 m. However, the lowermost
184 part of the unweathered section and the section below (starting at a depth of about 65 m down
185 to the final depth of 73.90 m) show for most of the elements a significant increase or decrease
186 in element concentrations respectively.

187 Throughout the core, the actinide metal uranium (U) has element concentrations
188 between 3.1 and 5.3 ppm (mean value \sim 4.1 ppm); the exception is the lower part of the core
189 at the depth of about 67.82 m towards the base of the core where U concentrations are
190 between 6.8 and 11.9 ppm (mean value \sim 8.7 ppm) (Fig. 5). These values are above the
191 average for PAAS of 3.1 ppm (Taylor and McLennan, 1985).

192 Thorium (Th) concentrations range between 11.0 and 48.6 ppm (Fig. 5), with a mean value of
193 17.7 ppm. This includes three samples with significant higher values (22.8 ppm at the depth
194 27.27 m, 26.6 ppm at the depth of 67.82 m and 48.6 ppm at the depth of 68.42 m) and two
195 samples with significant lower values (11.0 ppm at the depth of 62.34 m and 11.6 ppm at the
196 depth of 64.55 m) than the mean value of 17.7 ppm.

197 Throughout the core down to the depth of 67.59 m the Th/U ratios are quite constant
198 with 3.6 to 4.8, whereas starting at the depth of 67.82 m towards the base of the core the Th/U
199 ratios are 1.7 to 2.2 and thus significantly lower than in the section above (Fig. 5). The
200 exception is the sample at 68.42 m depth, which has a Th/U ratio of 4.4. Note that this sample
201 has the highest Th content of all samples (48.57 ppm).

202 Authigenic (non-detrital) U content (Wignall and Myers, 1988), calculated as

203

$$204 U_{\text{authigenic}} = (\text{total U}) - \text{Th}/3,$$

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206 and Th/U ratios show similar but inverse patterns. Positive values for $U_{\text{authigenic}}$ (1.97 to 4.06
207 ppm) are only observed in the lower section of the core, at the depth of 67.82 m toward to the
208 base of the core (Fig. 5).

209 An interesting parameter is cerium (Ce), which is commonly examined as Ce-
210 anomaly. Ce-anomaly values are commonly used in marine deposits for reconstructing
211 palaeo-redox conditions and sea-level changes (e.g. Murray et al., 1990; Wilde et al, 1996;
212 Pattan et al., 2005, and references therein). This is because Ce is sensitive to changes in the
213 redox state of the ocean but lanthanum (La) and promethium (Pr) are not. In the present study,
214 the Ce-anomaly values were calculated according to Murray et al. (1990):

215

216 $\text{Ce-anomaly} = \text{Ce}/\text{Ce}^* = \text{Ce}_{\text{SN}}/(0.5\text{La}_{\text{SN}} + 0.5\text{Pr}_{\text{SN}})$,

217

218 where SN indicates normalization to post-Archaean Australian Shale (PAAS; Nance and
219 Taylor, 1976), with values taken from McLennan (1989). Values of $\text{Ce}/\text{Ce}^* > 1$ are considered
220 to be positive, whereas values < 1 are considered to be negative. The whole-rock Ce-anomaly
221 values of the studied samples fluctuate around 0.93 (± 0.06), with exceptions of 0.78 and 1.08
222 at the depths of 55.53 m and 73.20 m respectively (Fig. 5).

223 Potassium (K), expressed as K_2O , varies between 2.94 and 3.67 wt%, with a mean
224 value of 3.37 wt%, at depths between 20.80 m and 64.02 m (Fig. 5). The section below,
225 between 64.55 and 73.21 m, has K_2O contents between 1.48 and 2.68 wt%, with decreasing
226 values toward the base of the core.

227 Th/K ratios vary around 5 for most samples down to a depth of 64.55 m, whereas
228 samples at the depth of 65.23 m and below show higher Th/K ratios of up to ~ 18 (Fig. 5).

229 Rubidium (Rb) and K_2O contents show similar patterns (Fig. 5). Rb values vary between 117
230 and 167 ppm, with a mean value of 140 ppm, at depths between 20.80 m and 63.45 m,
231 whereas samples at the depth of 64.02 m and below show (after a transitional interval) lower
232 K_2O contents, with values decreasing toward ~ 60 ppm at the depth of 73.21 m (Fig. 5).

233 Interestingly, strontium (Sr) and Rb contents show similar but inverse patterns (Fig. 5). Sr
234 values vary between 66 and 100 ppm, with a mean value of 83 ppm, at depths between 20.80
235 m and 63.45 m, whereas samples at the depth of 64.02 m and below show (after a transitional
236 interval) higher Sr contents, with values increasing toward ~ 188 ppm at the depth of 73.21 m
237 (Fig. 5). Note that Rb/Sr ratios and K_2O contents show similar patterns.

238 Phosphorous (P), expressed as P_2O_5 , shows little variation and has concentrations
239 between 0.07 and 0.20 wt%, with few samples having slightly higher values (Fig. 5);

240 Supplementary Table S3). Note that two samples from the uppermost section of the core at
241 the depths of 20.80 m and 27.27 m have significantly higher P_2O_5 values of 0.34 and 0.59 wt
242 % respectively.

243 Titanium (Ti), expressed as TiO_2 , and niobium (Nb) show similar trends (Figs 5, 6).
244 TiO_2 and Nb contents vary between 0.95 and 1.29 wt% and between 19 and 25 ppm
245 respectively. Both elements show their highest values at the depths of 27.27 m (1.23 ppm
246 TiO_2 , 24 ppm Nb) and 67.82 m (1.29 wt% TiO_2 , 25 ppm Nb).

247 Scandium (Sc) shows a distinctive pattern (Fig. 6). In the weathered section, Sc values
248 range from 16 to 27 ppm (mean value \sim 23 ppm), while in the unweathered section they are
249 mainly lower and range between 11 and 30 ppm (mean value \sim 15 ppm). The lowermost
250 section between depths of 68.42 m and 73.21 m has again higher Sc values (25–31 ppm; mean
251 value \sim 28 ppm), which are even higher than those of the weathered section between 20.80 m
252 and 46.20 m depths.

253 Vanadium (V) shows little variance between the weathered and unweathered sections
254 (Fig. 6). Most of the samples have V values between 110 and 150 ppm (mean value \sim 130
255 ppm). The two highest values of 164 and 160 ppm occur at depths of 71.44 and 72.07 m,
256 respectively. Note that the sample at the depth of 27.27 m has also an elevated V content (150
257 ppm).

258 Chromium (Cr) shows little variance between the weathered and unweathered sections
259 (Fig. 6). Concentrations vary between 70 and 110 ppm, with a mean of 90 ppm. Values less
260 than 70 ppm are observed at depths of 43.84 m (66 ppm), 62.34 m (60 ppm) and 64.55 m (63
261 ppm), and values higher than 110 ppm occur at depths of 27.27 m (111 ppm), 67.05 m (114
262 ppm), 67.97 m (111 ppm) and 68.42 m (111 ppm).

263 Manganese (Mn) concentrations allow a clear subdivision of the core into three
264 sections, which seems to coincide with the subdivision based on the grade of weathering (Fig.
265 6). In the weathered section, between 20.80 and 46.20 m, Mn concentrations vary from 258 to
266 648 ppm (mean value ~ 413 ppm). Concentrations in the unweathered section are between
267 494 and 2412 ppm (mean value ~ 1290 ppm). The exceptions are single values of 6048 ppm
268 and 4042 ppm at depths of 64.55 m and 67.40 m, respectively, as well as values of 374, 388
269 and 179 ppm at depths of 46.60 m, 67.59 m and 67.82 m, respectively, which are the
270 uppermost and the two lowermost samples of the unweathered section. Samples from the
271 lowermost section of the core show Mn concentrations less than 160 ppm.

272 Copper (Cu) concentrations mainly vary between 30 and 51 ppm (mean value ~ 43
273 ppm), the exception is a single peak of 64 ppm at 61.51 m depth and values of less than 30
274 ppm in the deepest part of the core between 68.42 and 73.21 m depth (Fig. 6).

275 With the exception of a few single peaks, zinc (Zn) and cobalt (Co) show similar
276 patterns with an increase in element concentrations with increasing depth, which is especially
277 apparent in the lower part of the unweathered section (Fig. 6). However, the deepest part of
278 the unweathered section, starting at 67.82 m records an abrupt decline of Co and Zn
279 concentrations to values of less than 10 and 50 ppm respectively. Such low values
280 characterise the 67.82 to 73.12 m interval.

281 Element concentrations of nickel (Ni) are around 50 ppm and do not show much
282 variation within most of the core to a depth of 62.34 m (Fig. 6). The 62.75 to 67.59 m interval
283 records elevated Ni contents of up to 86 ppm and even two single peaks with values of 162
284 and 157 ppm (at 64.02 m and 67.59 m respectively) are present. The remaining 67.82 to 73.12
285 m interval shows a subsequent decrease in Ni concentration from 50 to 10 ppm.

286 Element concentrations of the light element lithium (Li) vary between 71 and 129 ppm
287 (mean value ~ 110 ppm), the exception is a single peak at the depth of 57.59 m (182 ppm of
288 Li) and values of less than 70 ppm in the lowermost part of the core between 68.42 m and
289 73.21 m depth (Fig. 6).

290 The light element beryllium (Be) shows an interesting pattern. Its concentrations are
291 between 2.2 and 3.8 ppm throughout the core between 20.80 and 64.55 m depth. Higher
292 values than 3.8 ppm (up to 7.6 ppm) are recorded between 65.23 and 69.12 m depth, and the
293 lowermost part of the core is again characterised by low Be concentrations of about 2.3 to 2.7
294 ppm (Fig. 6). Interestingly, Li/Be ratios mainly fluctuate between 30 and 40 ppm at depths
295 between 20.80 m and 65.74 m, the exception is a sample at the depth of 43.84 m with a Li/Be
296 ratio of about 21 (Fig. 6). Samples between 66.21 m and 73.21 m have Li/Be ratios of less
297 than 30 with the Li/Be ratios showing a continuous decrease down to values of about 20 ppm.

298 Element concentrations of tin (Sn) vary between 3 and 5 ppm (mean value ~ 4.2 ppm).
299 The exception is the sample at 67.05 m depth with about 6 ppm of Sn (Fig. 6). Moreover,
300 from 20.80 m to 73.21 m depths there seems to be a trend towards higher Sn values with
301 increasing depth.

302 Throughout the core, yttrium (Y) concentrations mainly vary between 20 and 40 ppm
303 (mean value ~ 29 ppm), the exceptions are few samples with higher values (see Fig. 7).

304 Zirconium (Zr) concentrations are mainly ranging between 90 to 140 ppm (mean value
305 ~ 113 ppm); the exception is a single sample at the depth of 65.23 m with 189 ppm of Zr (Fig.
306 7).

307 Throughout the core, element concentrations of the alkali metal caesium (Cs) mainly vary
308 between 6 and 8 ppm (mean value ~ 7 ppm), the exceptions are few samples with higher and
309 lower values respectively (Fig. 7).

310 Barium (Ba) shows an interesting pattern (Fig. 7). After a slightly fluctuating pattern
311 with Ba concentrations between 618 and 720 ppm in the weathered section and the uppermost
312 part of the unweathered section between 20.80 and 62.75 m depth, the Ba concentration
313 decreases between 63.14 m and 67.97 m depth to a value of about 460 ppm, followed by an
314 increase in Ba concentrations (values up to 811 ppm) in the deepest section of the core after a
315 single spike of 1403 ppm of Ba at the depth of 68.42 m.

316 Throughout the core, hafnium (Hf) concentrations are between 3 and 4 ppm (mean
317 value ~ 3.4 ppm), the exceptions are samples at the depths of 62.34 m, 64.55 m, 65.23 m and
318 67.40 m with Hf concentrations of about 2.8, 2.9, 5.0 and 2.7 ppm respectively (Fig. 7). For
319 almost all samples, the Zr/Hf ratios range between 32 and 35, with a mean value of ~ 34 (not
320 shown on any diagram).

321 Element concentrations of tantalum (Ta) do not show any obvious pattern. The Ta
322 values fluctuate around 1.5 ppm, with only two single peaks at 27.27 m and 67.82 m depth
323 showing significantly higher values of up to almost 1.8 ppm of Ta (Fig. 7).

324 Throughout the core, total concentrations of the rare earth elements (REE) vary
325 between 200 and 310 ppm (mean value ~ 246 ppm), with exceptions at depths of 27.27 m,
326 67.82 m and 68.42 m where the total REE concentrations are 534, 394 and 825 ppm
327 respectively (Fig. 7).

328 As expected, the REEs from lanthanum (La) to lutetium (Lu) show similar patterns
329 and do not show much variation for each element (Fig. 8). The exceptions are two samples
330 from the uppermost section of the core, at 20.80 m and 27.27 m depths, and two samples from
331 the lower section of the core, at 67.59 m and 68.42 m depths, which have significantly higher
332 values for most of the REEs. Regarding the last two samples, following observation can be
333 made. At 67.59 m depth, there is an increase towards higher values from lanthanum (La) to

334 lutetium (Lu) whereas at 68.42 m depth the REEs behave exactly opposite with decreasing
335 values from lanthanum (La) to lutetium (Lu). Note that of all analysed samples the sample at
336 67.59 m depth has also the highest concentration of yttrium (155 ppm) (Fig. 7).

337

338 *3.1.2. Binary plots*

339

340 TOC and HI do not correlate with U (Fig. 9). The highest TOC content of 0.75 wt% has a U
341 content of 4.7 ppm, whereas the highest U content of 11.9 ppm shows only a TOC content of
342 0.46 wt%. Note that the highest U content belongs to a sample from the deepest part of the
343 unweathered core section. It therefore cannot be excluded that the TOC content of 0.46 wt%
344 has already been slightly influenced by weathering and hence may already be an artifact.
345 Originally, the TOC content of this U-rich sample might have been higher. Uranium also
346 shows no correlation with Zr concentrations (Fig. 10a). Hafnium (Hf) however correlates
347 positively with Zr, where $R^2 = 0.94$ (Fig. 10b). Rubidium (Rb) correlated positively with K_2O ,
348 where $R^2 = 0.90$ (Fig. 11a), but negatively with strontium (Sr), where $R^2 = 0.61$ (Fig. 11b). It
349 is worth noting that samples with high U concentrations (>6 ppm) have Rb/Sr ratios of less
350 than ~ 1 (Fig. 12a). Furthermore, most of the samples with high U concentrations have Th/K
351 ratios greater than 9 (Fig. 12b).

352 Niobium (Nb) correlates positively with TiO_2 , where $R^2 = 0.96$ (Fig. 13a), and nickel
353 (Ni) correlates positively with cobalt (Co), where $R^2 = 0.90$ (Fig. 13b). However, for the latter
354 calculation, samples with Ni/Co ratios of about 4 and greater were excluded (i.e., the sample
355 at 64.02 m depth and samples from 67.59 to 69.12 m depths).

356

357 *3.1.3. Normalised REE diagrams*

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359 Shale samples from borehole JA-2 (Fig. 14) show similar REE patterns, regardless of depth,
360 however, REE abundances are higher in samples at depths of 20.80 m, 27.27 m and 68.42 m
361 (Fig. 14a,b,m,n). One exception is the sample at 67.59 m depth, which shows a distinct REE
362 pattern. All samples show chondrite-normalised patterns with light REE enrichment and flat
363 heavy REE patterns with negative europium (Eu) anomalies. PAAS-normalised REE
364 concentrations show almost flat patterns with light REE enrichment. The sample from 67.59
365 m depth shows similar chondrite- and PAAS-normalised patterns for the light REE but
366 significant enrichment in the middle and heavy REE (Fig. 14m,n).

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368 *3.2. XRD analysis*

369

370 XRD analysis revealed that quartz, K-feldspar, kaolinite and illite form the prominent mineral
371 assemblage (Fig. 15; Supplementary Table S4). Chlorite, siderite and pyrite are also present in
372 many samples but only in minor amounts. With the exception of two samples, quartz, K-
373 feldspar, kaolinite and illite show constant values with only minor fluctuations throughout
374 most of the core from 20.80 m to about 65 m depths, whereas from 65 m towards the base of
375 the core either a significant increase or decrease of these minerals is recorded. The
376 kaolinite/illite ratio fluctuates around 1 from 20.80 m to about 65 m depths, whereas the
377 deeper section of the core shows a constant increase of the kaolinite/illite values to up to
378 almost 4 (Fig. 15). The K-feldspar/quartz ratios are between 0.2 and 0.5 from 20.80 m to
379 about 65 m depths, whereas the deeper section of the core records a constant decrease in the
380 K-feldspar/quartz ratio (Fig. 15). The K-feldspar content correlates negatively with Th/K and
381 positively with K₂O (Fig. 16). The K-feldspar content also correlates negatively with Rb (Fig.

382 17a), whereas the illite content correlates positively with the Rb content, where $R^2 = 0.83$
383 (Fig. 17b). The K-feldspar/illite ratios correlate positively with the Sr content (Fig. 18a) and
384 show a negative correlation with the K-feldspar/quartz ratios (Fig. 18b).

385

386 **4. Discussion**

387

388 *4.1. Whole-rock geochemistry*

389

390 *4.1.1. Element relationships with depth*

391

392 Core from JA-2 in Jebel Asba can be subdivided into three sections based on the grade of
393 weathering, which is expressed by colour changes from orange/brown (upper weathered
394 section) to dark grey (unweathered section) and further to light grey/reddish (lower weathered
395 section) (Fig. 4). Trace elements such as Mn and Sc show changes from the weathered into
396 the unweathered section whereas the majority of the major oxides, trace elements and REE
397 seem to be unaffected, or at least little affected, by weathering processes. The exception is the
398 transition from the unweathered section into the lower weathered section. Here, most of the
399 major oxides, trace elements and REE show either an abrupt or gradual shift towards lower or
400 higher element concentrations.

401 In the upper weathered section and in the unweathered section down to 67.59 m depth,
402 the U contents are about 4.1 ppm, which can be seen as normal (background) value of U for
403 the Tanezzuft Formation shales in Jebel Asba. The elevated U concentrations (6.8–11.9 ppm)
404 found in the deepest part of the core (67.82–73.21 m depth) are not related to heavy mineral
405 (zircon) enrichment. Here, the U enrichment is of authigenic origin as suggested by positive

406 values for $U_{\text{authigenic}}$ (1.97 to 4.06 ppm). U enrichment in sediment is commonly seen as an
407 indication of reduced oxygen levels in bottom waters and increased amounts of organic matter
408 (McManus et al., 2005). This is a possible explanation for the observed U enrichment in the
409 deepest section of the JA-2 core.

410 With Th concentrations being fairly constant throughout the core and U concentrations
411 showing a significant increase in the lower part of the core (Fig. 5), the Th/U ratios allow a
412 clear subdivision of the core into two sections. Throughout the core down to 67.59 m depth
413 the Th/U ratios are quite constant with 3.6 to 4.8, whereas starting at the depth of 67.82 m
414 towards the base of the core the Th/U ratios are 1.7 to 2.2; here they are significantly lower
415 than in the section above (Fig. 5). The exception is the sample at 68.42 m depth with Th/U of
416 4.4.

417 Before an explanation is given for these different Th/U ratios, the following outline
418 will help in understanding of the behaviour and mobility of U and Th in the sedimentary
419 environment. Geochemically, U and Th behave similarly, except under oxidising conditions
420 (McLennan et al., 1993, and references therein). Thorium is relatively immobile and is present
421 chiefly in the detrital clay minerals (e.g., Pattan et al., 2005, and references therein). It is not
422 affected by redox conditions and is present as insoluble Th^{4+} in the marine environment.
423 Uranium, however, is mobile under oxidising conditions as soluble U^{6+} . Under strongly
424 reducing conditions, U^{6+} may be reduced to the immobile U^{4+} , leading to U enrichment in
425 sediments, while oxidising environments can cause U loss from sediments (Klinkhammer and
426 Palmer, 1991; Jones and Manning, 1994; Wignall and Twitchett, 1996). Average shale such
427 as PAAS is an integrated average of the composition of the upper continental crust and has a
428 Th/U ratio of 3.8 (Taylor and McLennan, 1985). Under normal oxidising conditions, marine
429 shale commonly retains this ratio or higher because the soluble form of U will be favoured

430 (Guo et al., 2007). Yet, some U may be sequestered during early diagenesis due to reducing
431 conditions in pore waters related to organic decomposition (Guo et al., 2007). Wignall and
432 Twitchett (1996) have suggested that depositional environments with anoxic conditions lead
433 to shale Th/U ratios of 0 to 2, and this has been commonly used as a guideline in subsequent
434 studies. For example, Kimura and Watanabe (2001) showed that only sediment with Th/U
435 ratios <2 exhibited no recognizable bioturbation in their study of the lower Cambrian shales
436 from Iran, thus providing firm evidence that Th/U of ~ 2 seems to be an appropriate cut-off
437 point in distinguishing anoxic from oxic bottom waters.

438 Returning to the JA-2 core sample, shales from 20.80 m to 67.59 m depths exhibit
439 fairly constant Th/U ratios of 3.6 to 4.8, whereas the deeper section of the core has Th/U
440 ratios of 1.7 to 2.2, with one exception of 4.4 at 68.4 m depth. Thus, most parts of the core
441 between 67.82 and 73.21 m depths has Th/U ratios in the range of the proposed cut-off point
442 between anoxic and oxic bottom waters (Wignall and Twitchett, 1996). This would suggest an
443 anoxic environment during the period of deposition recorded in this cored interval. The
444 presence of authigenic U seems to confirm this statement, as sediment enriched in authigenic
445 U tends to have been deposited under highly reducing conditions that allow a large amount of
446 organic matter to accumulate to which U is fixed (Wignall and Myers, 1988). However,
447 Wignall and Myers (1988) also noted that carbonate and phosphate minerals could
448 incorporate U, which would limit the application of authigenic U content to identify anoxic
449 environments in the sedimentary record. This is likely the case for the core sample from 68.42
450 m depth, which has a U content of 11 ppm accompanied by a P_2O_5 content of 0.77 wt% (Fig.
451 5). The latter is about 7 times higher than the average P_2O_5 content observed in the JA-2 core.

452 Ce anomalies of the studied samples are around 0.93 (± 0.06), with exceptions of 0.78
453 and 1.08 at the depths of 55.53 m and 73.20 m respectively (Fig. 5). Thus, with the exception

454 of these two samples, the shales of the JA-2 core were likely deposited during fairly stable
455 palaeo-ocean water redox conditions. It is pertinent here to discuss briefly the behaviour of Ce
456 in ocean water. Ce^{3+} acts like other REE but oxidised Ce^{4+} is less soluble and is easily
457 adsorbed by any Mn-, Fe-oxyhydroxide (Möller et al., 1994) or organic particles (Holser,
458 1997). This consequently results in Ce depletion with negative anomalies in seawater and
459 positive or less negative anomalies in the sediment. In an anoxic environment, Ce is mobilised
460 and released into seawater as Ce^{3+} , causing its positive anomalies in seawater and depletion
461 with negative anomalies in contemporaneous sediments (De Baar et al., 1985; Wilde et al.,
462 1996). Note that some organisms remove phosphate from seawater and thus inherit the REE
463 pattern of seawater. Their Ce anomaly will be opposite in the form to that of coeval sediment.
464 It is however worth noting that any primary signature may be overprinted by late diagenetic
465 modification (MacLeod and Irving, 1996; Holser, 1997). The use of the whole-rock Ce
466 anomaly of sediment to reconstruct palaeo-ocean redox conditions needs to be applied with
467 caution (Patton et al., 2005) if no other parameters are available.

468 Significant changes throughout the core are exhibited by K_2O , Th/K, Rb, Sr and
469 Rb/Sr, with either increasing or decreasing values towards the base of the core (Fig. 5). A
470 decrease in K_2O content accompanied by increasing Th/K values toward the base of the core
471 suggests a decrease in K-feldspar content. This may reflect a change in the source area or of
472 climate; a more humid warm climate would have led to intensive weathering and dissolution
473 of K-feldspar in the source area.

474 The change in Rb, Sr and Rb/Sr values with depth seems to confirm a change in
475 palaeo-climate conditions. Due to their different geochemical behaviour, Rb and Sr are easily
476 fractionated during common processes at the Earth's surface such as weathering (e.g., Jin et
477 al., 2001, 2006). Because of that, changes of Rb/Sr ratios have been used as proxy for

478 chemical weathering intensity. Weathering profiles often show a negative relationship
479 between the Sr concentration and the Rb/Sr ratio due to an affinity of Rb for clay minerals
480 and Sr loss to solution during weathering (e.g., Jin et al., 2001, 2006). Studies on weathering
481 profiles and loess–palaeosol successions provide evidence that the Rb/Sr ratios in weathering
482 products increase notably with the enhancement of weathering intensity (e.g., Jin et al., 2001,
483 2006). Consequently, intensification of weathering increases the supply of Sr into the basin,
484 resulting in lower Rb/Sr ratios in lake and marine sediments (e.g., Jin et al., 2001, 2006).
485 Transferring this to the JA-2 core, the constant increase in Rb/Sr values from the base toward
486 the top of the core suggests that the source area providing the sediment that forms the lower
487 part of the JA-2 core between 73.21 and about 67 m experienced an enhancement of
488 weathering intensity compared to the core above.

489 The elevated value of phosphorous for the sample at 27.27 m depth (Fig. 5) is likely
490 related to the occurrence of a phosphatic phase, which could reflect either detrital input from
491 the continent (e.g., detrital apatite) or a biogenic origin. Since this sample has also elevated
492 Ti, Th, Rb, Y and REE values (Figs 5, 7 and 8; Supplementary Table S3), a major detrital
493 influx from the continent is most likely.

494 The Sc content shows significant changes throughout the core (Fig. 6), with ~23 ppm
495 between 20.80 and 46.20 m depth, ~15 ppm between 46.60 and 67.21 m depth, and ~28 ppm
496 between 67.40 and 73.21 m depth. The Sc values in the latter section are even higher than
497 those of the weathered section between 20.80 m and 46.20 m depths. Before an explanation is
498 given for these different Sc values, the following outline will help understanding of the
499 geochemical behaviour of Sc. Because the radius of Sc^{3+} (0.81 Å) is close to that of Fe^{2+} (0.74
500 Å), and the electronegativity of Sc^{3+} ($E_{\text{Sc}} = 1.3$) is much smaller than that of Fe^{2+} ($E_{\text{Fe}} = 1.65$),
501 Sc exhibits a great tendency to enter a suitable crystal lattice to replace Fe^{2+} during magmatic

502 crystallisation (Ringwood, 1955). Although the behaviour of Sc is complex, there seems to be
503 a close geochemical coherence between Sc^{3+} and Fe^{2+} (plus Fe^{3+}). Moreover, Sc^{3+} can
504 substitute for Al^{3+} and Ti^{3+} . Scandium is mainly associated with ferromagnesian minerals and
505 biotite, and it can be enriched in phosphorites (Kabata-Pendias and Mukherjee, 2007).
506 Judging from these evidences, it is suggested that Sc enrichment in the lower and upper
507 sections of the JA-2 core may simply be related to Fe enrichment due to intense chemical
508 weathering. Note that Sc is commonly taken as a reliable indicator of terrigenous material,
509 mainly aluminosilicates, which may provide an alternative explanation for the observed Sc
510 values in the JA-2 core. Unfortunately, an extensive discussion here concerning the behaviour
511 of Sc in fine-grained clastic sediment is hampered by the lack of published literature.

512 Elements such as Mn, Co and Zn show low values in the weathered section between
513 67.82 and 73.21 m depths, compared to the section between 20.80 and 67.59 m depths. The
514 element concentrations are even lower than those of the upper continental crust (Mn ~ 600
515 ppm, Co ~ 10 ppm, Zn ~ 71 ppm; Taylor and McLennan, 1985). The depletion in the lower
516 weathered section may simply be a result of element leaching due to intensive chemical
517 weathering.

518 Interestingly, high Ni/Co ratios occur in the lower part of the JA-2 core. Ni/Co ratios
519 are 4.1 to 8.6 between 67.59 and 69.12 m depths and 2.8 to 3.5 between 71.44 and 73.21 m
520 depths, compared to only about 2.2 in the section between 20.80 and 67.40 m depths. Ni is
521 controlled by the sulphide content since Ni resides in framboidal pyrite and covaries with
522 sulphur (Jones and Manning, 1994). Jones and Manning (1994) used Ni/Co to identify the
523 oxygen status during shale deposition. They concluded that shale deposited under oxic
524 conditions (860–2.0 ml l⁻¹ oxygen) would usually have Ni/Co ratios <5, shale deposited under
525 dysoxic conditions (2.0–0.2 ml l⁻¹ oxygen) would have Ni/Co ratios between 5 and 7 whereas

526 anoxic conditions lead to Ni/Co ratios of ≥ 7 . Therefore, the presence of high Ni/Co ratios in
527 shales of the lower part of the JA-2 core would suggest dysoxic to anoxic conditions during
528 their deposition. However, judging from the extraordinary low Co values it is more likely that
529 the Ni/Co ratios of the lower part are modified by element mobilisation due to intensive
530 chemical weathering.

531 The element concentrations of Y and Zr are fairly constant throughout the core with a
532 few single peaks occurring. The high Y value of 155 ppm at 67.59 m depth is accompanied by
533 elevated HREE concentrations and thus suggests garnet enrichment in this sample. The high
534 Zr value of 189 ppm at 65.23 m depth is probably caused by zircon enrichment. Nearly
535 constant Zr/Hf ratios (32 to 35) throughout the JA-2 core suggest that zircon is the main
536 contributor for Zr and Hf in the analysed sediment.

537 Ba concentrations decrease from high values of about 810 ppm in the lowermost
538 section of the core to values of about 443 ppm at 67.40 m depth, followed by an increase in
539 Ba concentration to values of about 700 ppm towards the top of the core (Fig. 7). The
540 exception is a value of 1403 ppm Ba at 68.42 m depth. In marine sediments, breakdown of
541 organic matter releases Ba into the water column, which in the presence of sulphate forms
542 barite (BaSO_4). Thus, Ba is mainly a residue of biogenic material and is therefore often taken
543 as a palaeo-productivity indicator (e.g., Dymond et al., 1992; McManus et al., 1998, and
544 references therein). However, diagenetic redistribution of Ba limits its use as a palaeo-
545 productivity indicator in nearshore deposits, and therefore, Ba from such sediments should not
546 be used for palaeo-productivity reconstructions (Dymond et al., 1992). For example, a
547 diagenetic Ba front can form at the base of the sulphate zone (Dymond et al., 1992, and
548 references therein).

549 Returning to the JA-2 core, the high value of Ba (1403 ppm) at 68.42 m depth is
550 accompanied by high values of P₂O₅ (0.77 wt%), U (11 ppm) and total REE (825 ppm). This
551 suggests a detrital origin for Ba, probably associated with a U–REE-bearing phosphate. The
552 high Ba values in the lowermost section of the core may be explained either by sedimentary
553 influx of Ba-rich detrital material or by post-depositional redistribution of Ba due to intensive
554 chemical weathering. The constant increase of the Ba content in the unweathered section
555 toward the top may reflect an increase in palaeo-productivity. However, Ba does not correlate
556 with the TOC content, and therefore, Ba cannot be used as a palaeo-productivity indicator in
557 the JA-2 core.

558 High total concentrations of the REE of 534 ppm and 825 ppm at 27.27 m and 68.42
559 m depths, respectively, are accompanied by high P₂O₅ values of 0.59 wt% and 0.77 wt%,
560 respectively (Figs 5 and 7). This suggests that detrital phosphate is likely enriched at these
561 depths causing positive peaks for total REE and P₂O₅ concentrations.

562

563 *4.1.2. Binary plots*

564

565 TOC and HI do not correlate with U (Fig. 9). Therefore, other U-bearing phases than those of
566 organic matter must be present, which significantly control the total U content of sediment.
567 The prime candidate is the heavy mineral zircon, which can incorporate significant amounts
568 of U (300–3000 ppm of U; Bateman, 1985). Zircon yields a background value for U in the
569 sediment. The positive correlation between Hf and Zr (Fig. 10b) clearly suggests zircon is the
570 major Hf source in the sediment.

571 The positive correlation between Rb and K₂O (Fig. 11a) suggests that Rb is fixed in K-
572 feldspar since K₂O correlates positively with the K-feldspar content determined by XRD (Fig

573 16b). Although Rb correlates positively with the K-feldspar content (Fig. 17a), Rb shows a
574 much better positive correlation with the illite content (Fig. 17b). Therefore, illite and minor
575 K-feldspar is likely the carrier of Rb in the JA-2 sediments. The negative correlation between
576 Rb and Sr (Fig. 11b) reflects the different behaviour of Rb and Sr during chemical weathering
577 (see Section 3.1.1. for discussion). Note that high Sr and low Rb contents (plus $Rb/Sr < 1$) in
578 the highly weathered section ($Th/K > 9$), in the deepest part of the JA-2 core are accompanied
579 by high kaolinite contents ($>35\%$) and high kaolinite/illite ratios (>1.5). Therefore, elevated
580 U concentrations (>6 ppm) of samples from this part of the core are likely related to intense
581 chemical weathering. The significant change in whole-rock geochemical composition and
582 mineralogy in the lower part of the JA-2 core is also reflected in a dramatic drop of the
583 abundance of the chitinozoans (Thusu et al., 2013), potentially related to the oxidation noticed
584 on the core samples. Two possible explanations are as follows: (a) a temporary emersion
585 event may have occurred during the latest Hirnantian–earliest Rhuddanian post-glacial
586 rebound, which led to the weathering of older strata. Interestingly, a hiatus has been predicted
587 to occur between the Hirnantian shale and the Tanezzuft ‘hot’ shales in core of the Murzuq
588 Basin (unpubl. data, Repsol Oil Operations, Tripoli, cited by Fello et al., 2006, p. 109). (b)
589 Groundwater circulation in a minor fault as observed in the lower part of the core is likely to
590 generate the oxidation of the sediment and of its organic matter in the deeper part of the core.

591 The positive correlation between Nb and TiO_2 (Fig. 13a) is due to the presence of
592 detrital rutile as it is the most prominent TiO_2 polymorph and a major carrier of Nb and Ti
593 (e.g., Meinhold, 2010). The positive correlation between Ni and Co (Fig. 13b) is due to their
594 similar chemical properties, allowing them to substitute each other in various phases.

595

596 4.1.3. Normalised REE diagrams

597

598 REEs are widely used to study marine sediments as they are an extremely coherent group of
599 elements (e.g., Elderfield and Greaves, 1982; McLennan, 1989; McLennan et al., 1993). The
600 REEs exist predominantly in the trivalent oxidation state, and their chemical properties vary
601 gradually along the series from lanthanum (La) to lutetium (Lu). Cerium (Ce) and europium
602 (Eu) are exceptions because Ce can be oxidised to a tetravalent state (Ce^{4+}) and then occurs as
603 a solid phase (CeO_2) that is highly insoluble in seawater (Elderfield, 1988). Reduction of Eu
604 to a divalent state (Eu^{2+}) may also occur (De Baar et al., 1983; Elderfield, 1988). Here, we
605 refer to Elderfield (1988), McLennan (1989) and McLennan et al. (1993) for details about the
606 geochemical behaviour and mobility of REEs and their use in sediment geochemistry.

607 Normalised REE concentrations in shale samples from the shallow borehole JA-2
608 (Fig. 14) show similar patterns suggesting no significant change in the source area through
609 time. The exceptions are two samples at 67.59 m and 68.42 m depths respectively. The
610 sample from 68.42 m depth has a similar REE pattern as the others samples but all REEs are
611 enriched resulting in a higher total REE whole-rock content (Fig. 14m,n). This can be
612 explained by REE scavenge in a phosphate phase since this sample has the highest phosphate
613 content of all analysed samples. The sample from 67.59 m depth has a similar LREE pattern
614 as the other samples but significant higher concentrations of HREE (Fig. 14m,n). This can be
615 explained by detrital enrichment in garnet since this sample has also a high whole-rock
616 yttrium content.

617

618 *4.2. XRD analysis*

619

620 Only minor fluctuating values for the quartz, K-feldspar, kaolinite and illite contents
621 throughout most of the core from 20.80 m to about 65 m depth suggest that sediment from
622 this part of the core was most likely sourced by the same hinterland, which did not experience
623 significant changes in climatic conditions. Post-depositional weathering on the whole-rock
624 mineralogy had only minor or no influence. However, the sediment between 65 m and the
625 base of the core shows a significant drop in illite and K-feldspar contents accompanied by an
626 increase in the contents of kaolinite and quartz. Hence, the kaolinite/illite and
627 K-feldspar/quartz ratios show increasing and decreasing values respectively. The deeper part
628 of the JA-2 core therefore records enhanced palaeo-weathering in the sediment source area
629 (see Section 3.1.2. for discussion).

630

631 *4.3. Note on U content in sediment as TOC indicator*

632

633 An important element of our work on the Tanezzuft Formation is to test the relationship
634 between U and TOC content. This is because the U content of Silurian shales in North Africa,
635 measured by portable gamma-ray spectrometry (PGRS), is commonly taken as a proxy for the
636 TOC content of the sediment in the search for possible ‘hot’ shales (e.g., Lüning et al., 2003;
637 Lüning and Fello, 2008). Although this technique seems to work well in certain areas of
638 North Africa and Arabia, especially for samples with high TOC content, there are a number of
639 facts to consider regarding the actual potential sources of U in sedimentary rocks.

640 The most important source of U is dissolved U carried from the world’s rivers to the
641 oceans. As already mentioned above, this source of U can be removed from ocean water by
642 diffusion across the sediment-water interface and eventual reduction may lead to the residence
643 in organic-rich shales (Klinkhammer and Palmer, 1991; Brumsack, 2006). This form of U is

644 called authigenic U. Changes of the U concentration in sediment with time are controlled
645 primarily by the U concentration of the source material settling from the water column, and
646 secondarily, by the organic content of this material and the sedimentation rate (Klinkhammer
647 and Palmer, 1991). This process is so effective that about 75% of the U being supplied to the
648 oceans is being removed by diffusion into suboxic sediments (Klinkhammer and Palmer,
649 1991). Thus, U is considered as being associated with the organic matter in the sediment
650 rather than the clay minerals. Yet, in marine sediments organic matter seems to be associated
651 with different types of clay minerals due to processes of adsorption and entrapment (e.g.,
652 Bader et al., 1960; Bishop and Philp, 1994, and references therein) and therefore U may be
653 indirectly related to clay minerals as well (see also Chabaux et al., 2003). In addition, U may
654 be enriched in sediment due to the accumulation of zircon as a major carrier of U. For
655 example, zircon could be concentrated in heavy mineral sands (placer deposits). Uranium may
656 also be enriched through U mineralisation. One example is the Upper Palaeozoic and Lower
657 Mesozoic continental sedimentary succession in the Air mountains of Niger (e.g., Bowden et
658 al., 1981). Uranium was derived from igneous rocks and their eroded cover and was
659 consequently concentrated in the sediment matrix and on secondary Fe-oxide coatings
660 surrounding lithic and crystal fragments (Bowden et al., 1981).

661 Thus, there is one major and at least three other potential sources of U in sedimentary
662 rocks. Alternatives to the common association of U with organic matter seem to have been
663 overlooked in the studies of the North Africa Silurian shales. Klinkhammer and Palmer
664 (1991) addressed the subject of U source in sediment and its mobilisation thoroughly. Further
665 research is needed to clarify the applicability of U concentrations as a tracer to detect 'hot'
666 shales.

667

668 **5. Conclusions**

669

670 Elemental geochemistry of 47 shale samples from the latest Hirnantian–earliest Rhuddanian
671 Tanezzuft Formation collected from the 20.80–73.21 m interval in borehole JA-2 clearly
672 shows the mobility of individual trace elements related to surface weathering. For example,
673 Mn is depleted and Sc is enriched in the weathered section. Throughout the core from 20.80
674 m to 67.59 m interval concentrations of U range between 3.1 and 5.3 ppm, while the deeper
675 section (67.82–73.21 m) shows U contents between 6 and 12 ppm. TOC content do not
676 correlate with U concentrations. For example, the highest TOC of 0.75 wt% (HI = 187 mg S₂/
677 g TOC) is associated with a U value of 4.7 ppm. Moreover, the highest U value of 11.9 ppm
678 corresponds to an intermediate TOC value of only 0.46 wt% (HI = 246 mg S₂/g TOC). This
679 observation demonstrates that the correlation between U and TOC may break down at low
680 TOC and U contents and organic matter is not the only source for U accumulation in
681 sediments. Therefore, total U contents determined with portable gamma-ray spectrometry
682 (PGRS) at outcrop may not always reflect the TOC content of the sediment.

683 Calculated whole-rock Ce anomalies of the analysed shale samples fluctuate around
684 0.93, which suggests no significant change in redox conditions throughout the cored section,
685 except perhaps at depths of 55.53 m and 73.20 m where the Ce-anomaly values are 0.78 and
686 1.08 respectively.

687 The positive correlation between Rb and K₂O suggests that Rb is fixed in K-feldspar
688 since K₂O correlates positively with the K-feldspar content. In general, quartz, K-feldspar,
689 kaolinite and illite form the prominent mineral assemblage. Chlorite, siderite and pyrite are
690 also present in many samples but only in minor amounts. Kaolinite/illite and
691 K-feldspar/quartz ratios are increasing and decreasing, respectively, from about 65 m depth

692 towards the base of the core. Although Rb correlates positively with the K-feldspar content, it
693 shows a much better positive correlation with the illite content. Therefore, illite and minor K-
694 feldspar is likely the carrier of Rb in the JA-2 sediments. The negative correlation between Rb
695 and Sr reflects the different behaviour of Rb and Sr during chemical weathering. High Sr and
696 low Rb contents (plus $Rb/Sr < 1$) in the highly weathered section ($Th/K > 9$), in the deepest
697 part of the JA-2 core are accompanied by high kaolinite contents ($>35\%$) and high
698 kaolinite/illite ratios (>1.5). This significant change in whole-rock geochemical composition
699 and mineralogy is also reflected in a dramatic drop of the abundance of the chitinozoans
700 (Thusu et al., 2013), possibly related to oxidation noticed on the core samples. Therefore,
701 elevated U concentrations (>6 ppm) of samples from this part of the core are likely related to
702 intensive chemical weathering due to humid and warm palaeo-climate. A temporary emersion
703 event may have occurred during the latest Hirnantian–earliest Rhuddanian post-glacial
704 rebound, which resulted in the weathering of older strata. Groundwater circulation in a small
705 fault as observed in the lower part of the core also has the potential to generate the oxidation
706 of the sediment and of its organic matter in the deeper part of the core. This faulting may be
707 synsedimentary as this part of the core should be near the base of the Tanezzuft Formation
708 and there is a lot of post-depositional remobilisation of the Mamuniyat Formation into the
709 Tanezzuft Formation in the vicinity (CASP unpublished data).

710 The present study clearly demonstrates that the relationship between the content of
711 total organic carbon (TOC) and the actinide metal uranium is more complex for latest
712 Hirnantian to Rhuddanian shales than currently assumed. This may limit the use of the U
713 content, determined by PGRS at outcrop (particularly at low concentrations of U and TOC),
714 to identify potential ‘hot’ shales in Libya or elsewhere. Thus, there is clearly the need for

715 further investigations to address this subject, which may help developing new models for
716 ‘hot’ shales deposition.

717

718 **Declaration of competing interest**

719

720 The authors have no conflicts of interest to declare.

721

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723

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735

736 **Appendix A. Supplementary data**

737

738 Supplementary data to this article can be found online at <https://doi.org/xxxxxx>

739

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941

942 **Figure captions**

943

944 **Fig. 1.** Geological map of Libya and neighbouring countries showing location of the Kufra
945 Basin in SE Libya (after Meinhold et al., 2011). The location of the borehole JA-2 in southern
946 Jebel Asba at the eastern margin of the Kufra Basin (Meinhold et al., 2013b; this study) and
947 of the borehole CDEG-2a at the eastern margin of the Murzuq Basin (Paris et al., 2012;
948 Meinhold et al., 2013a) are indicated.

949

950 **Fig. 2.** Generalized stratigraphic column for Upper Ordovician–ower Silurian strata in Jebel
951 Asba in SE Libya, with main lithologies, thicknesses, and depositional environment (modified

952 after Meinhold et al., 2013b). It is referred to Gindre et al. (2012) for details about the
953 sedimentology and facies analysis.

954

955 **Fig. 3.** Landsat image (NASA Landsat Program) of southern Jebel Asba in SE Libya with the
956 distribution of Tanezzuft Formation shales superimposed and the location of the borehole JA-
957 2 (modified after Meinhold et al., 2013b).

958

959 **Fig. 4.** Summary of the stratigraphic distribution of selected source rock data, trace element
960 concentrations, mineralogical composition and of palynological and kerogen parameters in
961 shales from borehole JA-2 in southern Jebel Asba, SE Kufra Basin. The lithology, bulk
962 gamma-ray log, total organic carbon (TOC) and hydrogen index (HI) values were taken from
963 Meinhold et al. (2013a), the uranium (U) values and mineralogical composition are from this
964 study, and the chitinozoan abundance and kerogen data are from Thusu et al. (2013).

965 Palynological examination of samples suggest that the unweathered section belongs to the
966 *Euconochitina moussegoudaensis/Spinachitina oulebsiri* Chitinozoan Zone (Thusu et al.,
967 2013). Note that only 0.5 m of casing was retrieved; the rest had fallen into the borehole. The
968 deflection of the shale line to the left between 20 and ~32 m indicates the position of the
969 fallen section of casing (marked with a red arrow).

970

971 **Fig. 5.** Stratigraphic distribution of selected trace element concentrations and of
972 palaeoenvironmental sensitive parameters in shales from borehole JA-2 in southern Jebel
973 Asba, SE Kufra Basin. The TOC and HI values were taken from Meinhold et al. (2013a).

974

975 **Fig. 6.** Stratigraphic distribution of selected trace element concentrations and element ratios in
976 shales from borehole JA-2.

977

978 **Fig. 7.** Stratigraphic distribution of selected trace element concentrations and total REE in
979 shales from borehole JA-2.

980

981 **Fig. 8.** Stratigraphic distribution of the REE concentrations in shales from borehole JA-2.

982

983 **Fig. 9.** (a, b) Total Organic Carbon (TOC) and Hydrogen Index (HI) versus U content cross
984 plots for samples from borehole JA-2.
985

986 **Fig. 10.** (a, b) U and Hf contents versus Zr content for samples from borehole JA-2. (b) Hf
987 and Zr are well correlated due to the resistance in zircon.
988

989 **Fig. 11.** (a, b) K₂O and Sr contents versus Rb content for samples from borehole JA-2. (a)
990 K₂O and Rb are well correlated probably due to the resistance in K-feldspar.
991

992 **Fig. 12.** (a, b) Rb/Sr and Th/K contents versus U content for samples from borehole JA-2.
993

994 **Fig. 13.** (a) Nb versus TiO₂ cross plot. The positive correlation between Nb and TiO₂ suggests
995 rutile as major source for Nb in the sediment. (b) Ni versus Co cross plot shows positive
996 correlation between both elements with depletion of Ni and Co, respectively, in the weathered
997 sections.
998

999 **Fig. 14.** REE diagrams for drill core from borehole JA-2. The samples are arranged with
1000 increasing depth. Samples in (a, b) come from the upper weathered section. Samples in (c–f)
1001 appear unweathered; organic matter is preserved. Samples in (g–l) come from the
1002 unweathered section; organic matter is preserved. In samples from 67.21 m to 67.97 m depths
1003 (m, n) organic matter is preserved, although the abundance is low in the sample from 67.97 m
1004 depth. Samples in (o, p) come from the lower weathered section; no organic matter is
1005 preserved.
1006

1007 **Fig. 15.** Stratigraphic distribution of the whole-rock content of selected minerals and mineral
1008 ratios in shales from borehole JA-2.
1009

1010 **Fig. 16.** (a) K-feldspar contents versus Th/K cross plot. (b) K-feldspar versus K₂O contents
1011 cross plot. The inset (c) shows the K-feldspar versus kaolinite contents cross plot.
1012

1013 **Fig. 17.** (a) K-feldspar versus Rb contents cross plot. The inset shows the negative
1014 correlation between the K-feldspar content and Th/K. (b) Illite versus Rb contents cross plot
1015 shows positive correlation between illite and Rb.

1016

1017 **Fig. 18.** (a) Sr versus K-feldspar/illite contents cross plot. (b) K-feldspar/quartz versus K-
1018 feldspar/illite contents cross plot.