

1 Are Spherulitic Lacustrine Carbonates an Expression of Large-  
2 Scale Mineral Carbonation? A case study from the East  
3 Kirkton Limestone, Scotland.

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28

29 **ABSTRACT**

30 Lacustrine carbonate deposits with spherulitic facies are poorly understood, but are key to  
31 understanding the economically important “Pre-Salt” Mesozoic strata of the South Atlantic.  
32 A major barrier to research into these unique and spectacular facies is the lack of good  
33 lacustrine spherulite-dominated deposits which are known in outcrop. Stratigraphy and  
34 petrography suggest one of the best analogue systems is found in the Carboniferous of  
35 Scotland: the East Kirkton Limestone. Here we propose a hydrogeochemical model that  
36 explains why the CaCO<sub>3</sub>, SiO<sub>2</sub>, Mg-Si-Al mineral suite associated with spherular radial calcite  
37 facies forms in alkaline lakes above basaltic bedrock. Demonstrating links between igneous  
38 bedrock chemistry, lake and spring water chemistry and mineral precipitation, this model  
39 has implications for studies of lacustrine sediments in rift basins of all ages. Using empirical  
40 and theoretical approaches, we analyze the relationship between metal mobilization from  
41 sub-surface volcanoclastic rocks and the potential for precipitation of carbonate minerals,

42 various Mg-bearing minerals and chalcedony in a lacustrine spherulitic carbonate setting.  
43 This suite of minerals is most likely formed by in-gassing of CO<sub>2</sub> to a carbon-limited alkaline  
44 springwater, consistent with the reaction of alkali igneous rocks in the subsurface with  
45 meteoric groundwater. We suggest that an analogous system to that at East Kirkton caused  
46 development of the 'Pre-Salt' spherulitic carbonate deposits.

47

48 **Keywords:** Palaeozoic, magnesium silicate, calcite, hydrolysis, Pre-Salt, palaeogeography,  
49 lake, PHREEQC, Europe, Sediment mineralogy

50

## 51 **1. INTRODUCTION**

52 Fibro-radial spherulitic calcite components are relatively well known on a small scale from  
53 vadose, lacustrine and marine environments (Verrecchia et al., 1995; Braissant et al., 2003;  
54 Arp et al., 2012; Wanas, 2012; Casado et al., 2014; Bahniuk et al., 2015). However, deposits  
55 constituted of more than a few grains of spherulitic habit are rare, and probably limited to  
56 specific processes and depositional conditions that are currently poorly constrained.

57 Comparatively little studied, there has been increasing interest in understanding how such  
58 voluminous lacustrine spherulitic calcite deposits, and the SiO<sub>2</sub> and Mg-Si-Al suite of  
59 minerals typically associated with them, were precipitated. This increased interest has been  
60 further motivated by the need to explain the economically-significant and spatially  
61 voluminous early Cretaceous 'Pre-Salt' carbonate reservoirs of Brazil and Angola (Wright,  
62 2012; Wright and Barnett, 2015). The origin of these highly unusual deposits, which

63 occupied rift lakes formed during opening of the South Atlantic, is controversial (Wright,  
64 2012; Mercedes-Martín et al., 2016).  
65 Crucial first-order questions, such as the source(s) of the calcium and silica being deposited,  
66 remain unanswered. The sheer masses of minerals precipitated from the Cretaceous lakes  
67 imply a major mass-transfer process operated at the time, but this process has not been  
68 identified. What is clear is that the petrographic appearances of these sediments is  
69 markedly different from known Recent “meteoene” or “tufa” carbonate deposits (Wright,  
70 2012). Equally, the very high volume of carbonate emplaced demonstrates that these  
71 systems were not metal-limited as most modern “thermogene” or “travertine” deposits are  
72 (Guido and Campbell, 2011; Renaut et al., 2013). Such geologically unusual deposits imply  
73 an unusual mass transfer mechanism operated during rifting of the South Atlantic.

74

### 75 **1.1. Fibro-Radial Calcite and the Great Pre-Salt Controversy**

76 In the ‘Pre-Salt’ South Atlantic rift lake rocks, fibro-radial carbonate components ‘float’  
77 within Mg-rich clay deposits (Dias, 1998; Terra et al., 2010; Wright and Barnett, 2015). The  
78 precise genetic relationship between these Mg-Si and CaCO<sub>3</sub> phases is a subject of ongoing  
79 controversy that needs resolving if the origin of the ‘Pre-Salt’ deposits is to be elucidated  
80 (Mercedes-Martín et al., 2016). Hypotheses based on petrographic observations variously  
81 suggest fibro-radial calcite arises from displacive concretionary crystal growth within Mg-Si  
82 matrices (Dorobek et al., 2012), or as early diagenetic features from Mg-Si gel catalysis  
83 (Wright and Barnett, 2015) or as a consequence of crystal growth in the presence of specific  
84 organic compounds (Mercedes-Martin et al, 2016). All three hypotheses are yet to be

85 rigorously experimentally tested, and a major barrier to effective testing is a lack of suitable  
86 deposits that can be investigated beyond proprietary and confidential drill core material of  
87 the South Atlantic rift lakes. Some partial analogues are known from the literature, for  
88 example minor spherulitic facies are reported from the distal facies of Jurassic hot spring  
89 systems from Deseado Massif, Argentina (Guido and Campbell, 2011). Here we focus on the  
90 mechanisms leading to the precipitation of carbonates and silicates in a lacustrine  
91 Carboniferous analogue from Scotland, UK.

92

### 93 **1.2. The East Kirkton Limestone: an interesting case study of rifting-related spherulitic** 94 **limestones**

95 The Carboniferous East Kirkton Limestone of the Midland Valley graben of Scotland (Fig. 1)  
96 contains calcium carbonate spherulites, spherulitic bioherms, calcite-smectite laminites and  
97 primary chert (Rolfe et al., 1993; Walkden et al, 1993). It occurs as a Member of the upper  
98 part of the West Lothian Oil Shale Formation (Smith et al., 1993), and its petrology,  
99 paleontology, stratigraphy and isotope geochemistry were well described in studies from  
100 the 1980s and 1990s (Wood et al., 1985, McGill, 1994; McGill et al, 1994; Clarkson et al,  
101 1993; Rolfe et al., 1993; Walkden et al., 1993; Goodacre, 1999). However, despite this  
102 significant effort to understand the East Kirkton Limestone, aspects of the system could not  
103 be elucidated two decades ago. A pivotal question lies in unravelling the source of the  
104 calcium and silica mass deposited in the lake, which is implicit in ongoing debates over  
105 whether the water in the lake was affected by deep-sourced “geothermal” springs (McGill et  
106 al., 1994).

107

108 The West Lothian Oil-Shale was deposited during a phase of rapid extension of the Midland  
109 Valley Basin, and these strata were strongly affected during their deposition by right lateral  
110 strike-slip movement which created half-grabens with tilted blocks forming inter-basin highs  
111 (Whyte, 1993; Read et al., 2002). Rift evolution was pulsed, with each phase of activity  
112 producing voluminous calc-alkaline extrusive igneous products (Monaghan and Parrish,  
113 2006). These products were interbedded as volcanoclastic rocks below, within and above the  
114 East Kirkton Limestone, indicating that the lacustrine phase was short-lived and coincided  
115 with an active volcanic pulse.

116 Basins opened throughout the South Atlantic in the Mesozoic from the Berriasian, due to  
117 rifting followed by strong thermal subsidence (Karner et al., 2003). In the southern basins of  
118 interest to this study (Moulin et al., 2005), rifting was active from the Barremian to base  
119 Aptian (Chaboureau et al., 2013). The active rifting was characterised by widespread, largely  
120 trachytic, volcanism (Teboul et al., 2017) which was particularly voluminous in the southern  
121 sector, encompassing the Santos / Campo and South Kwanza basins (Chaboureau et al.,  
122 2013). The Pre Salt carbonate formations developed during Early Aptian as accommodation  
123 was created by thermal sag of these rift basins (Karner et al., 2003). Volcanism continued  
124 within the Santos (Moreira et al., 2007) and Campos (Rangel et al., 1994) basins into the  
125 Aptian, reflecting that some lithospheric stretching continued into the period of extensive  
126 carbonate deposition. As at East Kirkton, lacustrine carbonate formations are therefore  
127 underlain by thick calc-alkaline volcanic materials, and deposition is associated within minor  
128 ongoing extrusive volcanic activity.

129 Overall, the East Kirkton Limestone seems an exceptional case study to better understand  
130 the origin of the mineral phases developed in rift volcanic lake settings such as those  
131 forming the South Atlantic 'Pre-Salt' deposits (sensu Dias, 1998, and Terra et al., 2010). The  
132 East Kirkton Limestone is also an important geoheritage site in its own right, famous for  
133 being the place where the earliest known well-preserved amphibian reptile skeleton was  
134 discovered (*Westlothiana lizziae*; Wood et al., 1985), so our findings have inherent value in  
135 further constraining a globally important early reptilian habitat.

136

## 137 **2. MATERIALS AND METHODS**

138 The type section of the East Kirkton Limestone is a quarry face (Fig. 1), where a heavily  
139 silicified spring emergence zone occurs at the northern limit giving way to layered  
140 carbonate, chalcedony and volcanoclastic deposits on its southern edge. This deposit was  
141 logged and sampled in August 2014. In addition, a series of boreholes (BH1, BH2 and BH3)  
142 drilled during 1987 and 1988 from the immediate area around the quarry were accessed,  
143 logged and sampled via the BGS Core Repository at Keyworth (UK) in February 2015. In  
144 particular, borehole BH2 is comprised of thick altered volcanoclastics attributed to unit 61 of  
145 the East Kirkton Limestone (see Rolfe et al., 1993), and borehole BH3 hosts more than 60  
146 cm-thick tuffaceous rocks. Geochemical analyses were performed from samples in borehole  
147 BH3.

### 148 **2.1. Optical and Energy-Dispersive X-Ray Spectroscopy (EDS) analysis**

149 Optical microscopic examinations of thin sections were made with a Nikon Microphot FX  
150 microscope interfaced with a Nikon DS-Fi2 camera, and Nikon Elements D software. An

151 Oxford Instruments Peltier-cooled type X-Max 80 EDS system integrated with a Zeiss EVO60  
152 Scanning Electron Microscopy was used to determine the abundance of specific elements  
153 through the X-rays energy spectrum. Rasterization of particular areas within the sample was  
154 implemented to obtain the chemical abundance of elements and create from matrix points,  
155 using a standard method within the INCA Energy software.

## 156 **2.2. X-ray powder diffraction**

157 X-ray powder diffraction data were collected from ground samples mounted in stainless  
158 steel sample holders. A PANALYTICAL Empyrean diffractometer operating in Bragg-Brentano  
159 geometry with copper  $K\alpha_1$  ( $\lambda = 1.540546 \text{ \AA}$ ) and a PIXEL detector was used for the data  
160 collection.

## 161 **2.3. Sr Isotopes**

162 The mobile fraction of strontium (i.e.  $\text{HNO}_3$  soluble) from samples taken from within the  
163 East Kirkton Limestone and from the altered igneous rocks of BH1 (Table 1) were extracted  
164 from powdered samples in PFA Teflon (Savillex) beakers on a hotplate at 140-150°C using  
165 ultrapure  $\text{HNO}_3$ . Analysis follows standard procedures (Henderson et al., 1994; Pin et al.,  
166 1994) with multiple  $\text{HNO}_3$  elutions from a Triskem Sr-spec resin packed Bio-Rad glass  
167 column. Pure strontium concentrates were loaded on to Re filaments using Ta emitter  
168 solution and analyses carried out on a VG sector 54-30 thermal ionisation Mass  
169 spectrometer at SUERC.

## 170 **2.4. Organic Geochemistry**

171 Lipid biomarkers were extracted from c.2.8 – 4.0g of freeze-dried and homogenised sample,  
172 following the microwave-assisted extraction methodology of Kornilova and Rosell-Melé

173 (2003). Known concentrations of 5 $\alpha$ -cholestane and hexatriacontane (Sigma-Aldrich) were  
174 added as internal standards. Each total lipid extract was hydrolysed using 8% KOH in  
175 methanol, heated for 1 hr at 70°C and left overnight. Neutral fractions were recovered using  
176 repeated liquid extraction with hexane, then separated into apolar, ketone and polar  
177 fractions using silica column chromatography and *n*-hexane, dichloromethane and methanol  
178 as eluents, respectively. The apolar fractions were analysed by gas chromatography-mass  
179 spectrometry (GC-MS), using a 30m HP-5MS fused silica column (0.25 mm i.d. 0.25 $\mu$ m of 5%  
180 phenyl methyl siloxane). The carrier gas was He, and the oven temperature was  
181 programmed as follows: 60-200°C at 20°C/min, then to 320°C (held 35 min) at 6°C/min.  
182 The mass spectrometer was operated in full-scan mode (50-650 amu/s, electron voltage  
183 70eV, source temperature 230°C). Quantification was achieved through comparison of  
184 integrated peak areas in the total ion chromatograms and those of the internal standards.  
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196 areas in the total ion chromatograms and those of the internal standards.

197

### 198 **3. RESULTS**

199 The general stratigraphy, mineralogy and geochemistry of the East Kirkton Limestone were  
200 previously described by Clarkson et al., 1993; Rolfe et al., 1993; Smith et al., 1993; Walkden  
201 et al., 1993; McGill et al, 1994; Goodacre, 1998. The most significant facies (Fig. 2, Fig. S1)  
202 and a representative sedimentary facies log (borehole BH3, Fig. 3) are provided to illustrate  
203 the main stratigraphic features. The mineral assemblages and stratigraphic context of these  
204 deposits are comparable to those documented so far in the South Atlantic 'Pre-Salt' rift  
205 lakes (*sensu* Bertani and Carozzi, 1985; Dias, 1998; Terra et al., 2010; Tosca and Wright,  
206 2015; Saller et al., 2016). We make this claim on the basis of: i) the occurrence of meter-  
207 scale beds yielding abundant partially eroded fibro-radial, spherical calcite components  
208 about 1mm in size and displaying sweeping extinction; ii) the presence of serpentine-rich  
209 floatstone of spherulitic components; iii) the laminated nature of the alternations of Mg-Si  
210 and CaCO<sub>3</sub> mineral phases throughout; and the presence of significant chalcedony and  
211 calcite cementing both Mg-Si and Ca phases (Fig. 4), iv) presence of mature hydrocarbons  
212 stored in spherulitic biohermal reservoir facies (Fig. S1F).

213

214 Thin section and XRD analyses (Figs. 4 and 5) both demonstrate that the primary carbonate  
215 mineralogy is dominantly calcite, with silica and dolomite as secondary phases: the  
216 composition and mineral paragenesis of this rock is consistent with currently published data

217 on South Atlantic 'Pre-Salt' deposits (Bertani and Carozzi, 1985; Dias, 1998; Terra et al.,  
218 2010; Tosca and Wright, 2015; Saller et al., 2016). It is possibly coincidental that the East  
219 Kirkton Limestone contains abundant mature hydrocarbons (Fig. 6), which have likely  
220 migrated into this reservoir facies from the black lacustrine West Lothian Oil-shale, however  
221 this does illustrate that it occurs in a hydrocarbon-prone basin context analogous to the Pre  
222 Salt and that migration of mature hydrocarbons and their formation waters are shared  
223 features of the paragenesis of both deposits.

224

### 225 **3.1. Stratigraphic relationships**

226 Borehole BH-3 (Fig. 3) displays a soil and rock cover in the first 3 m. Spherulitic carbonates  
227 are found between 2.8 and 3.6 m and between 4.3 and 6.2 m depth occurring as laminites,  
228 which are formed by the alternation of carbonate-rich and organic-rich laminae hosting  
229 abundant calcite spherulitic components (Fig. 2B, C; Fig. S1A, B). In some cases, a large  
230 number of spherulites are found floating in clay/organic to mudstone-rich matrices  
231 producing floatstone textures (Fig. 2D). Soft-sediment deformation (slumps, creeping of  
232 laminae, Fig. 2A, Fig. S1B) and diverse biota is occasionally recognised in laminites (Fig. S1C).  
233 Some cm-scale calcareous-rich tuff layers are interbedded within the sequence (from 3.6 to  
234 3.8m depth, Fig. S1D) which hardly ever contains spherulitic components. Three organic-rich  
235 shale packages (3.8 to 4.3 m; 6.2 to 7.3 m, and 7.8 to 13.5 m depth) previously named Little  
236 Cliff Shale Member by Rolfe et al., (1993) are also recorded. These authors identified  
237 pelecypods (*Curvirimula scotica*), plants (*Lepidodendron*), fish scales, ostracods (*Carbonita*),

238 and arthropods. A 50cm-thick layered carbonate interval (Fig. 3A) is recorded between 7.3  
239 and 7.8 m depths displaying nodular to tabular beds of wackestone to floatstone textures.  
240 Evidence of slumps and convolute beds is present and peloids, fish scales and ostracods  
241 allochems are common. In the bottom of the borehole (between 13.5 and 14.6 m depth) a  
242 greenish to dark orange tuff is recognised (Fig. 3, Fig. S1D). This unit is characterised by a  
243 pyroclastic texture with mm-thick angular to subangular lapilli clasts surrounded by fine-  
244 grained vesicular and amygdaloidal ash and shards (Fig. S1D). In some cases, calcite  
245 pseudomorphs after altered amygdale textures were observed emplaced within plagioclase  
246 or olivine phenocrysts (Fig. 2E), and some of these alkali minerals showed alteration  
247 textures to serpentine-like clay minerals. In addition, centimetre-sized irregular cavities  
248 filled with sequential generations of fibroradial/spherulitic chalcedony and drusy  
249 megaquartz cements (Fig. 2F) are also present in some spherulitic biohermal carbonate  
250 units (not shown in the log, Fig. S1F)..

251

### 252 **3.2. Petrological observations**

253 XRD analyses of the tuffs underlying the East Kirkton section indicate they have now  
254 completely replaced to calcite (Fig. 5A). The spatially-resolved EDS map of the altered tuff  
255 (across the white square in Fig. 5A) shows that pure calcite cement occurs as a light  
256 coloured fabric under plane-polarized light (top left in Fig. 3A, corresponding to high  
257 concentrations of Ca in Fig. 5B). A greenish brown area rich in Al, Mg and Fe (center and top-  
258 right in Fig. 5A, corresponding to high concentrations of these elements in Fig. 5B) is a

259 serpentine-like clay alteration product (Fig. 5C), similar to that encountered in the lacustrine  
260 deposits located higher in the East Kirkton stratigraphy (Fig. 5). A pale green region in the  
261 bottom left (Fig. 5A) is rich in K and Al and likely contains un-altered components of the  
262 original feldspar mineral phase.

263

### 264 **3.3. Strontium isotope data**

265 Results of strontium isotope analysis (Fig. 7) demonstrate that a substantial component of  
266 this metal was ultimately derived from a mantle source. Also, comparison with the BH3  
267 material and published data for the Midland Valley volcanic rocks indicate that BH3 volcanic  
268 tuffs and the lacustrine carbonate deposit are geochemically compatible, and probably co-  
269 developed, whereas both are less radiogenic than the original volcanic rocks.

270

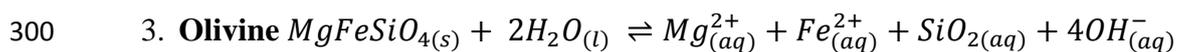
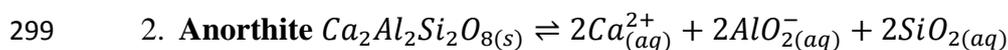
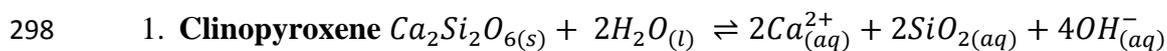
## 271 **4. DISCUSSION**

272 Overall, the tectono-stratigraphic context and mineral paragenesis recognised at East  
273 Kirkton are compellingly similar to the Pre-Salt deposits, representing a unique opportunity  
274 to study the hydrogeochemical processes enabling the development of these unusual  
275 deposits in detail. As with Pre Salt deposits, we interpret the East Kirkton deposit as an  
276 alkaline lake fed by springs with a high dissolved mass. Interpretation that the East Kirkton  
277 Limestone formed in an alkaline lake fed by a hot-spring are not new (McGill et al., 1993;  
278 Walkden et al., 1993). However, no previous study has been able to deduce the origin of the  
279 carbonate and silica-rich solutions contributing to the lake water mass. Here we present  
280 new petrographical analyses showing that the tuff in borehole BH3 underlying the

281 Limestone deposit (Fig. 3, Fig. 5, and S1D) displays textural and chemical evidence of  
282 replacement and alteration (Fig. 2E, 5) and only a faint geochemical signature of the original  
283 mineralogy can be identified. This alteration moved the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio away from the  
284 composition of unaltered regional igneous rocks, towards a composition also seen in the  
285 spherulitic carbonate deposits vertically above (Fig. 7). We infer that these two systems  
286 were in connection, and that the altering water was derived from meteoric input (Walkden  
287 et al., 1993).

288 The composition of Midland Valley Carboniferous extrusive igneous rocks nearby  
289 (Monaghan and Parrish, 2006) indicate that the original mineralogy of this material was a  
290 fairly standard pyroxene-olivine-feldspar assemblage, and this is compatible with the  
291 remnant Mg, Fe, K, Al found within the weathered tuffs (Fig. 5). The dominance of Ca in the  
292 weathered residue indicates that the feldspars were close to the anorthite end member and  
293 the pyroxenes were close to the Ca-rich end member in the original mineralogy. These  
294 minerals are known to be prone to weathering by infiltrating water, and undergo the  
295 following hydrolysis reactions (Equations 1-3), which are essentially the metasomatic  
296 reactions involved in serpentinization (Müntener, 2010; Hövelmann et al., 2011).

297



301

302 In all three reactions, the dissolved products cause hydrolysis resulting in very alkaline  
303 solutions. Ultimately, the solution produced by these reactions: i) will have a very high pH;  
304 ii) will be reducing; iii) will be rich in Ca, Si, Al, Mg and Fe. The molar ratios of fluid reaching  
305 the Earth's surface will be determined by 1) the molar ratios in the original rock, and 2) the  
306 molar ratio of secondary precipitates left by the solution in the subsurface.

307

308 The abundance of carbonate secondary precipitates in BH1 (Fig. 5) shows that the  
309 precipitating fluid contained substantial amounts of dissolved inorganic carbon. This is  
310 common in both meteoene and thermogene settings (Pentecost, 2005), and results in  
311 significant deposition of carbonate minerals as observed in this case. Consequently,  
312 although the Midland Valley volcanic series can be expected to have contained >10%  
313 calcium by mass, springs reaching the surface having altered these rocks will be severely  
314 calcium-limited. This is observed in modern springs, even where pH has been raised above  
315 10 by reactions analogous to equations 1-3 (Jones and Renaut, 2010; Renaut et al., 2013). To  
316 explain the Ca-rich spring implied by the spherulitic nature of the deposits at East Kirkton  
317 (Wright and Barnett, 2015; Mercedes-Martín et al., 2016), and more dramatically the  
318 exceptionally large mass of calcium deposited within the Pre-Salt Formations (Dias, 1998;  
319 Terra et al., 2010), such calcium limitation cannot have occurred, and the amount of calcium  
320 available to the subsurface fluids must have exceeded the capacity of the dissolved carbon  
321 supply to remove it. This implies that the waters were not geothermally sourced but were  
322 meteoric, and that the whole East Kirkton system was consuming very large masses of  
323 carbon derived from the atmosphere. Large-scale geochemical systems fulfilling this

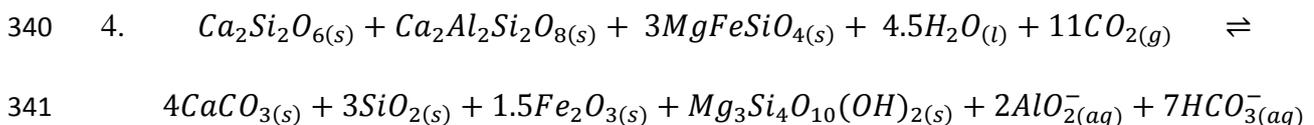
324 description occur today within exhumed ophiolites, for example the Soma Ophiolite in  
325 Oman (Matter and Kelemen, 2009). Springs fed from carbon-limited reactions in the  
326 subsurface have led to the deposition of an estimated  $10^7$  m<sup>3</sup> of carbonate on the surface,  
327 covering an area of ~200,000 m<sup>2</sup>, in the last ~50,000 years alone (Kelemen and Matter,  
328 2008). We propose that an analogous geochemical system led to the development of both  
329 the East Kirkton and Pre-Salt carbonate formations.

330

#### 331 **4.1. Understanding a Carbon-Limited, Hyperalkaline Spring System**

332 On emergence at the surface, a carbon-limited solution produced by weathering alkaline  
333 tuff would rapidly equilibrate by reacting with atmospheric CO<sub>2(g)</sub> to produce a range of  
334 mineral products. Summatively, reactions 1-3 and 4 result in a balanced transfer of mass  
335 from clinopyroxene, olivine and feldspar to calcite, silica and serpentine-like clay (stevensite  
336 at high pH and high Mg/ Si ratios; Tosca and Masterton, 2014) and Mg-Al phases, and these  
337 reactions are essentially identical to those reported from weathering ophiolite systems  
338 (Kelemen and Matter, 2008).

339



342

343 Our hypothesis is that there is no geothermal heating from active magma systems from  
344 which excess CO<sub>2</sub> could be provided, however this does not imply the spring was necessarily  
345 cold. Reactions 1-4 are exothermic (Wenner and Taylor, 1971), so it is likely the waters

346 arising from them were warm. Temperatures as high as 60°C for the East Kirkton lake water  
347 have been inferred from  $\delta^{18}\text{O}$  in silica (McGill et al, 1993). We note that Walkden et al.  
348 (1993) estimated an average lake temperature of 20°C from oxygen isotopes in calcite  
349 spherules, however this facies may reflect a distal setting in which significant dissolved  
350 organic matter was present in solution (Mercedes-Martin et al., 2016) as reported in  
351 Patagonia (Guido and Campbell, 2011). The high-temperature siliceous facies and the low-  
352 temperature spherulite facies are therefore compatible with relatively high (proximal) and  
353 low (distal) spring influence respectively. In any case, the importance of identifying whether  
354 the water was hot or cold derives, in large part, from the value of raised temperature as a  
355 proxy for a non-karstic source for the calcium and carbonate ions. Our analysis indicates  
356 that these ions were sourced from igneous rock weathering regardless of spring water  
357 temperature, and so the emphasis on understanding temperature is much reduced.

358

359 The evolution of the solution, and the paragenesis of depositional products derived from it,  
360 can be explored by sequentially exposing a spring representative of carbon-limited reactions  
361 1-3 to  $\text{CO}_2(\text{g})$  at surface conditions using a simple thermodynamic approach via PHREEQC  
362 modelling (Parkhurst and Appelo, 1999; Fig. 8, See Supplementary Material). Here, we use a  
363 representative springwater from the Somail Ophiolite (see Supplementary material). We  
364 find that Mg-Si phases are most insoluble initially;  $\text{CaCO}_3$  phases precipitate in almost  
365 stoichiometric balance with the ingassing of carbon dioxide; and  $\text{SiO}_2$  phases increase in  
366 insolubility as pH falls (Fig. 8). Indeed, by allowing the system to achieve equilibrium with  
367 excess  $\text{CO}_2$ , we can also investigate the predicted paragenesis for the mineral assemblage.

368 Figure 4 shows that with increasing ingassing, serpentine-like Mg-Si phases remineralize to a  
369 combination of Mg-Al phases and dolomite as  $\text{OH}^-_{(\text{aq})}$  becomes unavailable below the pH  $\sim 10$   
370 transition, which is consistent with paragenesis concepts for the Pre-Salt (Wright and  
371 Barnett, 2015). Simultaneous deposition of calcite, silica, dolomite and serpentine-like clays  
372 around the lake shores implies an equilibrium pH of  $\sim 8$  for lake waters (Fig. 8), comfortably  
373 within the range of modern alkaline surface waters (Rogerson et al., 2014). Alternation of  
374 calcite- and silica-dominated phases in the more distal lake environments in this case is  
375 consistent with an oscillation of water chemistry around pH 7, presumably reflecting  
376 variable balance in the input flux of spring and ambient meteoric water. However, this result  
377 is unlikely to be unique and may reflect the specific chemistry of the spring system itself.  
378 The diagenetic changes implied by the succession of Mg-phases in Figure 8 indicate that  
379 secondary porosity is likely to develop. This is consistent with the behaviour of Mg-Si in the  
380 Pre-Salt system as more fully developed by Tosca and Wright (2015).

381

#### 382 **4.2. Is Carbon-limited Mass Transfer to Terrestrial Carbonates a Significant Sediment** 383 **Transport Process?**

384 The similarity of the sediments and mineral phases at East Kirkton to those of the larger  
385 South Atlantic Cretaceous lakes implies a strong similarity in their genetic processes, and  
386 therefore that similar mass-transfer geochemical processes are likely to have been  
387 operating on a very large scale in the early Mesozoic. Indeed, the geochemical signature of  
388 subsurface alteration of this type has also been reported for the igneous series underlying  
389 the 'Pre-Salt' carbonates. During rainy periods chemical weathering of basic volcanoclastic

390 rocks and basaltic magmas is thought to have promoted an active transport of dissolved  
391 cations (Na, Ca, K, Mg) into the Lagoa Feia lake ('Pre-Salt', Brazil; Bertani and Carozzi, 1985).  
392 In addition, extensive calcitization processes and trioctahedral smectite formation took  
393 place in the distal parts of the lacustrine terrigenous flats (Bertani and Carozzi, 1985).  
394 Serpentinization of the exhumed mantle in several Brazilian 'Pre-Salt' basins can have  
395 occurred down to depths of 6-8 km at the continental-oceanic crustal transition (Zalán et al.,  
396 2011), providing an enormous reservoir of dissolved cations from igneous source rocks for  
397 remobilisation in the 'Pre-Salt' lakes. Recent re-evaluation of the igneous series underlying  
398 the Kwanza Pre-Salt basin offshore of Angola again indicates meteoric alteration, and  
399 development of metal-rich fluids (Teboul et al., 2017). Our hypothesis only requires that this  
400 alteration is done by relatively carbon-poor meteoric waters so that subsurface reactions  
401 were carbon-limited not calcium-limited. In the case of the Kwanza basin, this is consistent  
402 with low temperature alteration yielding highly alkaline, Mg, Ca and Si-rich solutions and  
403 may have occurred early during alteration (Teboul et al., 2017). Later fluids, and thus  
404 equilibrium mineral phases in the altered igneous rocks, indicate high-temperature  
405 alteration from fluids rich in CO<sub>2</sub> (Teboul et al., 2017).  
406 The primary difference between the East Kirkton deposit (spatial scale ~100's m) and Pre  
407 Salt systems (~100s km) is scale, and some care is needed before mass transfer processes  
408 can be assumed to apply over 3 orders of magnitude. However, as the scale of the lake  
409 system being considered increases the potential to capture increasing numbers of large  
410 spring systems also increases. It is clearly impossible that a Pre Salt system could be fed by a  
411 single point source, as appears to be the case in East Kirkton. However, we see no reason

412 why multiple sources cannot be sufficient to condition a large lake watercolumn chemistry  
413 just as a single source conditions a small one. The primary difference will be multiple,  
414 potentially independently evolving, points of calcium, magnesium and silica supply to the  
415 lake to be active, likely giving rise to complex spatial and temporal variability in sedimentary  
416 facies and early diagenesis.

417 If this hypothesis is correct, the subsurface mass-transfer through pumping of aqueous  
418 solutions described at East Kirkton is capable of acting over scales of hundreds of  
419 kilometres. This is a basin-scale sedimentary process that has received very scant  
420 investigation, but may be repeated and predictable in basins where rapid extension and  
421 volcanic exhumation is taking place with dominantly low-lying, terrestrial conditions at the  
422 surface. We propose the East Kirkton Limestone as a type system for further investigation of  
423 this new carbon-limited mass transfer and depositional systems associated with subsurface  
424 alkaline rock weathering.

425

## 426 **5. CONCLUSIONS**

427 We hypothesise that the East Kirkton Limestone is the depositional end of a little recognised  
428 mass-transfer process originating with subsurface geochemical alteration of alkaline igneous  
429 volcanic rocks, acting through carbon-limited spring systems, which may have been heated  
430 by the reactions themselves, and terminating in potentially basin-scale lacustrine deposition  
431 in which minerals are formed from the mixture of spring water and atmospheric carbon.  
432 Today, this process occurs within exhumed ophiolites but may also be associated with a  
433 specific phase during crustal extension. The East Kirkton lithofacies and mineral assemblages

434 (carbonates, Mg-Si phases, and chalcedony) are so analogous to, and the geological  
435 background so coherent with, the South Atlantic Cretaceous 'Pre-Salt' strata that we  
436 conclude that similar processes are likely to have been acting there. Understanding the  
437 mass-transfer dynamics of hydrochemical systems in the subsurface will be fundamental to  
438 a process-based understanding of the origin of the spherical-radial carbonate phases  
439 recorded both at East Kirkton and in the 'Pre-Salt' deposits, and forms an intriguing new  
440 perspective on both the fate of metal mass remobilisation from extrusive igneous processes  
441 in these contexts and the geothermal significance of alkaline warm and hot springs.

442

443

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452

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616  
617  
618

## 619 **FIGURE CAPTIONS**

620 **Figure 1.** Geological setting of the East Kirkton Limestone Quarry (red square). Limestones  
621 occur interbedded within coeval tuffs and basalt lavas. Location of the studied borehole BH-  
622 3 in the study area (modified from Cameron et al, 1998).

623 **Figure 2.** Main facies types. A) Spherulitic carbonates affected by different scales of soft-  
624 sediment deformation. Hammer for scale. B) Spherulitic components are embedded in  
625 organic-rich muddy matrices displaying floatstone to laminite textures. C) Spherulites are

626 composed of fibro-radial calcite generating spherical or elongated particles seen in crossed  
627 Nichols. EDS analysis on carbonate spherulites confirms calcite mineralogy (Cc: calcite, Mgc:  
628 low-magnesium calcite). D) Floatstone of volcanic remains (Volc) and spherulites (Spher) in a  
629 serpentine-like amorphous matrix (Am. silicate). Calcite cements crosscut previous  
630 materials. Plane polarized light image. E) Calcite pseudomorphs [Cal and arrows] replacing  
631 former amygdaloidal textures [Am] in volcanic rocks. F) Diverse generations of fibroradial/  
632 spherulitic chalcedony [FSC] and drusy mega-quartz cements [DM] as cavity-filling minerals.  
633 Dolomite rhombs [D] forming tiny rims around the edge of the cavities.

634 **Figure 3.** Borehole BH3 sedimentary log. A) Solid lines show the vertical distribution of the  
635 main sedimentologic features. Cross references to figures are written in the log. Key. Sh:  
636 Shale, C: Carbonates, V: volcanics.

637 **Figure 4.** A) Spherulites are composed of fibro-radial calcite generating spherical or  
638 elongated particles seen in cross Nichols. B) Volcanic remains (Volc) and spherulites (Spher)  
639 produce a floatstone texture made of clay matrix (Mg/Al clay). Calcite cements (Cem)  
640 crosscut previous materials. Plane polarized light image.

641 **Figure 5.** A) Thin-section of altered basaltic rock (thin section in plane polarised light). B)  
642 Composition maps showing abundance of Ca, Mg, Fe, Al, K elements within the white  
643 square on A. C) XRD analysis reveal calcite mineralogy (Cc) for the products filling cavities  
644 within altered igneous rocks.

645 **Figure 6.** Carbon Preference Indices of n-alkanes from the East Kirkton limestone. Equal  
646 concentrations of odd- and even- alkanes (CPI = 1) indicate full thermal maturity. It is these

647 measurements reflect likely liquid hydrocarbons observed in thin section to have migrated  
648 into the pore space, and that these derive from the adjacent West Lothian Oil Shale  
649 Formation.

650 **Figure 7.** Compilation of Sr isotope data. EK Lst indicates whole rock and HNO<sub>3</sub>-soluble  
651 fractions of 5 carbonate-rich samples from the East Kirkton Limestone Member. EK leachate  
652 / whole rock indicate whole rock and HNO<sub>3</sub>-soluble fractions of 3BH1 volcanoclastic samples.  
653 Visean Seawater data taken from (Veizer et al., 1999), hydrothermal data taken from  
654 (Palmer and Edmond, 1989) Midland Valley Volcanic series data taken from (Smedley,  
655 1986).

656 **Figure 8.** Theoretical evolution of the solid mineral assemblage produced by natural  
657 hyperalkaline waters from serpentinization during ingassing of CO<sub>2</sub>. Note log scale on solid  
658 concentration axis, and linear scales otherwise. As ingassing is a progressive process, the X  
659 axis can also be read qualitatively as time or distance from source, making vertical sections  
660 of the diagram predictions of the mineral assemblage at specific water pH levels.

661

662 **Figure S1.** Facies types and stratigraphic features of the East Kirkton Quarry. A) Laminites  
663 display a flat-tabular bedding in outcrop. B) Laminites are composed of an alternation of  
664 carbonate-rich (lighter) and organic-rich laminae (darker) and are commonly displaying soft-  
665 sediment deformation features (creeping and micro-folding of laminae). C) Plant remains  
666 are common in the organic-rich intervals of laminites. D) Greenish to dark orange tuff  
667 characterised by a pyroclastic texture with mm-thick angular to subangular lapilli clasts. E)

668 Layered beds formed by an alternation of nodular to tabular limestone beds with organic-  
669 rich black clay. Slumps were present. F) Thin section of a spherulitic biohermal carbonate  
670 sample displaying the sequential stacking of mm-thick botryoidal calcite fans.

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## SUPPLEMENTARY MATERIAL

### PHREEQC MODELLING OF SOLUTION AND MINERAL ASSEMBLAGE COMPOSITION

A simple thermodynamic equilibrium model of reactions between likely spring-water solutions arising from meteoric water serpentinization of alkali igneous rocks was created using PHREEQC Version 3.1.7. Solution composition was drawn from Stanger (1986), who report a large number of springwater compositions from the Oman Mountains. The specific site used was Jalah Spring (site 69 of Stanger, 1986), where waters rise from the middle Harzburgite of the ophiolite series (Dewandel et al., 2005). These rocks and the purely meteoric waters interacting with them provide a close match to the system inferred for East Kirkton, and therefore the solutions produced should be similar in composition. As iron and aluminium composition of these waters are not reported by Stanger 1986, we use representative values for the same region taken from Dewandel et al., (2005). Composition of the initial solution used for the model is shown in Table S1.

This initial solution was allowed to equilibrate with the minerals identified within the East Kirkton Limestone deposit (calcite, dolomite, Mg-smectite, chalcedony). In addition, the high initial pH makes it very likely that Mg-Si phases would be stable under the anticipated conditions of the experiment, so equilibration with a representative mineral (sepiolite) was also permitted (Tosca and Wright, 2015). The charge balance in solution was allowed to freely equilibrate within the parameterization of PHREEQC, and constraint of mineral stabilities was taken from the Laurence Livermore National Laboratory database (lnl.dat).

Once equilibrium between the initial solution and the permitted solid phases has occurred, reaction with gaseous CO<sub>2</sub> was incrementally achieved by sequentially adding 0.01 moles of CO<sub>2(g)</sub> and calculating the new equilibrium point, including deposition (dissolution) of solid phases. This addition of CO<sub>2(g)</sub> was continued until calcite became soluble (the abundant calcite present at East Kirkton demonstrates this threshold as not exceeded) or dissolved carbon content of the water reached 1M.

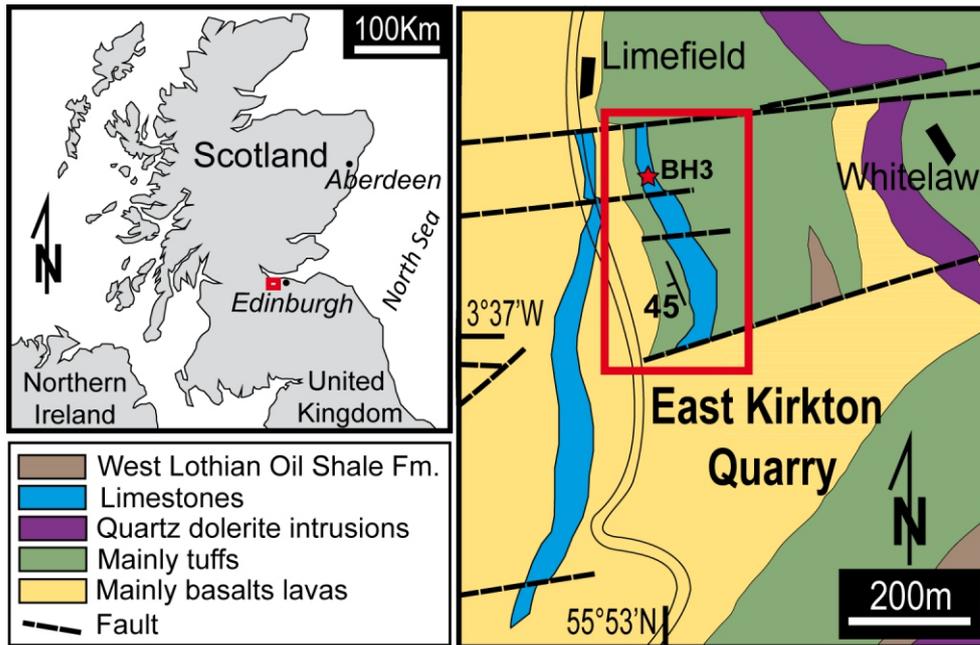
Temperature	34°C
pH	11.4
Al	0.05
Ca	1.530
Cl	11.17
Fe	4x10 <sup>-5</sup>
K	0.430
Mg	0.0017
Na	12.706
S	0.081
Si	0.568

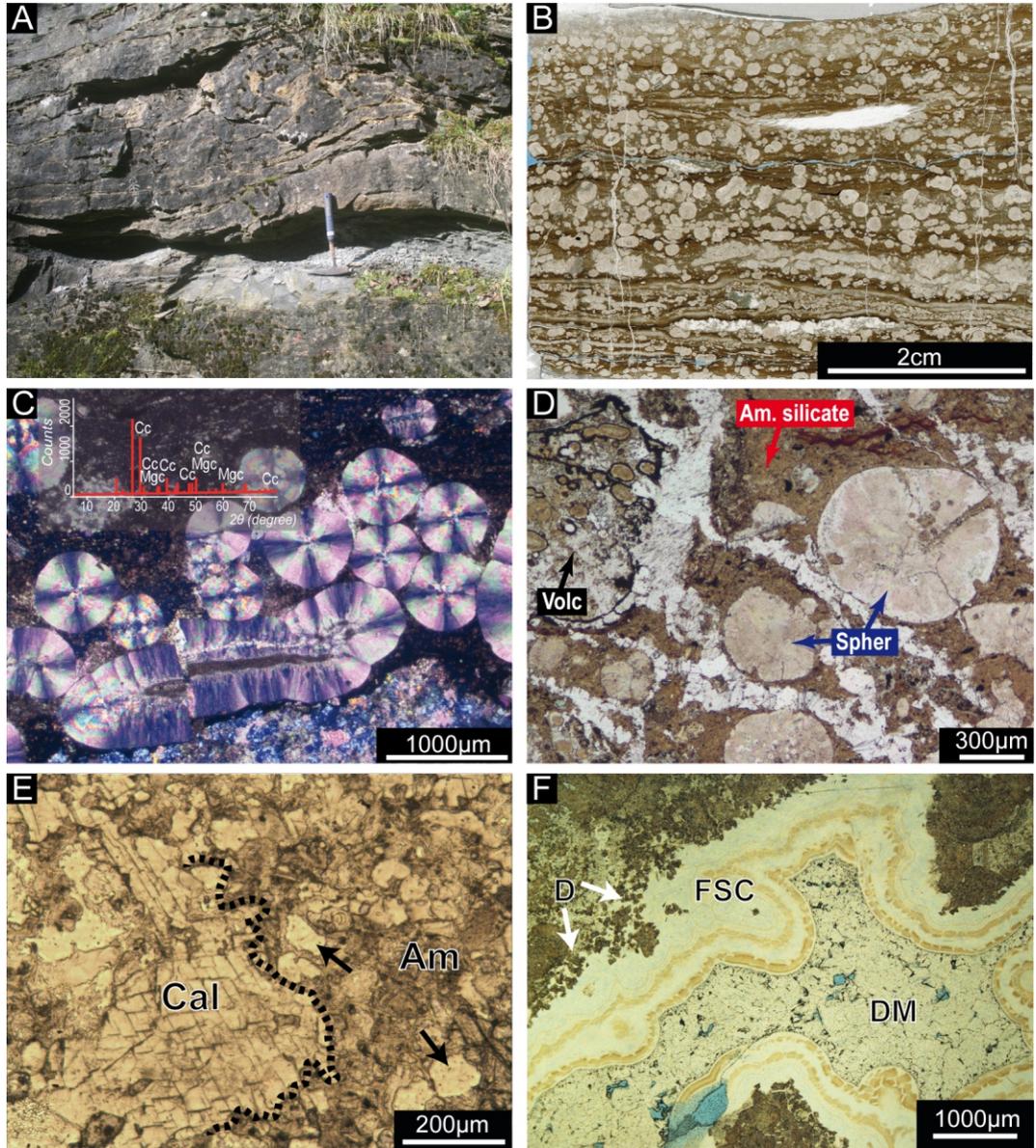
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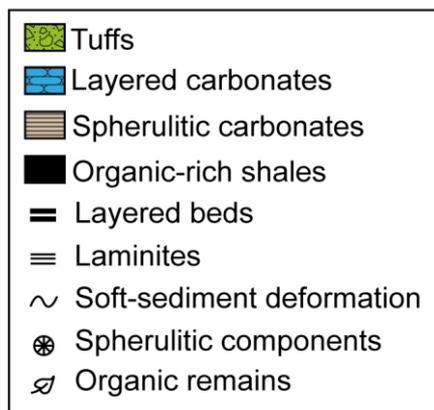
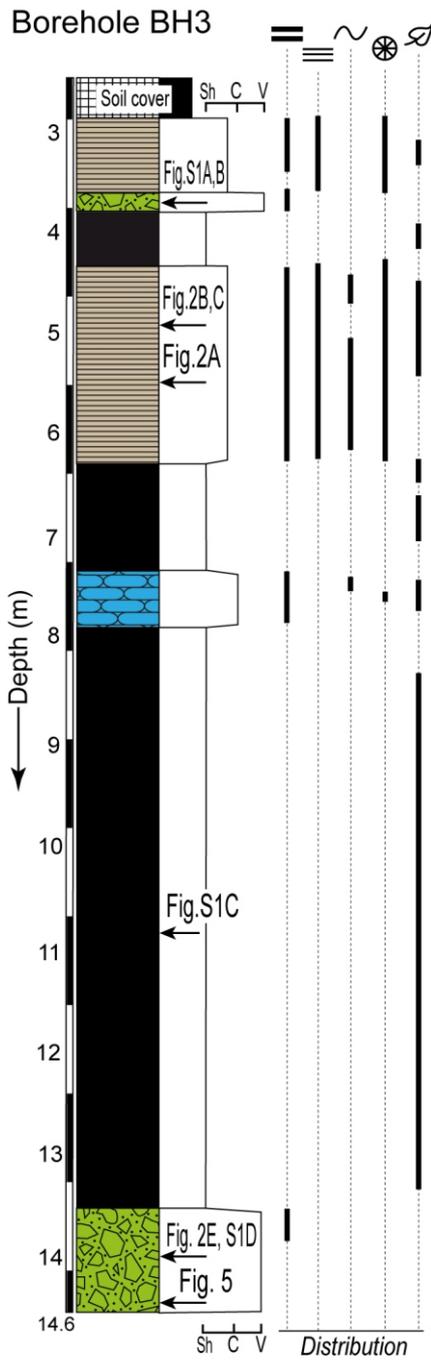
Table S1. Composition of initial solution used for modelling. All concentrations are given in millimoles.

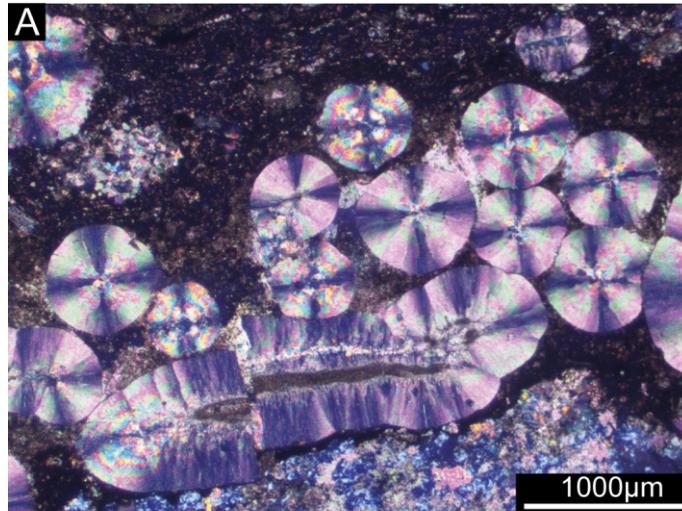
Table 1. Strontium isotope data used in this study. Position of samples shown in Figure 3. Results summarised in Figure 7.

Lab No	Sample Name	Sr 87/86	% Std Error	Abs error
H639	BGS 1	0.749678	0.0013	9.74581 x 10 <sup>-6</sup>
H640	BGS2	0.766026	0.0013	9.95834 x 10 <sup>-6</sup>
H641	EK 0	0.706511	0.0012	8.47813x 10 <sup>-6</sup>
H642	EK 3	0.706817	0.0014	9.89544 x 10 <sup>-6</sup>
H643	EK 6	0.70685	0.0015	1.06028 x 10 <sup>-5</sup>
H644	EK 25	0.70764	0.0013	9.19932 x 10 <sup>-6</sup>
H645	EK 30	0.706706	0.0016	1.13073 x 10 <sup>-5</sup>
H646	BGS 1WR	0.707575	0.0015	1.06136 x 10 <sup>-5</sup>
H647	BGS 2WR	0.708487	0.0015	1.06273 x 10 <sup>-5</sup>
H639 leachate	BGS 1 L	0.706418	0.0017	1.20091 x 10 <sup>-5</sup>
H640 leachate	BGS 2 L	0.706517	0.0014	9.89124 x 10 <sup>-5</sup>









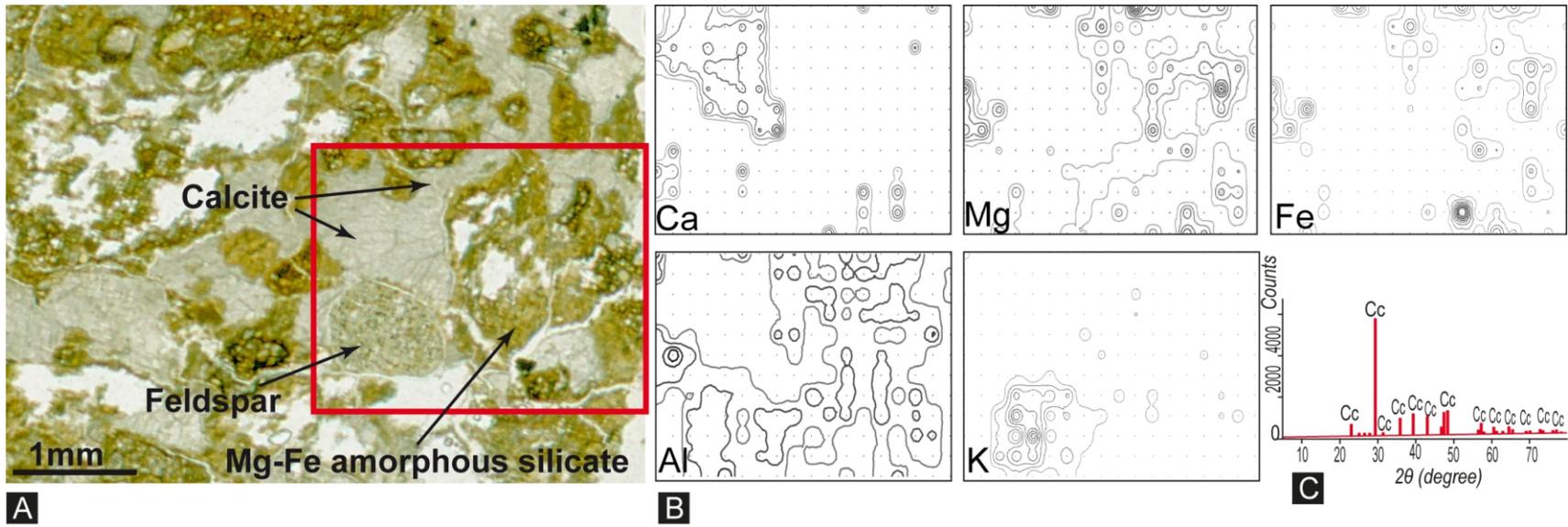


Figure 6

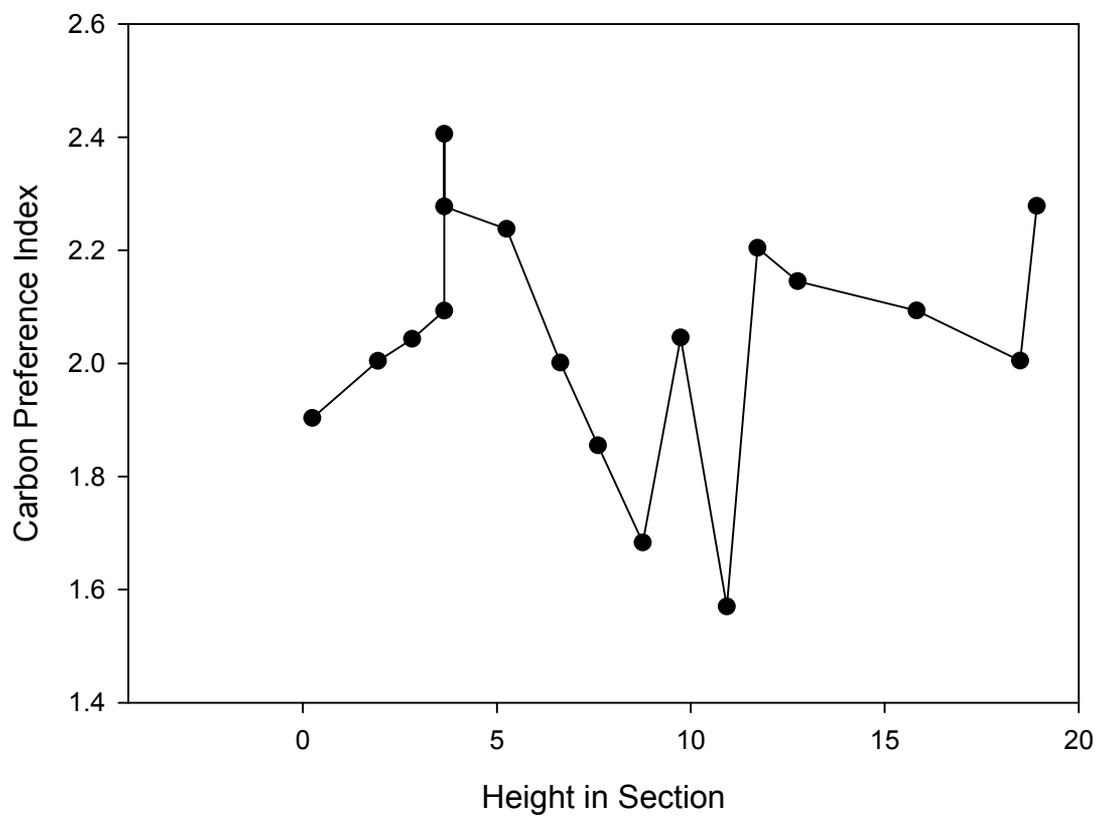


Figure 7

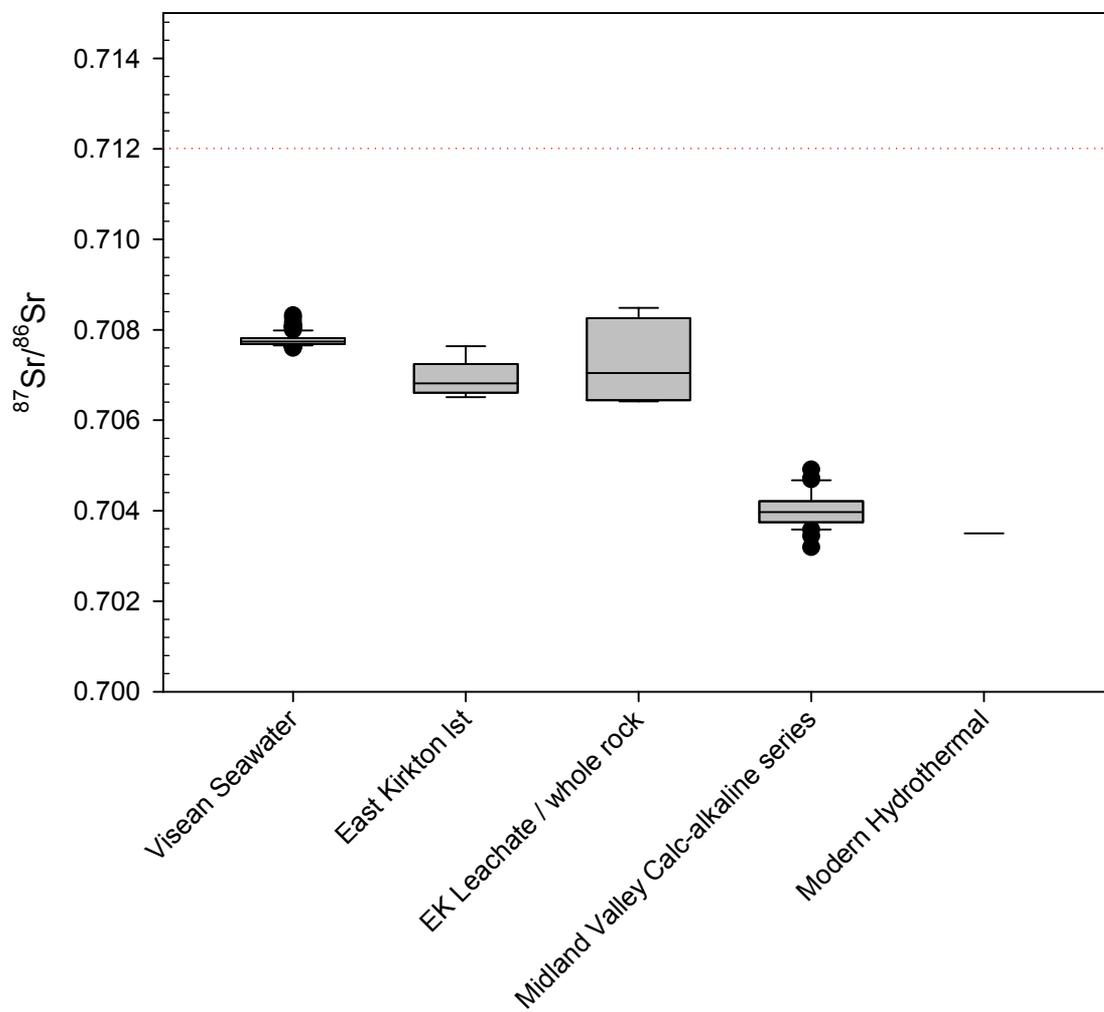


Figure 8

