

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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5 Mike Rogerson¹, Ramon Mercedes-Martín¹, Alexander T. Brasier², Rona A.R. McGill³, Tim J. Prior⁴,
6 Hubert Vonhof⁵, Simon M. Fellows⁴, John J. G. Reijmer⁶, Erin McClymont⁷, Ian Billing^{8,9}, Anna,
7 Matthews⁸ and Martyn Pedley¹
8

- 9 *1. Department of Geography, Environment and Earth Sciences, University of Hull,*
10 *Cottingham Road, Hull, UK. HU6 7RX. Tel. +44 (0)1482466051. m.rogerson@hull.ac.uk;*
11 *r.mercedes@hull.ac.uk; h.m.Pedley@hull.ac.uk*
12 *2. School of Geosciences, Meston Building, University of Aberdeen, Old Aberdeen, Scotland,*
13 *UK. AB24 3UE. Tel. +44(0)1224273449. a.brasier@abdn.ac.uk*
14 *3. Scottish Universities Environmental Research Centre (SUERC), Rankine Avenue, East*
15 *Kilbride G75 0QF. Tel. +44(0) 01355270158. Rona.McGill@glasgow.ac.uk*
16 *4. Department of Chemistry, University of Hull, Cottingham Road, Hull, UK. HU6 7RX. Tel.*
17 *+44(0)1482466389. t.prior@hull.ac.uk; s.m.fellows@hull.ac.uk*
18 *5. Max Planck Institute of Chemistry, Hahn-Meitnerweg 1, 55128, Mainz Germany. Tel*
19 *+4961313056605. hubert.vonhof@mpic.de*

20 6. Faculty of Earth and Life Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1085,
21 1081HV, Amsterdam, The Netherlands. 1081HV. Tel. +31 20 59 87360. h.b.vonhof@vu.nl;
22 j.j.g.reijmer@vu.nl

23 7 Department of Geography , Durham University , Lower Mountjoy , South Road, Durham ,
24 DH1 3LE, UK

25 8 BP Exploration - Integrated Subsurface Description & Modelling, Bldg H, Desk W172
26 Chertsey Road, Sunbury on Thames, TW16 7LN

27 9 University of Derby, Kedleston Road , Derby, DE22 1GB

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 CaCO₃, SiO₂, 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 CO₂ 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 SiO₂ 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 CaCO₃ 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. 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 HNO_3 . Analysis follows standard procedures (Henderson et al., 1994; Pin et al.,
166 1994) with multiple 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 α -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 μ 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 CaCO₃ 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

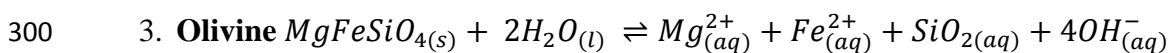
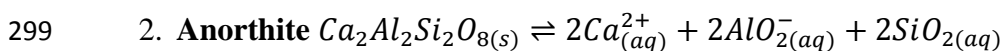
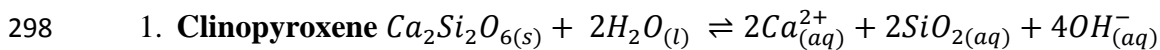
271 **4. DISCUSSION**

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

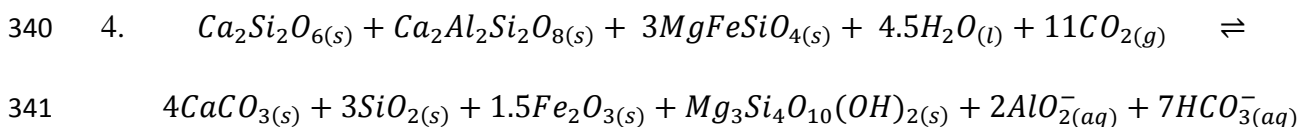
324 description occur today within exhumed ophiolites, for example the Somaïl Ophiolite in
 325 Oman (Matter and Kelemen, 2009). Springs fed from carbon-limited reactions in the
 326 subsurface have led to the deposition of an estimated 10^7 m³ of carbonate on the surface,
 327 covering an area of ~200,000 m², 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_{2(g)} 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 CO₂ 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; CaCO_3 phases precipitate in almost
365 stoichiometric balance with the ingassing of carbon dioxide; and SiO_2 phases increase in
366 insolubility as pH falls (Fig. 8). Indeed, by allowing the system to achieve equilibrium with
367 excess 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 ~ 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 ~ 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 CO₂ (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

453 **REFERENCES CITED**

454 Arp, G., Helms, G., Karlinska, K., Schumann, G., Reimer, A., Reitner, J., and Trichet, J., 2012,
455 Photosynthesis versus exopolymer degradation in the formation of microbialites on the

456 atoll of Kiritimati, Republic of Kiribati, Central Pacific: Geomicrobiology Journal, v. 29, no.
457 1, p. 29-65.

458 Bahniuk, A.M., Anjos, S., França, A. B., Matsuda, N., Eiler, J., McKenzie, J. A., and
459 Vasconcelos, C., 2015, Development of microbial carbonates in the Lower Cretaceous
460 Codó Formation (north-east Brazil): Implications for interpretation of microbialite facies
461 associations and palaeoenvironmental conditions: Sedimentology, v. 62, no. 1, p. 155-
462 181.

463 Bertani, R.T., and Carozzi, A.V., 1985. Lagoa Feia Formation (Lower Cretaceous) Campos
464 Basin, offshore Brazil: rift valley type lacustrine carbonate reservoirs – II: Journal of
465 Petroleum Geology, v. 8, no. 2, p. 199-220.

466 Braissant, O., Cailleau, G., Dupraz, C., and Verrecchia, E.P., 2003. Bacterially induced
467 mineralization of calcium carbonate in terrestrial environments: the role of
468 exopolysaccharides and amino acids: Journal of Sedimentary Research, v. 73, p. 485-490.

469 Cameron, I. B., Aitken, A. M., Browne, M. A. E., Sepsenson, D. (1998). Geology of the Falkirk
470 district: memoir for 1: 50 000 geological sheet 31E (Scotland). London, The Stationery
471 Office. 106pp.

472 Casado, A.I., Alonso-Zarza, A. M., and La Iglesia, A., 2014. Morphology and origin of dolomite
473 in paleosols and lacustrine sequences. Examples from the Miocene of the Madrid Basin:
474 Sedimentary Geology, v. 312, p. 50-62.

475 Chaboreau, A.C., Guillocheau, F., Robin, C., Moulin, M., Aslanian, D., 2013. Paleogeographic
476 evolution of the central segment of the South Atlantic during the Early Cretaceous times :
477 paleotopographic and geodynamic implications. Tectonophysics 604, 191-223.

478 Clarkson, E.N.K., Milner, A.R., and Coates, M.I., 1993. Palaeoecology of the Viséan of East
479 Kirkton, West Lothian, Scotland: Transactions of the Royal Society of Edinburgh: Earth
480 Sciences, v. 84, p. 417-425.

481 Dewandel, B., Lachassagne, P., Boudier, F., Al-Hatali, S., Ladouche, B., Pinault, J.-L., Al-
482 Suleimani, Z., 2005. A conceptual model of ophiolite hard-rock aquifers in Oman based
483 on a multiscale and a multidisciplinary approach. Hydrogeology Journal 13, 708-726.

484 Dias, L.J., 1998, Análise sedimentológica e estratigráfica do Andar aptiano em parte da
485 margem leste do Brasil e no platô das Malvinas: considerações sobre as primeiras
486 incursões e ingressões marinhas do oceano Atlântico Sul Meridional [Ph.D. thesis]: Brazil,
487 Universidade Federal do Rio Grande do Sul, 411p.

488 Dorobek, S., Piccoli, L., Coffey, B. and Adams, A., 2012. Carbonate rock-forming processes in
489 the Presalt “sag” successions of Campos Basin, offshore Brazil: evidence for seasonal,
490 dominantly abiotic carbonate precipitation, substrate controls, and broader geologic
491 implications: AAPG Hedberg Conference “Microbial Carbonate Reservoir
492 Characterization” Abstracts. Houston Texas.

493 Goodacre, I.R., 1999. Microbial carbonates in lacustrine settings: an investigation into the
494 Carboniferous East Kirkton Limestone [Ph.D. thesis]: Scotland, University of Aberdeen,
495 253p.

496 Guido, D.M., Campbell, K.A., 2011. Jurassic hot spring deposits of the Deseado Massif
497 (Patagonia, Argentina): Characteristics and controls on regional distribution: Journal of
498 Volcanology and Geothermal Research, v.203, 35-47.

499 Henderson, G., Martel, D., O'Nions, R., Shackleton, N., 1994. Evolution of seawater $^{87}\text{Sr}/^{86}\text{Sr}$
500 over the last 400 ka: the absence of glacial/interglacial cycles: *Earth and Planetary*
501 *Science Letters*, v.128, 643-651.

502 Hövelmann, J., Austrheim, H., Beinlich, A., and Anne Munz, A., 2011. Experimental study of
503 the carbonation of partially serpentinized and weathered peridotites: *Geochimica et*
504 *Cosmochimica Acta*, v.75, p. 6760-6779.

505 Jones, B., Renaut, R.W., 2010. Calcareous Spring Deposits in Continental Settings.
506 *Sedimentology*, v.61, 177-224.

507 Karner, G.D., Driscoll, N.W., Barker, D.H.N, 2003. Syn-rift region subsidence across the West
508 African continental margin; the role of lower plate ductile extension, In: Arthur, T.J.,
509 MacGregor, D.A.S., Cameron, N.R. (Eds.), *Geological Society of London, Special*
510 *Publications* 207, 105-129

511 Kelemen, P.B., Matter, J., 2008. In situ carbonation of peridotite for CO₂ storage.
512 *Proceedings of the National Academy of Sciences*, v.105, 17295-17300.

513 Matter, J.M., Kelemen, P.B., 2009. Permanent storage of carbon dioxide in geological
514 reservoirs by mineral carbonation. *Nature Geoscience*, v.2, 837-841.

515 McGill, R.A.R., 1994. *Geochemistry and petrography of a Lower Carboniferous, lacustrine,*
516 *hot spring deposit: East Kirkton, Bathgate, Scotland [Ph.D. thesis]: Scotland, University of*
517 *Glasgow*, 173p.

518 McGill, R.A.R., Hall, A.J., Fallick, A. E., and Boyce, A. J., 1994. The paleoenvironment of East
519 Kirkton, West Lothian, Scotland: stable isotope evidence from silicates and sulphides:
520 *Transactions-Royal Society of Edinburgh: Earth Sciences* v. 84, p. 223-237.

521 Mercedes-Martín, R., Rogerson, M., Brasier, A. T., Vonhof, H. B., Prior, T. J., Fellows, S. M.,
522 Reijmer, J.J.G., Billing, I., Pedley, H. M., 2016. Growing spherulitic grains in saline,
523 hyperalkaline lakes: experimental evaluation of the effects of Mg-clays and organic acids.
524 *Sedimentary Geology* v. 335, p. 93-102

525 Monaghan, A.A., and Parrish, R.R., 2006. Geochronology of Carboniferous-Permian
526 magmatism in the Midland Valley of Scotland: Implications for regional tectonomagmatic
527 evolution and the numerical time scale: *Journal of the Geological Society* v.163, p. 15-28.

528 Moreira, J.L.P., Madeira, C.V., Gil, J.A., Machado, M.A.P., 2007. Bacia de Santos. *Boletim de*
529 *Geociencias da Petrobras* 15, 531-549.

530 Moulin, M., Aslanian, D., Olivet, J., Contrucci, I., Matias, L., Geli, L., Klingelhoefer, F., Nouze,
531 H., Rabineau, M., Labails, C., Rehault, J., Unternehr, P., 2005. Geological constraints on the
532 evolution of the Angolan margin based on reflection and refraction seismic data (ZaiAngo
533 Project). *Geophysical Journal International* 162, 793-810.

534 Müntener, O., 2010. Serpentine and serpentinization: a link between planet formation and
535 life: *Geological Society of America*, v. 38, no. 10, p. 959-960.

536 Palmer, M.R., Edmond, J.M., 1989. The Strontium Isotope Budget of the Modern Ocean.
537 *Earth and Planetary Science Letters* 92, 11-26.

538 Parkhurst, D.L., and Appelo, C A.J., 1999. User's guide to PHREEQC (Version 2): A computer
539 program for speciation, batch-reaction, one-dimensional transport, and inverse
540 geochemical calculations. 312 p.

541 Pentecost, A., 2005. *Travertine*. Springer, Berlin.

542 Pin, C., Briot, D., Bassin, C., Poitrasson, F., 1994. Concomitant separation of strontium and
543 samarium-neodymium for isotopic analysis in silicate samples, based on specific
544 extraction chromatography. *Analytica Chimica Acta* v. 298, 209-217.

545 Rangel, H.D., Martins, F.A.L, Esteves, F.R., Feijo, F.J., 1994. Bacia de Campos. *Boletim de*
546 *Geosciencias da Petrobras* 8, 203-217.

547 Read, W.A., Browne, M.A.E., Stephenson, and D. Upton, B.J.G., 2002. Carboniferous, *in*
548 Trewin, N. H., ed., *The Geology of Scotland*, 4th. Geological Society, London, p. 251–300.

549 Renaut, R.W., Owen, R.B., Jones, B., Tercelin, J.J., Tarits, C., Ego, J.K., Konhauser, K.O., 2013.
550 Impact of lake-level changes on the formation of thermogene travertine in continental
551 rifts: Evidence from Lake Bogoria, Kenya Rift Valley. *Sedimentology*, v.60, 428-468.

552 Rogerson, M., Pedley, M., Kelham, A. and Wadhawan, J., 2014, Linking mineralisation
553 process and sedimentary product in terrestrial carbonates using a solution thermodynamic
554 approach: *Earth Surface Dynamics* v. 2, p. 197-216.

555 Rolfe, W.D.I., Durant, G.P, Baird, W. J., Chaplin, C, Paton, R. L., and Reekie, R. J., 1993, The
556 East Kirkton Limestone, Viséan, of West Lothian, Scotland: introduction and stratigraphy:
557 *Transactions of the Royal Society of Edinburgh: Earth Sciences*, v. 84, no. 3-4, p. 177-188.

558 Saller, A., Rushton, S., Buambua, L., Inman, K., McNeil, R., & Dickson, J.T., 2016. Presalt
559 stratigraphy and depositional systems in the Kwanza Basin, offshore Angola. *AAPG*
560 *Bulletin*, 100(7), 1135-1164.

561 Smith, R.A., Stephenson, D. and Monroe, S.K., 1993. The geological setting of the southern
562 Bathgate hills, West Lothian, Scotland: *Transactions of the Royal Society of Edinburgh:*
563 *Earth Sciences*, v. 4, no. 3-4, p.189-196.

564 Smedley, P.L., 1986. The relationship between calc-alkaline volcanism and within-plate
565 continental rift volcanism: evidence from Scottish Palaeozoic lavas. *Earth and Planetary*
566 *Science Letters* 77, 113-128.

567 Stanger, G., 1986. *The hydrogeology of the Oman Mountains*. Open University.

568 Teboul, P.-A., Kluska, J.-M., Marty, N.C.M., Debure, M., Durlet, C., Virgone, A., Gaucher, E.C.,
569 2017. Volcanic rock alterations of the Kwanza Basin, offshore Angola - Insights from an
570 integrated petrological, geochemical and numerical approach. *Marine and Petroleum*
571 *Geology* 80, 394-411.

572 Terra, G.J.S., Spadini, A.R., França, A.B., Sombra, C.L., Zambonato, E.E., Juschaks, L.C.d.S.,
573 Arienti, L.M., Erthal, M.M., Blauth, M., Franco, P.P., Matsuda, N.S., da Silva, N.G.C.,
574 Junior, P.A.M., D'Avila, R.S.F., deSouza, R.S., Tonietto, S.N., dos Anjos, S.M.C., Campinho,
575 V.S. and Winter, W.R., 2010, *Classificação de rochas carbonáticas aplicável às bacias*
576 *sedimentares brasileiras: Bulletin Geoscience Petrobras, Rio de Janeiro, v.18, p. 9-29.*

577 Tosca, N.J., and Wright, V.P., 2015. Diagenetic pathways linked to labile Mg-clays in
578 lacustrine carbonate reservoirs: a model for the origin of secondary porosity in the
579 Cretaceous pre-salt Barra Velha Formation, offshore Brazil, *in* Armitage, P. J., Butcher, A.
580 R., Churchill, J. M., Csoma, A. E., Hollis, C., Lander, R. H., Omma, J. E., and Worden, R. H.,
581 eds., *Reservoir quality of clastic and carbonate rocks: analysis, modelling and prediction:*
582 *Geological Society, London, Special Publications, 435, SP435-1.*

583 Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G.A.F., Diener, A.,
584 Ebner, S., Goddérís, Y., Jasper, T., Korte, C., Pawellek, F., Podlaha, O.G., Strauss, H.,

585 1999. $^{87}\text{Sr}/^{86}\text{Sr}$, ^{13}C and ^{18}O evolution of Phanerozoic seawater. *Chemical Geology* 161,
586 59-88.

587 Verrecchia, E. P., Freytet. P., Verrecchia, K. E., and Dumont, J-L., 1995, Spherulites in calcrete
588 laminar crusts: biogenic Ca CO_3 precipitation as a major contributor to crust formation:
589 *Journal of Sedimentary Research*, v. 65A, no. 4, p. 690-700.

590 Walkden, G. M., Roddy Irwin, J., and Fallick, A. E., 1993, Carbonate spherules and botryoids
591 as lake floor cements in the East Kirkton Limestone of West Lothian, Scotland:
592 *Transactions of the Royal Society of Edinburgh: Earth Sciences*, v. 84, no. 3-4, p. 213-221.

593 Wanas, H. A., 2012. Pseudospherulitic fibrous calcite from the Quaternary shallow lacustrine
594 carbonates of the Farafra Oasis, Western Desert, Egypt: A primary precipitate with
595 possible bacterial influence: *Journal of African Earth Sciences*, v. 65, p. 105–114.

596 Wenner, D.B., and Taylor, H.P., 1971. Temperatures of serpentinization of ultramafic rocks
597 based on $\text{O}18/\text{O}16$ fractionation between coexisting serpentine and magnetite:
598 *Contributions to Mineralogy and Petrology*, v. 32, no. 3, p.165-185.

599 Whyte, M. A., 1993. Scottish Carboniferous fresh-water limestones in their regional setting:
600 *Transactions of the Royal Society of Edinburgh: Earth Sciences*, v. 84, no.3-4, p. 239-248

601 Wood, S. P., Panchen, A. L. and Smithson, T. R., 1985. A terrestrial fauna from the Scottish
602 Lower Carboniferous: *Nature*, v. 314, p. 355-356.

603 Wright, V. P., 2012. Lacustrine carbonates in rift settings: the interaction of volcanic and
604 microbial processes on carbonate deposition, *in* Garland, L. E. Neilson, S. E., Laubach, and

605 Whidden, K. J., eds. *Advances in carbonate exploration and reservoir analysis: Geological*
606 *Society, London, Special Publications 370, p. 39-47.*

607 Wright, V. P., Barnett, A. J., 2015, *An abiotic model for the development of textures in some*
608 *South Atlantic early Cretaceous lacustrine carbonates, in Bosence, D. W. J., Gibbons, K.*
609 *A., le Heron, D. P., Morgan, W. A., Pritchard, T. and Vining, B. A., eds. Microbial*
610 *Carbonates in Space and Time: Implications for Global Exploration and Production:*
611 *Geological Society, London, Special Publications 418, p. 209-219.*

612 Zalán, P.V., Severino, M.D.C.G., Rigoti, C.A., Magnavita, L.P., and Bach, J.A., 2011. *An entirely*
613 *new 3D-view of the crustal and mantle structure of a South Atlantic passive margin-*
614 *Santos, Campos and Espírito Santo basins, Brazil. AAPG, Annual Convention and*
615 *Exhibition, Houston, Abstracts, p. 12.*

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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 HNO₃-soluble
651 fractions of 5 carbonate-rich samples from the East Kirkton Limestone Member. EK leachate
652 / whole rock indicate whole rock and HNO₃-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 CO₂. 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 CO₂ was incrementally achieved by sequentially adding 0.01 moles of CO_{2(g)} and calculating the new equilibrium point, including deposition (dissolution) of solid phases. This addition of CO_{2(g)} 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.

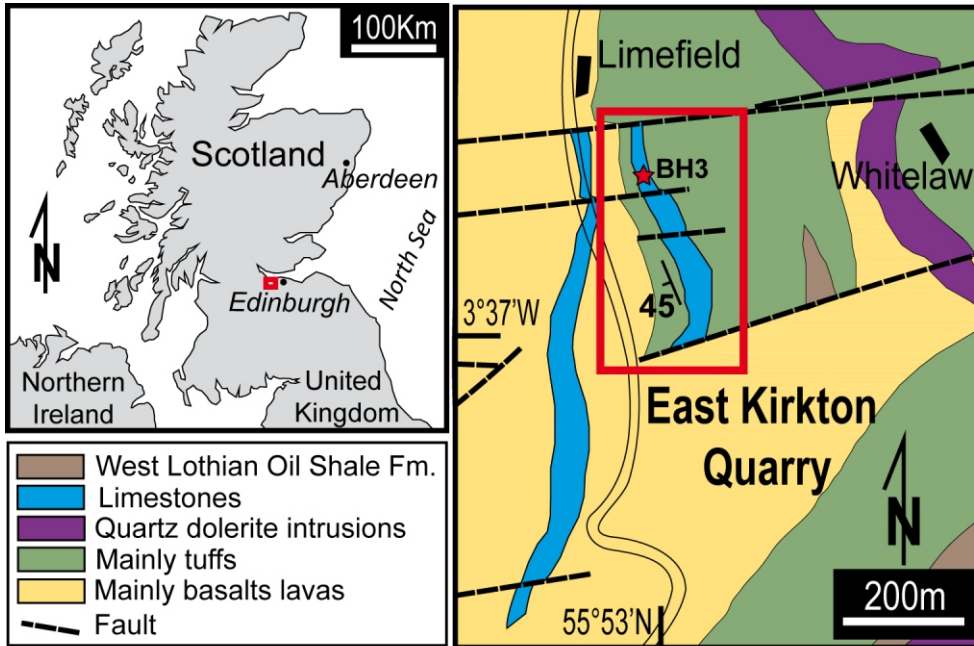
Temperature	34°C
pH	11.4
Al	0.05
Ca	1.530
Cl	11.17
Fe	4x10 ⁻⁵
K	0.430
Mg	0.0017
Na	12.706
S	0.081
Si	0.568

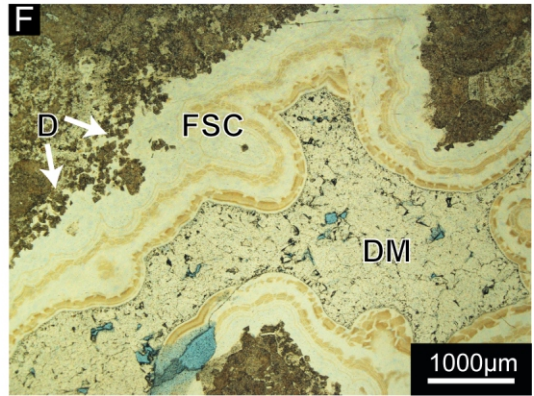
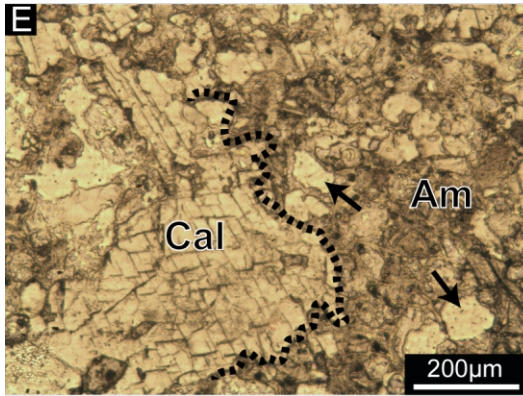
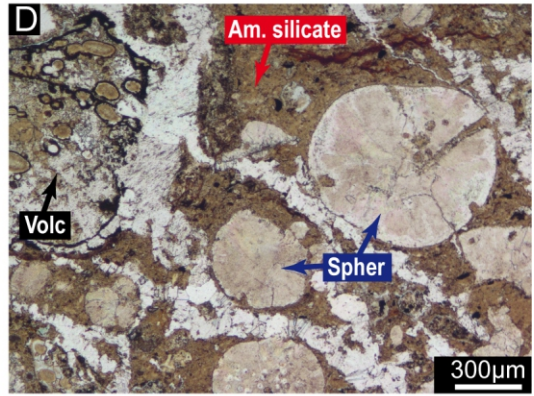
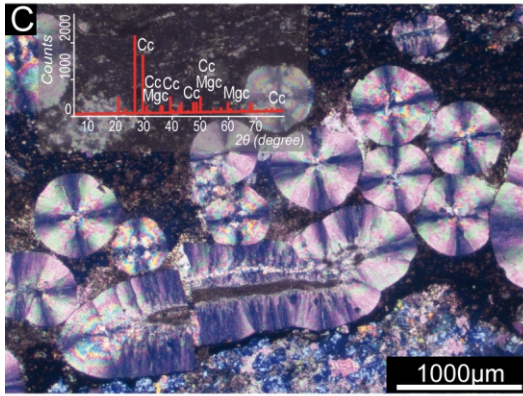
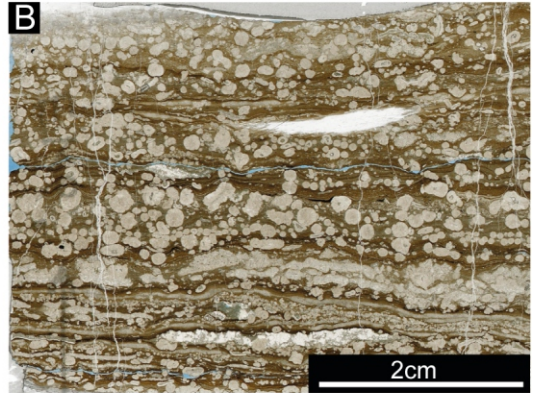
701
702
703
704

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

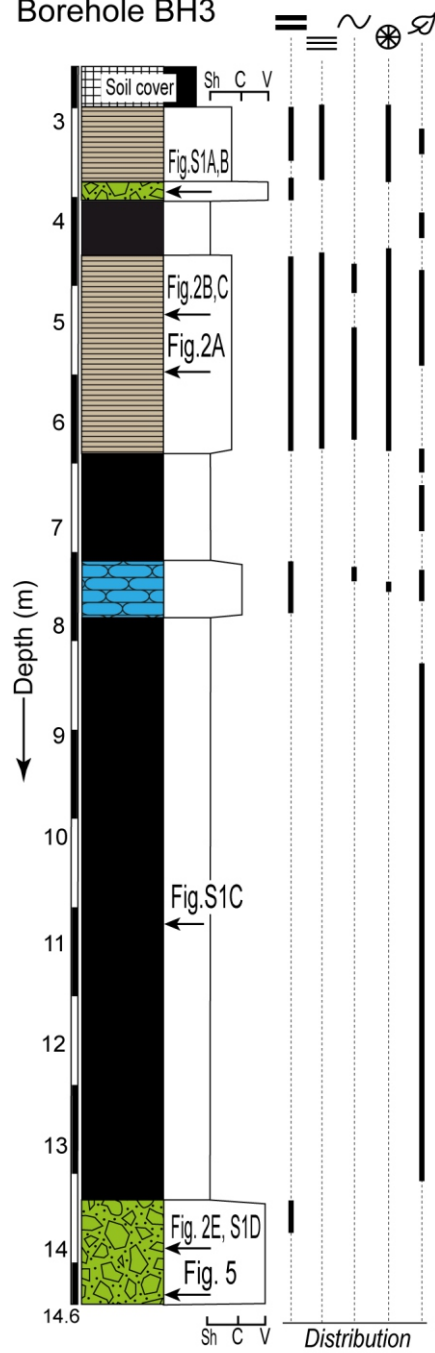
Table 1. Strontium isotope data used in this study. Position of samples shown in Figure 3. Results summarised in Figure 7.










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

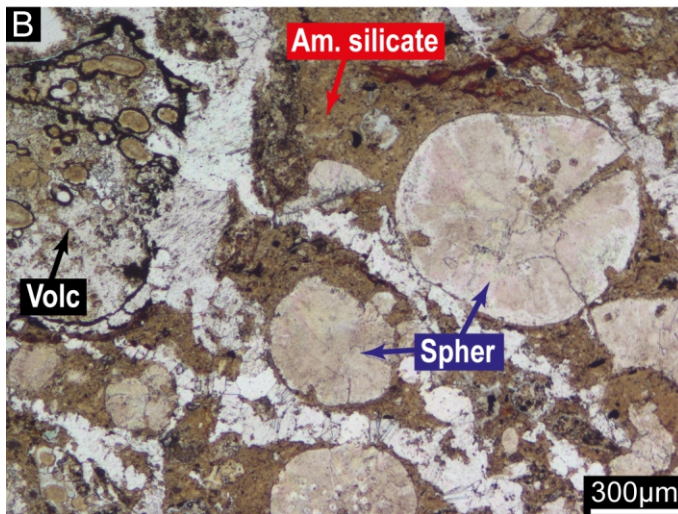
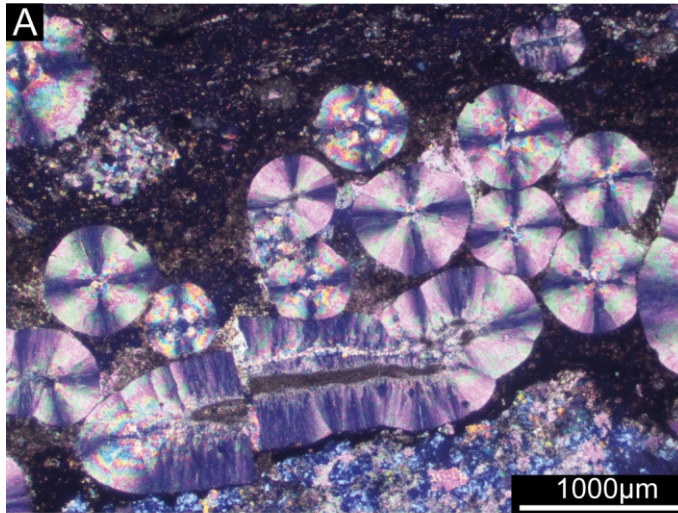


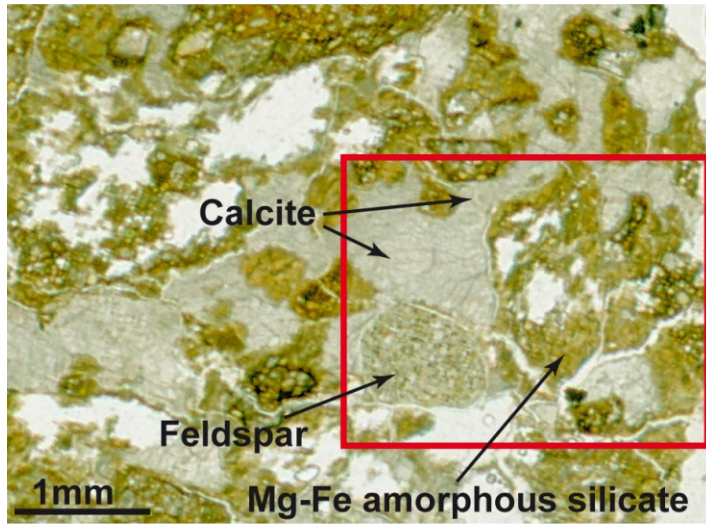


Borehole BH3

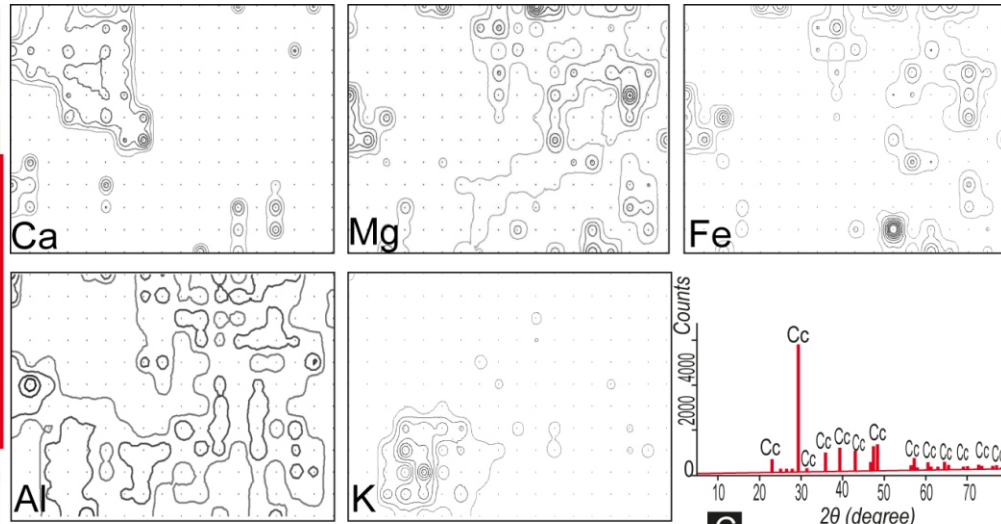


-  Tuffs
-  Layered carbonates
-  Spherulitic carbonates
-  Organic-rich shales
-  Layered beds
-  Laminites
-  Soft-sediment deformation
-  Spherulitic components
-  Organic remains





A



B

C

Figure 6

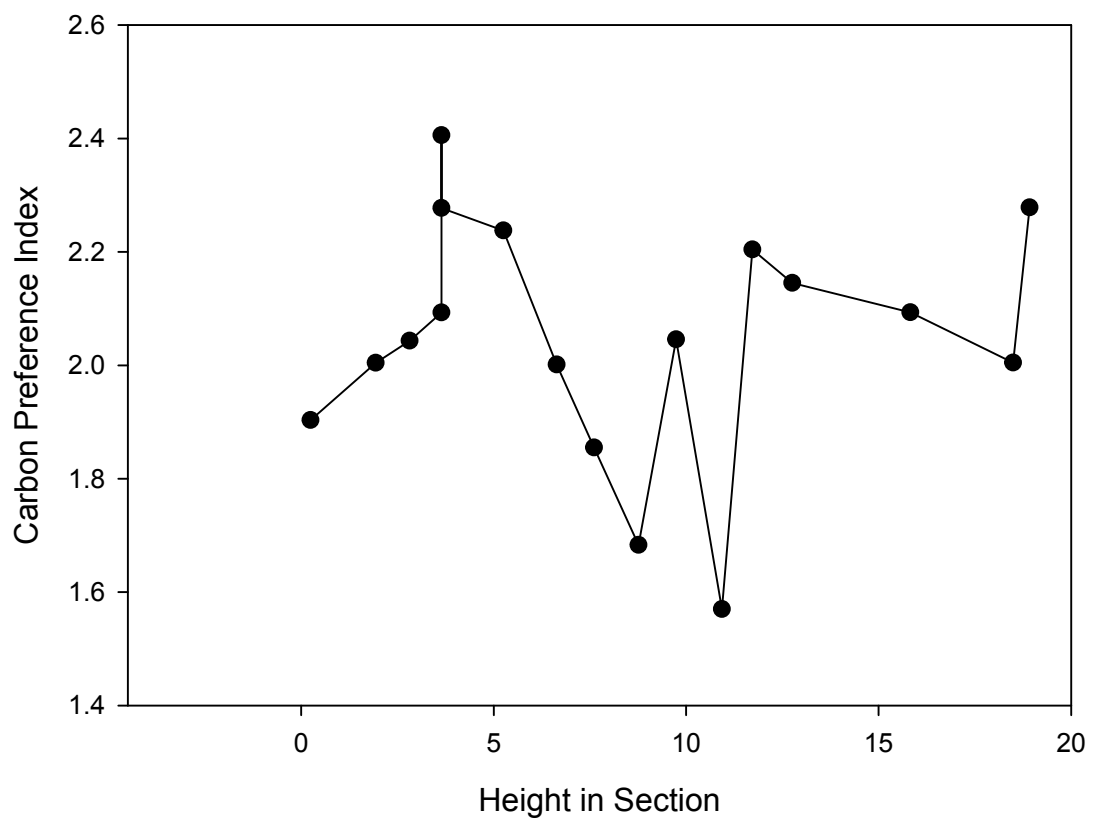


Figure 7

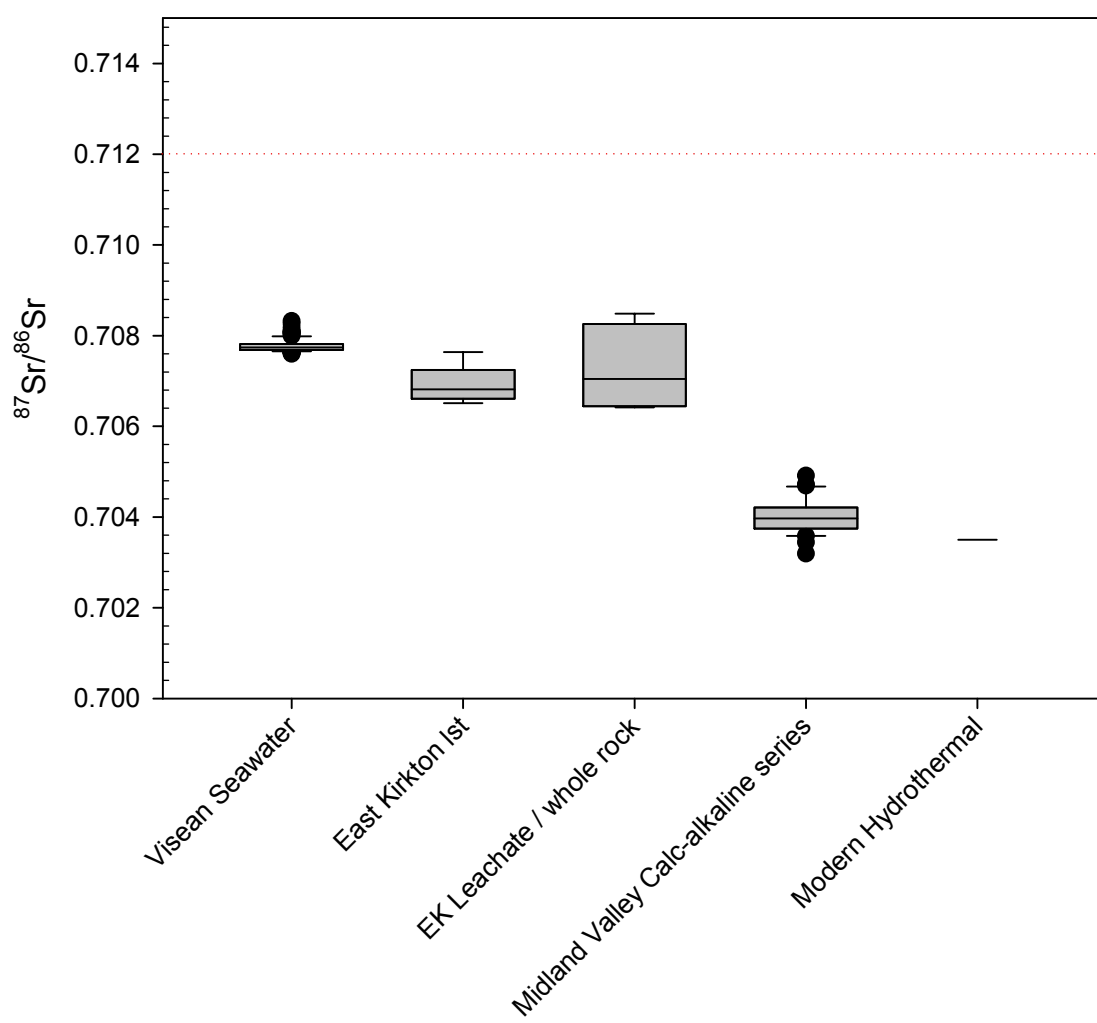


Figure 8

