

A depositional model for spherulitic carbonates associated with alkaline, volcanic lakes

Ramon Mercedes-Martín^{1*}, Alexander T. Brasier², Mike Rogerson¹, John J.G. Reijmer^{3,4}, Hubert
Vonhof⁵ and Martyn Pedley¹

1. School of Environmental Sciences, University of Hull, Cottingham Road, HU6 7RX, Hull, UK. (* Email:
r.mercedes@hull.ac.uk).

2. School of Geosciences, Meston Building, University of Aberdeen, Old Aberdeen, Scotland, UK. AB24 3UE.

3. Faculty of Earth and Life Sciences, VU University of Amsterdam, De Boelelaan 1085, 1081HV Amsterdam,
The Netherlands.

4. College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and Minerals,
Dhahran 31261, Saudi-Arabia

5. Max Planck Institut für Chemie, Hahn-Meitnerweg 1, 55128 Mainz, Germany.

ABSTRACT

The South Atlantic Aptian ‘Pre-salt’ reservoirs are formed by a combination of spherulitic carbonates and Mg-rich clays accumulated in volcanic alkaline lake settings with exotic chemistries. So far, outcrop analogues characterised by metre-thick successions deposited in lacustrine scenarios are elusive so disentangling the genesis of spherulitic carbonates represents a major scientific challenge with business impact. In particular the controls on spatial distribution and the environment of spherulitic facies formation remain poorly constrained, little studied, and hotly debated. To shed light on this conundrum, a spherulitic carbonate-rich, alkaline volcanic lacustrine succession has been analysed at outcrop scale: the Carboniferous East Kirkton Limestone (Scotland). Despite clays being very scarce and limited to layers of amorphous Mg-Si minerals, a diverse array of spherulitic calcitic

1 components were formed, including coated grains, crusts, and build-ups. This setting enables
2 the mechanisms of spherulitic calcite development and the patterns of sediment accumulation
3 to be explored in a geobiological and hydrochemical scenario similar to the ‘Pre-Salt’
4 subsurface occurrences but divorced from clay influence. The integration of logs, borehole
5 data, outcrop photomosaics and petrographic observations collectively allowed the
6 reconstruction of a depositional model for the East Kirkton lacustrine succession. In this
7 model, calcite spherule nucleation took place at the sediment-water interface in the littoral
8 zone, driven by the co-occurrence of 1) high alkalinity, 2) Ca-Mg rich hydrochemistry, and 3)
9 microbial-derived colloidal exopolymeric substances. These environmental conditions
10 permitted the coeval development of spherulitic cementstone build-ups and spherulitic
11 grainstone-packstone within the wave-agitated zone, and the accumulation of floatstones and
12 laminites of spherulitic grains in deeper lake regions by means of downslope reworking. This
13 model is consistent with the previously documented microbial bloom occurrences and
14 highlights the need to better understand the complex ‘microbe-solution’ interactions before
15 any reliable facies model is envisaged.
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39 **Keywords:** spherule, spherulitic, calcite , alkaline, lacustrine, volcanic, Carboniferous, Pre-
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48 **1. INTRODUCTION**

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51 Spherulitic textures from alkaline and volcanic-influenced lacustrine environments have risen
52 to prominence following their discovery in abundance in the Cretaceous subsurface rift lake
53 deposits of the South Atlantic (Terra et al., 2010; Luiz-Dias, 1998; Rezende and Pope, 2015;
54 Wright and Barnett, 2015; Saller et al., 2016). Spherules are defined as components formed
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1 by calcitic fibro-radial spherulitic polycrystals *sensu* Verrecchia et al., 1995. They are well
2 known from a wide variety of carbonate environments including soils, lakes, hyper-saline
3 lagoons, and marine tidal flat settings (Buczynski and Chafetz, 1993; Verrecchia et al., 1995;
4 Braissant et al., 2003; Spadafora et al., 2010; Pueyo et al., 2011; Arp et al., 2012; Wanas
5 2012; Bahniuk et al., 2015). However they rarely contribute the most abundant carbonate
6 grain in a deposit, and relevant outcrop examples of spherulitic limestone are scarce meaning
7 that the petrography of such carbonates is poorly constrained. Discoveries of the South
8 Atlantic ‘Pre-Salt’ hydrocarbon reservoirs of Brazil and Angola (Guardado et al., 2000;
9 Moreira et al., 2007; Carminatti et al., 2008; Cazier, et al., 2014) promoted interest in
10 deciphering the mechanisms capable of producing voluminous spherulitic carbonate deposits
11 in volcanic and lacustrine settings (e.g., Mercedes-Martín et al., 2015; Wright and Tosca,
12 2016), placing the need to build facies models for these systems beyond the ability to
13 understand their mode of formation.

14 Lacustrine depositional models have recently been proposed for the Aptian ‘Pre-Salt’
15 spherule-bearing succession of the Angolan margin of the Kwanza Basin (Saller et al., 2016),
16 and the Brazilian margin of the Campos and Santos Basins (Wright and Barnett, 2015; Sabato
17 Ceraldi and Green, 2016). These models commonly display the occurrence of spherulitic
18 calcitic components intermingled within stevensite clays in deep lake environments. The
19 ‘shrubby’ spherulitic boundstones generally occupied the shallow lake settings where coeval
20 clay minerals were less abundant (Sabato Ceraldi and Green, 2016; Saller et al., 2016).

21 Calcite spherule formation has previously been explained from both end-member
22 perspectives: a biotically-influenced origin (e.g., Verrecchia et al., 1995; Arp et al., 2012),
23 versus an abiotic mechanism (e.g., García-Ruiz, 2000; Wright and Barnett, 2015). In the case
24 of the ‘Pre-Salt’ deposits, the abiotic hypothesis has been built on the assumption that the
25 abundant smectite clays (stevensite) present in very alkaline lakes encouraged spherulitic

1 calcite particle generation in association with ‘clay-gel phases’ (Wright and Barnett, 2015;
2 Tosca and Wright, 2015).

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4 To elucidate the mechanisms forming these carbonates a better understanding of the
5 biochemistry and the source of the carbonate-precipitating waters is required. In the case of
6 volcanic-influenced alkaline lakes, the chemical composition of these waters depends on at
7 least three factors: 1) the balance between runoff and evaporation, commonly related to
8 whether the basin is internally or externally draining; 2) the chemical composition of the
9 basement and coeval extrusive rocks; and 3) the degree to which water can interact with these
10 rocks (Bertani and Carozzi, 1985; Rowe and Brantley, 1993; Romero and Melack, 1996;
11 Carroll and Bohacs, 1999; Bohacs et al., 2000; Narcisi, 2001; Bowser and Jones, 2002;
12 Radke et al., 2002; Kebede et al., 2005; Ayenew, 2008; Bergner et al., 2009; Gierlowski-
13 Kordesch, 2010; Pecoraino et al., 2015; Rogerson et al., 2017). A recurrent issue for these
14 systems is how much carbonate can be deposited, given the mass flux of calcium and
15 magnesium being supplied to surface systems (Renaut and Jones, 1997; Guido and Campbell,
16 2011). In addition, alkaline lakes are favourable habitats for a broad assemblage of microbial
17 communities, including both benthic and planktonic microbes. Biological productivity in
18 these lakes can be extremely high (Melack, 1981; Galat et al., 1990; Jones et al., 1998; Grant
19 and Jones, 2000; Stockner et al., 2000; Kandianis et al., 2008). The organisms in the lakes
20 may control carbonate precipitation directly (Stabel, 1986, Chafetz and Buczynski, 1992, Arp
21 et al., 2001; Dittrich and Obst, 2004; Dupraz et al., 2009; Pedley et al., 2009), or indirectly by
22 stimulating calcite crystal nucleation through the production and / or consumption of
23 extracellular polymeric substances (hereafter EPS) (Trichet and Défarge, 1995; Arp et al.,
24 1999; Dupraz et al., 2009; Decho, 2010). Several researchers have attempted to distinguish
25 these bio-mediating processes from abiotic carbonate precipitating mechanisms (Burne and
26 Moore, 1987; Kelts and Talbot, 1990; Kempe et al., 1991; Merz, 1992; Pedley, 1992; Jones
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1 and Renaut, 1995; Chafetz and Guidry, 1999; Schneider and Le Campion-Alsumard, 1999),
2 but the division remains controversial.
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7 The present study examines a spherule-rich carbonate deposit formed in a volcanic and clay-
8 poor lacustrine setting: the Lower Carboniferous East Kirkton Limestone in Scotland (Rolfe
9 et al., 1993; Walkden et al., 1993). The East Kirkton Limestone displays an abundant
10 assemblage of spherulitic calcite fabrics. Thus, a detailed petrographic study of such
11 components and the sedimentological analysis of the spherule-bearing facies at East Kirkton
12 can 1) help to better constrain the environmental conditions underpinning the formation and
13 accumulation of these carbonates, and 2) provide an analogue case for other spherulitic
14 carbonate occurrences like those in the Cretaceous ‘Pre-Salt’ lakes of the South Atlantic.
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29 **2. GEOLOGICAL BACKGROUND**

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31 Half-grabens and intervening highs in the Midland Valley of Scotland were generated during
32 the Early Carboniferous by N-S oriented fault systems, with a right lateral strike-slip
33 component (Rippon et al., 1996). The Carboniferous strata are divided into the Inverclyde
34 (Tournasian) and Strathclyde (Viséan) Groups (Whyte, 1993; Read et al., 2002; FIG. 1). The
35 Strathclyde Group comprises a varied succession of sedimentary and volcanic rocks,
36 characterised by carbonaceous beds and coals. It is interpreted as largely fluvial and
37 lacustrine in origin but affected by sporadic marine incursions (Browne and Monro, 1989).
38 Basaltic volcanism (basanite type) increased during Strathclyde Group deposition (Whyte,
39 1993; FIG. 1) leaving the Midland Valley divided into a series of semi-enclosed continental
40 basins. They were filled by fluvial, deltaic and lacustrine-lagoonal deposits (Fig. 1, 2A; Read
41 et al., 2002). Sediments of the West Lothian Oil Shale Formation (Upper Viséan) were
42 deposited in a large stratified freshwater lake complex developed under a humid tropical
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1 climate and collectively referred to as Lake Cadell (Greensmith, 1968) (Fig. 2B). The
2 accumulation of planktonic and benthic microorganisms gave rise to oil-shale deposits under
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4 exorheic, meromictic, and deep (50 to 100m) conditions (Loftus and Greensmith, 1988;
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6 Parnell, 1988). The East Kirkton Limestone formed within this lake complex (FIG. 2B, C),
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8 comprising black shales, laminated limestones, tuffaceous clastic carbonates, and massive
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10 limestones all yielding spherulitic calcite textures (Rolfe et al., 1993; Walkden et al., 1993;
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12 Read et al., 2002, FIG. 2B). The East Kirkton Limestone displays well-exposed quarried
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14 faces and relatively undisturbed depositional geometries. Exquisitely preserved skeletons of
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16 amphibians, fishes, plants and ostracods have also been found at this locality (Smithson, 1989;
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18 Clarkson et al., 1993; Rolfe et al., 1993; Scott et al., 1993; Walkden et al., 1993).
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20 Palynological evidence shows that the East Kirkton lake was surrounded by an extensive
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22 woodland dominated by gymnosperms, pteridosperms and, later on, by lycopods (Rolfe et al.,
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24 1993; Scott et al., 1993).
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34 ===== FIGURE. 1 and 2 HEREBOUTS =====
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39 **3. MATERIAL AND METHODS**

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41 Fieldwork including sedimentary logging (sections EK-1 and 2) and sampling at East Kirkton
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43 Limestone Quarry was carried out in August 2014 (Fig. 2C; Fig. 3), with consent of Scottish
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45 Natural Heritage and West Lothian Council. Thirty eight thin sections were examined using
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47 Olympus BH2 and Nikon Microphot FX microscopes, and 45 polished slabs were also
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49 optically studied. Seven of these specimens came from borehole cores named BH-1, BH-2
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51 and BH-3 stored at the British Geological Survey (BGS) at Keyworth, UK. Thin sections
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53 were imaged with a flat-bed scanner, and textures were mapped. Eight cuttings were carbon
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55 coated and imaged by Scanning Electron Microscopy (SEM) with a Zeiss EVO60 at the
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1 University of Hull. False colour Back-Scattered Electron images (BSE) were taken on thin-
2 sections to obtain micro-scale resolution compositional maps enabling delineation of different
3 mineral phases (carbonate, clay, volcanic) and their features. An Oxford Instruments Peliter-
4 cooled type X-Max 80 EDX system was used to determine the abundance of specific
5 elements through Energy Dispersive X-ray Spectroscopy (EDX) in thin-sections and cuttings.
6
7 X-ray powder diffraction data were collected from ground samples mounted in stainless steel
8 sample holders. A PANalytical Empyrean diffractometer operating in Bragg-Brentano
9 geometry with copper $K\alpha_1$ ($\lambda = 1.54060 \text{ \AA}$) and a PIXEL detector was used for data
10 collection. Sediment particle morphologies were described following Blott and Pye (2008).
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12 The term ‘oncoïd’ is used *sensu* Flügel (2004): ‘unattached, rounded, calcareous nodules
13 exhibiting concentric layers and overlapping laminae around a core’.
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15 Photograph-based outcrop panels were annotated to recognise the architectural relationships
16 within the sedimentary succession recorded from field (EK1, 2) and borehole core data (BH-1,
17 2 and 3). Existing BGS borehole log annotations were also integrated to complement the
18 absence of core record from BH-1, 2 and 3. Paleontological and sedimentological
19 descriptions from previous works (Clarkson et al. 1993; Rolfe et al., 1993), and other log
20 observations (illustrated in Goodacre, 1999) were also combined with the new results in this
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51 **4. FACIES DESCRIPTIONS**

52 Six facies have been identified and characterised on the basis of lithology and/or sedimentary
53 attributes. These facies are listed in Table 1, illustrated in Figs. 4, 5 and 6, and their outcrop
54 architecture shown in Fig. 7: (1) Laminites, (2) Spherulitic grainstone-packstone, (3)
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1 Spherulitic cementstone , (4) Volcanic and intraclastic calcareous tuffs, (5) Intraclastic
2 wackestone-floatstone, and (6) Shales.
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10 **4.1. Facies 1: Laminites**

11 Laminites are organised in 5 to 50 cm-thick, dark brown to yellowish, tabular and laterally
12 continuous beds. Laminites are made up of a sub-millimetre alternation of carbonate, organic
13 and silica laminae (Fig. 3, 4; Table 1) packaged into couplets of up to 4 cm-thick carbonate-
14 rich layers alternating with up to 3 cm-thick organic or fine-grained silica-rich layers.
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17 Microscopic deformation of laminae couplets (convoluted) and macroscopic evidence of soft-
18 sediment deformation (slumps) is common in the central region of the quarry, decreasing in
19 abundance towards the SSE (Fig. 3A to D). Laminites yielded a diversity of fossils such as
20 amphibians, scorpions, eurypterids, myriapods, ostracods, plant and wood remains (Wood et
21 al., 1985; Clarkson et al. 1993; Rolfe et al. 1993; Ruta and Clack, 2006). Spherulitic
22 components (see Section 6) were recognised within organic laminae (Fig. 4D, E), the latter
23 pinching out towards the edges of the grains (Fig. 4E). Spherulitic grains were less commonly
24 found in association with carbonate laminae. ‘Spherulitic laminites’ are laminites notably rich
25 in spherulitic components (Fig. 4D, E). The laminite facies was recorded in boreholes BH-1
26 to 3 and in EK-1 and 2 (Fig. 7). This facies is equivalent to the ‘Laminated limestones’ of
27 Rolfe et al. (1993).
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Carbonate laminae (Fig. 4A) are made of 30 µm to 1000 µm-thick pale to dark brown,
wrinkled to flat, continuous micritic to microsparitic calcite bands. Individual sparitic calcite
crystals can be up to 100 µm in diameter, having rhombohedral shapes and mosaic fabrics.
Remains of fish scales are present but scarce. Evidence of micro-faulting and micro-
disruption was also recognised in some intervals. Walkden et al. (1993) recorded average

1 element concentrations of 5920 ppm for Mg, 10962 ppm for Sr, 7585 ppm for Fe, and 387
2 ppm for Mn.
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4 *Organic-rich laminae* (Fig. 4A, B, D, E) are made up of 7 μm to 1500 μm -thick dark brown,
5 wrinkled to undulated, continuous, particulate detritus-rich laminae. Backscatter electron
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7 imaging revealed irregular darker patches of iron oxide minerals up to 50 μm in diameter,
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9 euhedral pyrite crystals 5-6 μm in diameter, and framboidal pyrite aggregates of up to 20 μm
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11 diameter (Fig. 4C). Ostracod carapaces and plant remains were also recorded.
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16 *Silica laminae* (Fig. 4B, D) are composed of up to 350 μm -thick dark brown, spatially
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18 irregular amorphous vitreous silica bands conformably interlayered with carbonate and
19
20 organic laminae. Silica is glassy in cross-polarized light, and laminae show inclusions of
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22 single euhedral and patchy subhedral calcite crystals and cracks filled by calcite (Fig. 4B)
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24 (McGill, 1994).
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36 **4.2. Facies 2: Spherulitic grainstone-packstone**

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38 This facies consists of 5 to 80 cm-thick, grey, spatially discontinuous layers of grainstone-
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40 packstone exhibiting poorly to moderately sorted spherulitic grains (FIG. 5A, see Section 6),
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42 ranging from fine to coarse sand size, and well-rounded to angular texture (Fig. 5B). Sub-
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44 angular volcanic lithoclasts averaging 2 cm in diameter and rare fragments of stacked fans
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46 (see Section 6) averaging 1 cm in diameter were also recognised. In some cases, a finer sub-
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48 centimetre scale alternation of spherulitic grains (coated grains and intraclasts, see Section 6)
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50 was observed. Packstone matrix is composed of red-brown, fine-grained amorphous Mg-Si
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52 phase rich in Mg, Al and Fe, as determined by X-ray diffraction and EDX spot analyses (see
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54 Facies 4). In some cases, millimetre-thick alternations of Spherulitic Crusts (see section 6)
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1 and Mg-Si bands were recognised. Amorphous Mg-Si phases are commonly replaced by
2 ferroan blocky to granular calcite cements following vein-like structures (FIG. 5B). This
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4 facies was identified in the central part of the quarry (BH-2 and EK-1, Fig. 7) being very rare
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7 in the SE part.
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10 11 12 **4.3. Facies 3: Spherulitic cementstone** 13

14 This facies is represented by up to 2 m-thick and 3 m-wide, dark grey, un-fossiliferous
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16 carbonate units with distinctive dome-shaped to lenticular morphologies and limited lateral
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18 continuity towards the SSE of the quarry (FIG. 5C, D, E). According to Clarkson et al., (1993)
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20 this facies extended laterally at least 50 m to the west of BH-2 (Fig. 7). Two main metre-thick
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22 build-up intervals were identified in BH-2 and EK-1, although tiny centimetre-thick layers
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24 were reported interbedded within Facies 1 (EK-1). This facies is sandwiched between Facies
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26 1 and 4 (FIG. 5C, D), and in some outcrops it passes laterally into Facies 2 (seen in BH-2 and
27
28 EK-1, Fig. 7). Spherulitic cementstone encompass a ‘clotted’ carbonate texture formed by
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30 calcite stacked fan fabrics (see Section 6) developing millimetre to centimetre-sized, crackle
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32 to mosaic pack-breccias filled by pale white quartz/chalcedony cements (FIG. 5F). This
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34 facies was only recorded in the NW and central part of the quarry and it is equivalent to the
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41 ‘Massive limestones’ of Muir and Walton (1957) and Rolfe et al. (1993).
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51 **4.4. Facies 4: Volcanic tuffs and intraclastic calcareous tuffs** 52

53 This facies consists of 5 cm to 5 m-thick, green to yellow, nodular and discontinuous beds of
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55 epiclastic tuffs interbedded throughout the entire succession, though more abundant and
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57 thicker units were identified at the top of the sequence (Fig. 7). These deposits can reach up
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1 to 7 m-thick in BH-1 and 3.3 m-thick in BH-2. Volcanic tuffs display a fabric of coarse-
2 grained lapilli clasts (up to 15 mm in diameter) floating in poorly sorted fine-grained
3 vesicular or amygdaloidal ash with shards (FIG. 6A left). Lapilli clasts exhibit a porphyritic
4 fabric of plagioclase, augite, olivine and magnetite phenocrysts (Fig. 6B). Calcite
5 pseudomorphs after olivine are also present. EDX spot analyses of lapilli show abundance of
6 Al, Ti and Ca, and minor amounts of K, Mg and Fe (FIG. 6D). Petrographic and chemical
7 analysis points to a basaltic to basanitic composition. Furthermore, centimetre to decimetre-
8 thick (averaging 20 cm in thickness), greenish to dark grey, heterogeneous layers of
9 intraclastic calcareous tuffs were systematically recorded intercalated within Facies 1 in EK-1
10 and 2, and BH-1, 2 and 3 (Fig. 6A right; Fig. 7). These layers display sharp and erosive basal
11 contacts, normal grading and load casts. Intraclastic calcareous tuffs comprise moderately
12 sorted, poorly rounded, coarse sand to coarse pebble-sized fragments of volcanic tuffs, coarse
13 sand-sized spherulitic grains and intraclastic carbonate laminae (Facies 1) embedded in
14 submillimetre-thick patches of irregularly banded amorphous Mg-Si minerals (kaolinite-
15 serpentine group) as indicated by X-ray diffraction analyses (Fig. 6C). Fine grained intervals
16 are normally made up of well sorted, very fine to medium sand-sized, dark black volcanic ash.
17 Up to 6 m-thick basaltic bodies are reported at the top of BH-1 though such rocks were not
18 stored at Keyworth (borehole annotations are reprinted in Fig. 7). Overall, this facies is
19 equivalent to the Geikie Tuff unit of Rolfe et al. (1993).

4.5. Facies 5: Intraclastic wackestone-floatstone

20 This facies comprises centimetre to decimetre-thick (up to 15 cm-thick) continuous, nodular
21 to tabular wackestone to floatstone layers (Fig. 6E, F) commonly observed in the upper parts
22 of EK-2 and BH-3, but decreasing in abundance towards the NW of the quarry (FIG. 7). In
23 some cases normal graded beds (wackestone grading to floatstone), and macroscopic and
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1 microscopic evidence of soft-sediment deformation was identified (slumps and convolute
2 beds). Carbonate allochems comprise millimetre-sized contorted laminae intraclasts (Facies
3 1), peloids, fish scales, ostracod shells, and very rare spherulitic components floating in a
4 micritic matrix. SEM BSE analyses reveal abundant euhedral pyrite framboids (up to 6 µm in
5 diameter), and kerogenous matter both within laminae intraclasts and the carbonate matrix.
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7 This facies is partially equivalent to the Little Cliff Shale of Rolfe *et al.* (1993).
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17 **4.6. Facies 6: Shales**

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19 This facies is constituted by up to 6 m-thick, blue-grey, laterally variable, organic-rich shales
20 (Fig. 5E). They were recognised in the upper parts of BH-1, BH-3 and EK-2, thinning
21 laterally northwards (Fig. 7). It contains sporadic thin continuous horizons of centimetre-
22 thick ironstone bands, and a wide array of fossiliferous remains such as bivalves
23 (*Curvirimula scotica*), fish scales and skeletons (actinopterygians, acanthodians, and sharks),
24 ostracod shells (*Carbonita*), arthropod cuticles, spores, lycopsids (*Lepidodendron*), and other
25 foliage remains (Rolfe *et al.*, 1993; Clarkson *et al.*, 1993). Shales alternate with Facies 5 as
26 seen in EK-2 (Fig. 6E) though Facies 4 can also be sporadically interbedded within shales
27 (e.g. BH-1). This facies is comparable to the ‘Little Cliff Shale’ described by Rolfe *et al.*
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51 **5. FACIES SUCCESSIONS**

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53 At outcrop and borehole scale, lithofacies are stacked repeatedly, forming metre-thick small-
54 scale, usually asymmetrical cycles (Fig. 7, 8). The East Kirkton sedimentary succession is
55 built by the stacking of these cycles which were distinguished on the basis of their bounding
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1 surfaces and/or abrupt facies changes. Four types were recognised across the carbonate
2 system studied (labelled A, B, C, and D).
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7 **5.1. Type-A Cycle**

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9 The thickness of this asymmetrical cycle varies between 1 and 3 m. It is composed of
10 millimetre to centimetre-thick shaly layers (Facies 6) (FIG. 7, 8), followed by up to 2.5 m-
11 thick spherulitic cementstone build-ups (Facies 3) which is sharply overlain by up to 1 m-
12 thick beds of grainstone-packstone of spherulitic grains (Facies 2). Evidence for paleosols or
13 paleokarst horizons is lacking, despite this cycle was appearing to locally develop on top of
14 an erosional surface (as seen in EK-1). This type of cycle can contain up to 15 cm-thick
15 intraclastic calcareous tuff layers (Facies 4) intercalated within Facies 2, centimetre-thick
16 levels of grainstone-packstone of spherulitic grains (Facies 2) and rare centimetre-thick
17 spherulitic-shaly limestone beds (Facies 6) intermingled within Facies 3. Type-A cycles were
18 exclusively recorded in the NW part of the quarry (EK-1 and BH-2, Fig. 7).
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36 **5.2. Type-B Cycle**

37 This type of cycle is constituted by up to 1.5 m-thick strata bounded by sharp surfaces and
38 forming asymmetrical sequences (Fig. 7, 8). They are constituted by a lower part of up to
39 1.1m-thick spherulitic laminite beds (Facies 1) grading upwards towards up to 40 cm-thick of
40 grainstone-packstone of spherulitic grains (Facies 2). Type-B cycles were only recognised in
41 the central part of the quarry (EK-1) (Fig. 7).
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53 **5.3. Type-C Cycle**

54 These basic accretional units are made up of 1 to 3 m-thick packages bounded by sharp
55 flooding surfaces. This asymmetrical cycle is composed by a lower portion of up to 1 m-thick
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1 (typically <25 cm-thick) organic-rich shales (Facies 6) commonly overlain by up to 2 m-thick
2 upper portion constituted by coarse-grained calcareous tuffs (Facies 4) grading to spherulitic
3 laminites (Facies 1) (Type-C1, Fig. 7, 8). Facies 4 tend to show basal sharp erosional surfaces
4 or undulating contacts due to plastic buckling on top of shale beds. In some cycles, laminites
5 are notably devoid of spherulitic grains defining Type-C2 cycles. Type-C1 cycles were
6 recognised in the NW part of the quarry (BH-2, EK-1 and BH-1) while Type-C2 were
7 identified in the SE region (BH-3 and EK-2) (Fig. 7).
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19 **5.4. Type-D Cycle**

20 These elemental cycles are constituted by up to 6 m-thick strata bounded by sharp facies
21 contrasts or flooding surfaces (Fig. 7, 8). They are organised by a metre-thick lower shale-
22 rich package (Facies 6) or laminites with absence of spherulitic grains (Facies 1) occasionally
23 alternating with centimetre-thick intraclastic calcareous tuff levels (Facies 4), and an upper
24 interval formed by an alternation of intraclastic wackestone-floatstone (Facies 5) and shales
25 (Facies 6). Type-D cycles were preferentially recorded in the upper and SSE part of the
26 quarry (EK-2 and BH-3) (Fig. 7).
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46 **6. PETROGRAPHY OF SPHERULITIC COMPONENTS**

47 Spherulitic components are characterised by a recurrent combination of several crystal fabrics:
48 Fibrous Calcite, Spherulitic Calcite, and Subhedral Silica (Table 2).
49 The Fibrous Calcite (*sensu* Schroeder, 1972; Longman, 1980, or Mazzullo, 1980) (FIG. 9A)
50 consists of needle-like and radially divergent crystals with length-to-width ratio of ~9.2:1
51 (>6:1 according to Folk, 1965) and typically average lengths and widths of ~83 µm and ~9
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µm respectively. In some cases, pervasive corrosion obliterated the characteristic fibrous terminations (FIG. 9A).

Spherulitic Calcite (*sensu* Schroeder, 1972; Davies, 1977, or Verrecchia et al., 1995) is made up of dense spheroidal to botryoidal coatings constituted by elongated, rectilinear fibro-radial calcite polycrystals with their *c* axes radiating from a previous substrate, and exhibiting sweeping extinction (FIG. 9B, C, D; 10A, C). A characteristic feature of Spherulitic Calcite crystals is their epitaxial growth on top of Fibrous Calcite, or other Spherulitic Calcite bodies (Fig. 9A, 9F). Polycrystals in Spherulitic Calcite are between 80 µm to 2 mm-length -length and up to ~10 µm-width.

Spherulitic Calcite coatings exhibit corrosion scars characterised by dentate or irregular surfaces (FIG. 9D, E). Younger generations of these fabrics were nucleated on previous surfaces, and sometimes they grew in optical and lattice continuity with the older crystals. In so doing they left subtle concentric lines between each growth stage (FIG. 9F). Trace element analyses indicate a Mg ferroan composition (average Mg content of 14345ppm), and Sr, Fe and Mn concentrations averaging 11500, 3400 and 390ppm respectively (Walkden et al., 1993).

Subhedral Silica is recognised as up to 40 µm diameter crystals that exhibit single-crystal and undulose extinction (FIG. 9A, C; 10D up) and partially seen replacing Fibrous Calcite, and less commonly replacing Spherulitic Calcite.

===== TABLE 2. HEREABOUTS =====

6.1. Petrography of Spherulitic Coated Grains

In two-dimensional sections, these grains display diverse sizes and morphologies (Table 2). Two types of particles were recognised according to their outlines. Around 85% are Type 1

1 Coated Grains, described as circular to sub-circular (50 to 700 μm -diameter) with rounded to
2 sub-rounded corners and edges, and irregular and/or abraded outlines (FIG. 9B, 10A, C). The
3 remaining 15% are Type 2 Coated Grains, which have elongated outlines (up to 4 mm length)
4 and similar roundness and irregularities to Type 1 (FIG. 9C, 10C, D). Most grains have
5 allochthonous particles in their cores, commonly lycopsids, ferns, gymnosperms or algal
6 fragments, and less frequently volcanic grains and peloids (FIG. 10D). Core dimensions
7 average between 50 μm to 3 mm in length and their shape are curled, elongated or sub-
8 circular.
9

10 Physical characteristics of cores are closely linked to the final external morphology of these
11 grains. Type 1 exhibit arcuate to spheroidal cores such as foliage particles and ash fragments
12 of 50 μm to 700 μm in length, and length to width (L:W) ratios of 2:1 (Fig. 4E; 9B). Type 2
13 have elongated and non-spheroidal cores such as plant debris with lengths up to 4mm, and
14 L:W ratios >2:1 (Fig 9C, 10D). Although some grains appear to lack cores, this likely reflects
15 that the plane of the thin-section did not cut through the particle core, or that core size was
16 very small (e.g. Fig. 9B, 10C).
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43 Spherulitic Coated Grains are composed of Fibrous Calcite, and Spherulitic Calcite.

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46 Microscopy including SEM–EDX analyses revealed the absence of Mg-Si mineral inclusions
47 within Spherulitic Calcite. Fibrous Calcite formed widespread calcite fringe coatings that
48 nucleated on and grew normal to the core surface (FIG. 9A and 10D). Spherulitic Calcite was
49 epitaxially nucleated upon Fibrous Calcite templates or on antecedent Spherulitic Calcite
50 coatings. In some cases, pervasive corrosion of these crystals is later filled by Subhedral
51 Silica. This adversely affected the continuity and terminations of fibrous crystals (FIG. 9A
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1 and 10D). Type 1 grains were dominated by Spherulitic Calcite adopting spheroidal coatings,
2 whereas non-spheroidal, elongated Type 2 grains were normally made of Spherulitic Calcite
3 displaying botryoidal fan-shaped coatings. 'Oncoidal' forms were represented by the <5% of
4 studied grains where concentric generations of Spherulitic Calcite grew in optical and lattice
5 continuity around a core (FIG. 9F).
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11 Some Spherulitic Calcite fibres experienced deflection during later stages of growth, and this
12 is visible where crystals reached >1mm in length (FIG. 10A, B). These deviations imparted
13 arcuate crystal terminations to the spherules. Some other grains have polished, and irregularly
14 dentate outlines (FIG. 10C).
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24 **6.2. Petrography of Spherulitic Crusts**

25 These crusts (FIG. 11; Table 2) are made up of a first generation of Fibrous Calcite fabrics
26 nucleating from core nuclei, and a second phase constituted by Spherulitic Calcite.
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29 Spherulitic Calcite encapsulated carbonaceous filaments (mono-specific, dark brown, double
30 walled filamentous structures and their fragments) (FIG. 11A to D). Preserved carbonaceous
31 filaments displayed circular to prismatic outlines in transverse cross-sections (~50 µm in
32 diameter) and elongated, parallel and smooth outlines in longitudinal cross-sections (at least 4
33 mm in length). Outer boundaries of Spherulitic Calcite bundles overlap and are fused together,
34 defining distinct planes (FIG. 11D). These planes display dissolution cavities filled by Mg-Si
35 minerals that in turn were replaced by younger Spherulitic Calcite (FIG. 11C, D). Spherulitic
36 Crusts were overlain by filament-free Mg-Si-rich layers (FIG. 11A).
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51 Circular to sub-circular abraded fragments of Spherulitic Crusts were found in Facies 1 and 4.
52 In these cases, the tubular moulds left by the decay of the filamentous inclusions became
53 filled by sparite (FIG. 11E, left) or amorphous Mg-Si minerals (FIG. 11E, right). Crusts were
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1 also seen growing around nuclei made of coated grains (FIG. 11F). Deflection of calcite
2 fibres around algae objects was observed (Fig. 11F, inset)
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10 11 12 **6.3. Petrography of Spherulitic Intraclasts**

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14 Two types of Spherulitic Intraclasts were recognised: Type 1 (90% in abundance), sub-
15 millimetre-sized individual objects, and Type 2 (10% in abundance), millimetre-sized
16 tubiform objects (FIG. 12; Table 2).
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20 Type 1 comprised elongated particles (100 to 500 µm long) constituted by laterally stacked
21 Spherulitic Calcite fans. Each intraclast measured up to 20-30 µm in width and most
22 exhibited flat and smooth bases (Fig. 12A). Some bases had slightly irregular and corroded
23 boundaries. Type 2 comprised individual tubiform particles reached 4 mm in length, and up
24 to 2 mm in width, each exhibiting an outer layer of laterally and vertically-stacked Spherulitic
25 Calcite. The latter have dimensions of 100 to 500 µm in width (Fig. 12B, C). In some cases,
26 corrosion cavities within Spherulitic Intraclasts were filled by Spherulitic Crusts (FIG. 12C,
27 D, E). Spherulitic Calcite fans can rarely incorporate fragments of carbonaceous filaments. In
28 such cases, calcite fibres around filaments displayed deflected growth trajectories (FIG. 12F).
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51 **6.4. Petrography of Stacked Fans**

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53 Carbonate ‘clots’ of Facies 3 (Spherulitic cementstones) are constituted by ‘botryoidal-like’
54 growths of laterally and vertically-stacked Spherulitic Calcite. Individual fans reach 100 to
55 1000 µm-thick, and 100 to 3000 µm in width (FIG. 13; Table 2). Composites of laterally-
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1 aligned fans have lengths of several centimetres. Some Spherulitic Coated Grains served as
2 initiation points for these fans. Scalloped solution pits and vertical cracks up to 200 µm deep
3 were observed on top surfaces (Fig. 13B, C). These corroded areas were successively
4 epitaxially covered by lighter and turbid and pale brown Spherulitic Calcite (FIG. 13D). In
5 some cases, chert replaced corroded fans (FIG. 13E). 10 to 50µm-thick continuous silica
6 laminae separate some of the Spherulitic Calcite fans (FIG. 13C). Centimetre-sized crackle to
7 mosaic pack-breccia interclast voids were filled with fibro-radial chalcedony cement (FIG.
8 13F).
9
10 Though Goodacre (1999) identified filamentous carbonaceous inclusions within stacked fans
11 attributed to cyanobacterial remains, none were found in our samples, resulting in similar
12 calcitic ‘shrubby’ textures to those illustrated in ‘Pre-Salt’ Campos Basin (Herlinger, 2016).
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14 However, intra-crystalline micro-porosity filled by kerogenous matter was observed in the
15 calcite fans as suggested by EDX and BSE analyses (FIG. 13A).
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39 **7. DISCUSSION**

40 **7.1. Geochemical considerations**

41 The occurrence of amorphous magnesium-silicate minerals in association with intraclastic
42 calcareous tuffs (Facies 4) is not surprising. Alteration of Mg-rich silicates (e.g., pyroxene or
43 olivine) from alkaline and ultramafic igneous rocks can have generated a range of Mg/Si-rich
44 phyllosilicate phases such those recorded in East Kirkton and probably in the ‘Pre-salt’
45 lacustrine basins (Rogerson et al., 2017). According to XRD and EDX analyses such Mg-Si
46 phases are compositionally similar to minerals of the kaolinite-serpentine group, $[(Mg,Fe)_3$
47 $Si_2O_5(OH)_4]$. Weathering by infiltrating water may have triggered the hydrolysis of basaltic
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1 lavas favouring the formation of hydrous magnesium iron phyllosilicates (see Rogerson et al.,
2 2017). A tropical and humid climate is supported by the abundant lycopod and fern
3 vegetation surrounding the lake margins (Clarkson et al., 1993; Scott et al., 1993).
4 Furthermore, water-rock interactions can have raised the pH and increased the alkalinity of
5 the aqueous solutions sourcing the East Kirkton lake (Pecoraino et al., 2015; Deocampo and
6 Renault, 2016;). Enhanced substrate hydrolysis can release alkali cations in solution (Ca, Mg,
7 Sr) encouraging elevated CaCO_3 supersaturation in the lake waters (Rogerson et al., 2017).
8 Moreover, the East Kirkton carbonates (laminites and spherulitic components) showed
9 $\delta^{18}\text{O}_{\text{calcite}}$ values of -11 to -2‰, and $\delta^{13}\text{C}_{\text{calcite}}$ values of 0 to 4‰ globally indicating
10 precipitation in a meteoric-sourced, dysaerobic to anoxic, volcanic lake (Walkden et al.,
11 1993). The lack of evaporite minerals and the depleted $\delta^{18}\text{O}_{\text{calcite}}$ values questions whether the
12 lake had persistent salinity departures.
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31 **7.2. Diagenesis and trace element concentrations**

32 Subhedral Silica is usually replacing early Fibrous Calcite in those spherules encapsulating
33 carbonaceous filaments. Filament decay may have generated favourable conduits for the
34 circulation of silica fluids into the permeable organic cores producing enhanced silicification
35 within and around Fibrous Calcite crystals soon after spherule formation (Fig. 14). In
36 addition, amorphous silica lamina in laminite facies was interpreted as primary in origin via
37 formation of silica gels because: 1) plastic deformation of slumped silica laminae show no
38 evidence of fracturing, 2) silica laminae is cut by tiny perpendicular cracks leaving the
39 overlying laminae unaffected (*sensu* McGill, 1994) (Fig. 4B).
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56 Furthermore, the Spherulitic Calcite textures show no evidence of an original aragonite
57 precursor neither the presence of neomorphic calcite fabrics selectively replacing aragonite.
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1 Strikingly, spherulitic fabrics contain high Mg and Sr concentrations as occur in the ‘Pre-salt’
2 shrubby carbonates where calcite was hypothesised to be directly precipitated from alkaline
3 lake waters (Saller et al., 2016). Enhanced strontium uptake into calcite minerals originally
4 precipitated in low-temperature alkaline experiments has been reported via initial formation
5 of amorphous calcium carbonate (ACC) precursor phases (Littlewood, et al., 2017). The
6 presence of dissolved Mg^{2+} ions can further stabilise ACC phases thus promoting Sr^{2+}
7 incorporation (Rodríguez-Blanco et al., 2012) and favouring the direct transformation of
8 ACC into calcite crystals (Loste et al., 2003; Rodríguez-Blanco et al., 2012) with high-
9 magnesium contents (Raz et al., 2000; Wang et al., 2012). The initial formation of ACC can
10 be achieved in moderate to high alkalinity environments with concomitant high Mg:Ca
11 contents (Wang et al., 2012) turning alkaline lake chemistries suitable for potential primary
12 precipitation of high-Mg calcites.
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31 **7.3. Sedimentology of spherulitic components**

32 The isopachous calcite rims of Fibrous Calcite grew upon organic cores in conditions
33 favourable for crystal nucleation. Such conditions may have included elevated pH and high
34 alkalinity linked to high $CaCO_3$ supersaturation, perhaps coupled with active water agitation
35 (e.g. Schroeder, 1972; Longman, 1980) and abundance of loose carbonaceous material to
36 form cores (Fig. 14). The epitaxial growth of Spherulitic Calcite on top of Fibrous Calcite
37 indicates that the crystalline substrate played a role in the development of these fabrics (Fig.
38 14). Indeed, the shape of the cores in Spherulitic Coated Grains (Type 1 and Type 2)
39 seemingly dictated the final external morphology (FIG. 10C). Absence of evidence for clay
40 or volcanoclastic inclusions within Spherulitic Calcite suggest that Spherulitic Coated Grains
41 developed at the sediment-water interface rather than within the sediment. Absence of
42 conspicuous biological inclusions further suggests that the type of microbial communities
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1 thriving at the time of spherule formation did not leave noticeable organic remains. Evidence
2 of clay cavity-filling textures within spherules is here consistent with late corrosion processes.
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4 All of this evidence points to a depositional environment capable of forming packstone,
5 grainstone and floatstone of Spherulitic Coated Grains regularly agitated by currents and
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7 supplied by plant debris (common nuclei) at or above the sediment-water interface.
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19 Conversely, Spherulitic Crusts tended to incorporate filamentous components into their
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21 crystal structure. Petrographic analysis suggests that Spherulitic Crusts grew within an
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23 intertwined framework of filamentous green algae (*Cladophora*-like) (FIG. 11C, 15).
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25 Deviation of the Spherulitic Calcite growth trajectories in proximity to algal fragments
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27 further suggests that crystallite trajectories were affected by the presence of these objects (Fig.
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29 11F). Overlapping of crystal fans is compatible with competitive growth of Spherulitic
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31 Calcite bundles that ceased when remaining space was filled. Lack of sediment inclusions
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33 indicates that growth occurred above the sediment-water interface (Fig. 15). In the East
34
35 Kirkton Lake, very rare Mg-Si mineral occurrences were recognised and these were found
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37 overlaying spherulitic crusts (Fig. 10A). Such phyllosilicate layers were largely devoid of
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39 carbonaceous filaments, consistent with a cessation of algal production during Mg-Si
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41 presence (Fig. 11A; 15).
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53 The Spherulitic Calcite forming Spherulitic Intraclasts are likely calcite encrustations on the
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55 external surfaces of subaquatic plants and algae or within internal cavities producing
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57 laterally-linked botryoids (Type 1) (FIG. 16). Similarly, tubular spherulitic aggregates may
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1 have originally encrusted macro-algal thallae (Type 2). Subsequent reworking of the organic
2 templates may have generated intraclastic textures seen in thin sections (FIG. 12, 16). The
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4 predominance of packstone-grainstone textures supports the contention that water agitation
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6 was a factor in their accumulation. Similar fibro-radial crystals have been reported as forming
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8 attached to the trichomes of freshwater cyanobacterium *Nostoc parmelioides* (Freytet and
9
10 Verrecchia, 1993), filling the axial voids of the freshwater algae *Zarramenella minorica*
11
12 (Freytet *et al.*, 1999), or the lysed cells of the green-alga *Cladophoropsis* (Arp *et al.*, 2003).
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24 Stacked Fan nucleation and growth likely required a static substrate (FIG. 17), and these
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26 facies may be partially analogous to stacked botryoidal micro-stromatolitic crusts (20 to
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28 60µm-thick) and globular aragonitic fans of Satonda Lake, Indonesia (Arp *et al.*, 2003). The
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30 crusts of Arp *et al.* (2003) veneered the outer moulds of green algal filaments and were
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32 terminated by smooth, undulating surfaces. East Kirkton Stacked Fans, however, lacked
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34 noticeable organic filaments (although these are mentioned by Goodacre, 1999), which raises
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36 questions over the spatial organisation of active calcite growth and the microbes that will
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38 inevitably have been present within this site.
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43 Petrography shows epitaxial Spherulitic Calcite nucleated on previously corroded fans (Fig.
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45 13D), indicating that corrosion occurred during growth stages, and that sustainable conditions
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47 for Spherulitic Calcite growth re-emerged after short-lived dissolution events (FIG. 17). Lack
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49 of clay or volcanoclastic materials within Stacked Fans suggests that they may have formed in
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51 an agitated subaqueous environment.
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7.4. Cyclostratigraphy and depositional model

Cycle data was integrated with the sedimentological observations of spherule-bearing lithofacies (Fig. 7) and spherulitic components (Fig. 14 to 17). This allowed the reconstruction of the depositional model for the East Kirkton sedimentary succession (Fig. 18) and comparisons with the 'Pre-salt' cyclostratigraphic data.

7.4.1. Littoral environment

Type-A cycles characterise the shallower lake environments where carbonate production took place in moderate to high energy conditions, perhaps in the littoral to proximal sublittoral setting towards the lake centre. This environment was located on the NNW side of the quarry (Fig 7). Type-A cycles reflect an initial transgressive phase (Facies 6) overlain by a regressive spherule-dominated stage (Facies 2 and 3) (Fig 7). The sporadic occurrence of poorly sorted spherulitic grainstone to packstone on top of these cycles points to intermittent low-energy periods enabling co-occurrence with Mg-Si minerals. Spherulitic Coated Grains, Spherulitic Crusts, and Spherulitic Intraclasts were penecontemporaneously nucleated in this setting, which hosted the optimal conditions for nucleation and growth of Spherulitic Calcite (Fig. 18). Moreover, the fact that Facies 2 and 3 are laterally linked or intermingled suggest that they formed in close temporal association. The local erosional truncation underlying Type-A cycles likely reflects a phase of lake contraction followed by the development of spherulitic cementstone build-ups during a resumed lake re-flooding (Fig. 7, 8). Intermittent input of undersaturated waters into the lake (*sensu* Driscoll and Newton, 1985; Reuss et al., 1987) could explain some early dissolution features in spherulitic textures. McGill (1994) and Walkden et al. (1993) documented cathodoluminescence banding in spherulitic components that would be coherent with E_H -pH variations of the fluids forming these grains. The shallow

1 water, high energy setting and simultaneous development of spherulitic cementstones of East
2 Kirkton compares well with the 'Pre-Salt' shrubby microbial boundstones from Brazil and
3 Angola, (Saller et al., 2016; Sabato Ceraldi and Green, 2016). In East Kirkton, Type-A cycles
4 are similar to those described for the 'Pre-salt' by Wright and Barnett (2015), and Sabato
5 Ceraldi and Green (2016). In the latter cases, the laminated argillaceous mudstone is placed at
6 the beginning of the cyclothems (Wright and Barnett, 2015) and considered as formed during
7 transgressive pulses (*sensu* Sabato Ceraldi and Green, 2016) as similarly occur with Facies 6
8 in this work. In some 'Pre-salt' cycles the occurrence of thin spherulitic grainstone with
9 intraclastic shrub material has been reported underlying the laminated mudstone indicating
10 potentially active reworking events before deposition of muddy facies. In the Scottish cycles
11 spherulitic grainstone to packstone represents the most regressive parts accumulated on top of
12 spherulitic cementstone packages or even occurring intermingled within them suggesting a
13 close origin for both facies.

34 7.4.2. *Sublittoral to shallow profundal environment*

35 Type-B and C cycles define the littoral to sublittoral settings respectively, which were located
36 in the central part of the quarry (Fig 7). Type-B cycles show an initial deepening phase
37 (Facies 1), and a subsequent shallowing phase (Facies 2). More distal Type-C cycles (C1 and
38 C2) display a transgressive pulse (Facies 6), and a regressive stage formed by the stacking of
39 Facies 1 and 4. Normal graded beds with erosive bases are best interpreted as pulses of
40 downslope sediment gravity transport triggered by slumping processes (e.g., Lowe, 1979)
41 generated during regressive intervals (Fig 7, 8). The fold axes of slumps and convolute beds
42 are similarly grouped sub-parallel to one another and parallel to the inferred paleo-slope
43 strike suggesting that soft-sediment deformation (slumping and convolute laminae) was likely
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1 triggered by slope gradients to the WNW (Woodcock, 1979; Strachan and Alsop, 2006) (Fig.
2 7B, Fig. 18).
3

4 Sub-millimetre scale continuous laminae formed under low energy depositional conditions
5 with limited siliciclastic input. Carbonate laminae are 2 to 4 times thicker than organic
6 laminae, suggesting brief intervals of carbonate-free sedimentation interrupting ongoing
7 calcite production triggered by photosynthesis in the water column (*sensu* Dittrich and Obst,
8 2004). Evidence of chipped and polished spherulitic grains, and abraded spherulitic crust
9 fragments within Type-B and C1 cycles points to reworking of these components from the
10 shallow lake factory areas (Fig. 18). Likewise, in the ‘Pre-Salt’ sag lakes clay-rich spherulitic
11 facies tend to occur in deeper environments below the platform margin where lower energy
12 enabled the deposition of finer-grained sediments (Saller et al., 2016; Sabato Ceraldi and
13 Green, 2016). Thus ‘Pre-salt’ cycles show spherule-stevensite floatstone packages capped by
14 calcite shrubs framestone beds (Wright and Barnett, 2015) or microbial crusts-reworked
15 spherules in an upward regressive trend (*sensu* Sabato Ceraldi and Green, 2016). Type-B
16 cycles in East Kirkton show similar stratal arrangement though low energy intervals are here
17 dominated by laminites instead of substantial clay beds.
18

19 Pinching out of organic laminae against spherulitic grains further indicates that East Kirkton
20 grains were systematically buried by muddy sediments (Fig. 4E). Type- C2 cycles are
21 apparently devoid of spherulitic grains indicating deposition of laminites in deeper
22 environments than Type-C1 (Fig 7). The occurrence of pyrite framboids, preserved biota,
23 absence of bioturbation, and trace element geochemistry (Clarkson et al., 1993; Rolfe et al.,
24 1993; Scott et al., 1993) is consistent with low oxygen conditions.
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56 7.4.3. *Profundal environment* 57 58 59 60 61 62 63 64 65

1 Type-D cycles indicate sedimentation in a profundal lake setting under low energy conditions
2 found predominantly in the SE part of the quarry (Fig. 7, 18). These cycles display an initial
3 shale-rich deepening interval (Facies 6) followed by carbonate-rich shallowing intervals
4 (Facies 5) (Fig 7). Graded and convolute beds are evidence for gravity flows and reworking
5 of semi-consolidated layers from lake margins to depocentres. Preservation of pyrite
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framboids and fauna and flora indicates conditions of water stagnation and oxygen depletion. These features imply the bottom was well below lake wave base, which is reliable with earlier suggestions that the lake was of sufficient water depth to sustain sporadic meromictic conditions and support nektonic vertebrate life (Parnell, 1988; Loftus and Greensmith, 1988; Clarkson et al., 1993). Similar anoxic conditions were reported in the ‘Pre-salt’ lakes during the sag 2 microbial interval when organic-rich shales and marls were deposited in the deeper parts (Sabato Ceraldi and Green, 2016).

===== FIGURE. 18 HEREBOUTS =====

7.5. Origin of Spherulitic Calcite: microbes versus stevensite

Nucleation of Spherulitic Calcite is a phenomenon that has been linked to bacterial and cyanobacterial activity, as demonstrated through laboratory experimentation (Buczynski and Chafetz, 1993; Verrecchia et al., 1995; González-Muñoz et al., 2000; Braissant et al., 2003; Ercole et al., 2007; Rodríguez-Navarro et al., 2007; Sánchez-Navas et al., 2009; Pedley et al., 2009). Microbial physiological processes (see Arp et al., 2003; Dupraz et al., 2009; Decho 2010) can alter the subaqueous carbonate equilibrium to effectively promote calcium carbonate precipitation that in some cases exhibits spherulitic morphologies (Verrecchia et al., 1995; Rodríguez-Navarro et al., 2007; Arp et al., 2012). However, in hyper-alkaline systems these metabolic activities are less likely to stimulate substantial calcification (Arp et al., 2001;

1 2012). In these settings bacterial degradation of the biofilm EPS significantly increases
2 supersaturation and promote calcification (Arp et al., 1999; Dupraz, et al., 2009; Decho,
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4 2010). Indeed, fibrous and radially-divergent aragonite layers are interpreted from lysed
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6 green algal structures in Satonda Lake (Arp et al., 2003). Similarly, millimetre-sized
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8 aragonite spherules grew and accumulated within deeper parts of cyanobacterial mats in the
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10 Recent Kiritimati Lake where progressive EPS degradation was attributed to spherule
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12 formation (Arp et al., 2012). In all these cases, calcite precipitation will be occurring in
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14 environments rich in dissolved EPS, which have been demonstrated to promote spherule
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16 formation (Braissant et al., 2003, Wolthers et al., 2008; Mercedes-Martín et al., 2016). This
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18 mechanism is highly likely to be responsible for the abundant spherulitic carbonates at East
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20 Kirkton, and the absence of fossilised bacteria suggesting that calcite mineralisation is
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22 forming within degrading EPS gels rather than within actively photosynthesising biofilms
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24 (*sensu* Trichet and Défarge, 1995; Arp et al., 2003; 2012) and in alkaline lakes (Walkden et
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26 al., 1993; Rogerson et al., 2017). Whether EPS molecules are produced from lake benthic
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28 biofilms or being sedimented as polymer gels from colloidal planktonic material onto the lake
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30 bottom (Decho, 1990; Hoagland et al., 1993; Passow et al., 2001; Passow, 2002) is unclear,
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32 but likely only relevant as an indicator of the water depth at which Spherulitic Calcite
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34 formation took place. This mechanism is supported by the abundance of bacterial and micro-
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36 algal planktonic organisms known from the Midland Valley Carboniferous oil-shale lakes
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38 (Loftus and Greensmith, 1988; Parnell, 1988; Raymond, 1991).

39 In the 'Pre-salt' lakes, stevensite clay was invoked to participate in the growth of calcitic
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41 spherules (Tosca and Wright, 2015; Wright and Barnett, 2015). In East Kirkton, amorphous
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43 clay is limited to tiny occurrences in the sublittoral slope settings where chemical (pH,
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45 alkalinity, saturation index) and physical (low energy) conditions enabled its formation and
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47 accumulation. At the same time, stevensite mineral formation is favoured at high pH, high
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1 salinity and high Mg/Si ratios (Tosca and Masterson, 2014) suggesting that the East Kirkton
2 lake did not undergo such conditions in low energy zones. Interestingly, the occurrence of
3 authigenic sparite in laminites (Fig. 4A) suggest that the sublittoral region was characterised
4 by lower pH/ saturation indexes than the littoral zone probably explaining why clay minerals
5 were volumetrically rare. Nevertheless, examples such as the East Kirkton Limestone
6 demonstrate that the formation of abundant spherulitic carbonates can be decoupled from clay
7 influence in alkaline lakes and that ‘microbial-solution’ interactions warrant further research.
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19 **7.6. Hydrological implications**

21 The sedimentary record of the East Kirkton lake displays two incomplete, large-scale
22 deepening-shallowing cycles bounded by an erosional surface interpreted as an unconformity
23 formed in the littoral lake portion (Fig. 7, 8). These larger-scale cycles may reflect a broad
24 deepening pulse, as Type-C2 and D cycles are progressively more abundant upwards in the
25 sedimentary sequence (Fig 7). A change towards a more humid climate is recorded by the
26 transition from gymnosperm to lycopsid vegetation in the lake margin (Scott et al., 1993),
27 and from tetrapods-arthropods to fishes-ostracods within the lake water (Clarkson et al.,
28 1993), thus the overall deepening trend of the lake appears to reflect increasing water
29 incursion. Variable water input is also reflected in the wide spectrum of $\delta^{18}\text{O}_{\text{calcite}}$ reported
30 from the ‘Pre-Salt’ spherulitic carbonates of Brazil (-6 to 5‰) and Angola (-2 to 3‰), which
31 fall within a broad range between fresher and more evaporative lake water conditions (Saller
32 et al., 2016; Sabato Ceraldi and Green, 2016). Although the unusual carbonate phases of East
33 Kirkton and the ‘Pre-Salt’ are certainly dependent on sufficiently high calcite supersaturation
34 to form, this is apparently decoupled from evaporation. The lack of sulphates, chlorides, or
35 their calcite/silica pseudomorphs even in the most regressive facies further indicates that the
36 lake was not truly endorheic. It therefore seems unlikely that hydrological closure was a
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pivotal precondition for the development of calcitic spherules (Saller et al., 2016; Sabato Ceraldi and Green, 2016)

8. CONCLUSIONS

1) A widespread assemblage of calcite spherulitic components (Coated Grains, Intraclasts, Crusts, and Stacked Fans) were formed in a clay-poor, volcanic and alkaline lacustrine system.

2) The carbonate factory of spherulitic components was located in the littoral lake region (Fig. 18). This setting experienced a combination of high alkalinity, metal-rich hydrochemistry, and microbe-derived organic acid interference with the mineral formation process. These conditions collectively encouraged widespread Spherulitic Calcite nucleation at the sediment-water interface.

3) *Spherulitic Coated Grains* were nucleated at the sediment-water interface on loose organic cores in an agitated environment (Fig. 14). Initial isopachous rims of Fibrous Calcite coated these cores. Spherulitic Calcite grew epitaxially upon Fibrous Calcite giving the characteristic spheroidal shape to the grains. *Spherulitic Crusts* grew at the sediment-water interface within an intertwined framework of filamentous green algae subsequently buried by amorphous Mg-Si matrices (Fig. 15). *Spherulitic Intraclasts* may have first formed as Spherulitic Calcite bodies laterally encrusted to organic templates. Later reworking produced the intraclastic texture (Fig. 16). *Stacked Fans* grew as laterally-stacked, Spherulitic Calcite nucleated upon static substrates building metre-thick lenticular spherulitic cementstones (Fig. 17). Spherulitic nucleation resumed upon corroded surfaces indicating that conditions of calcite supersaturation alternated with periods of undersaturation. Corrosive events are linked to input of fresher waters into the lake.

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4) Three lacustrine depositional settings were recognised: littoral, sublittoral, and profundal (Fig. 18). The *littoral* zone was characterised by coeval spherulitic cementstone build-ups and grainstone-packstone of spherulitic components formed in well-agitated, shallow environment. The *sublittoral* zone was define by metric scale, slumped beds, and sediment gravity deposition triggered by slope gradients. Significant down-slope resedimentation of spherulitic grains allowed spherulitic laminites to form in the sublittoral to profundal region. The *profundal* setting was constituted by abundant carbonate-shale alternations with highly preserved fossiliferous remains recording sporadic conditions of water stagnation, oxygen depletion and shedding episodes into lake depocentres.

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FIGURE CAPTIONS

FIGURE 1. Litho- and chronostratigraphical divisions of the Carboniferous in the Midland Valley of Scotland. The East Kirkton Limestone area is located in the red square. Modified from Read et al., (2002). Ages from Gradstein et al., (2012).

FIGURE 2. A) The Midland Valley isopachs during Strathclyde Group deposition (modified from Read et al., 2002). B) Paleogeographic map of the Lake Cadell in the West Lothian Oil Shale Formation. Extensive volcanic piles divided the Midland Valley into a series of semi-enclosed lacustrine-lagoonal basins (modified from Parnell, 1988). Marine incursions were intermittent. C) Geological map of the East Kirkton Limestone area, modified from Cameron et al., (1998).

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2 **FIGURE 3.** The East Kirkton Limestone Quarry area. A) Photomosaic of the studied quarry and
3 location of boreholes BH-1, BH-2 and BH-3, and logs EK-1 and EK-2 (inset) (reprinted from McGill,
4 1994). B) Metric-scale slumped beds inclined towards the WNW. C) Detail of B showing distorted
5 slumped laminites. D) Internal soft-sediment deformation within a flat-bounded bed.
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13 **FIGURE 4.** Laminites. A) Left: Flat tabular beds in outcrop. Right: Internal structure shows thicker
14 yellowish carbonate laminae [C] alternating with thinner darker organic laminae [O] or silica laminae
15 [Si] in X-Nichols. B) Composite image of alternating organic laminae [O] with primary silica laminae
16 [Si] seen vitreous in X-Nichols (left) and milky in plane light (right). Cracks in silica laminae are
17 filled by calcite (arrow). C) BSE image of pyrite framboids (EDX pattern, inset). D) Spherulitic
18 laminites with Spherulitic Coated Grains [SG] displaying loosely packed textures within organic
19 laminae. E) Organic laminae pinches out towards the edges of grains [arrows] displaying thickness
20 variations across them. (X-Nichols image).
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33 **FIGURE 5.** Spherulitic grainstone-packstone and Spherulitic cementstone. A) Laminated grainstone-
34 packstone with spherulitic grains alternating with thin amorphous Mg-Si clays [arrow]. B)
35 Moderately-sorted and well-rounded grainstone-packstone of spherulitic grains in an amorphous Mg-
36 Si matrix [arrow] locally replaced by blocky calcite, in X-Nichols. C) Dome-shaped spherulitic
37 cementstone build-ups (F3) tilted on top of slumped layers made of laminites (F1), volcanic tuffs (F4)
38 and shales (F6). Original depositional beds are inclined towards the left over the margin. D) An
39 incised surface [dotted line] on top of laminites (F1) is filled by volcanic and intraclastic tuffs (F4),
40 and overlaid by spherulitic cementstone (F3). E) Detail on C showing laminites (F1) overlaid by tiny
41 shrubby 'clotted' fabrics [arrow] vertically evolving to spherulitic cementstone build-ups (F3). F)
42 Polished slab of the spherulitic cementstone displaying clast-supported breccias filled with silica
43 cements [red arrow].
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FIGURE 6. Volcanic and intraclastic calcareous tuffs, Intraclastic wackestone-floatstone and Shales.

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2 A) Volcanic tuffs in core (BH-2) and intraclastic calcareous tuffs arrowed in BH-3. B) Volcanic tuff
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4 show porphyritic texture of phenocrysts floating in a cryptocrystalline glassy matrix. Plagioclase (Pg),
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6 Clinopyroxene (Cpx) and Olivine (Ol). C) Floatstone of Spherulitic Coated Grains (SG) in a red Mg-
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8 Si clay matrix [S]. Lapilli intraclasts [Lap] show vesicular textures. Clay XRD pattern at the bottom
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10 (red spot). D) BSE image of a floatstone with Spherulitic Coated Grains [SG], and lapilli fragments
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12 [Lap] in a Mg-Si matrix [S]. EDX analyses of amorphous Mg-Si phases (red spots) and volcanic
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14 minerals (blue spots). E) Intraclastic wackestone-floatstone alternating with Shales (left). Cores on the
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16 right showing laminites (F1) on top of shales (F6) and volcanic tuffs (F4) (arrow to base). F) Detail of
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18 E showing Intraclastic wackestone-floatstone of contorted carbonate laminae in a muddy matrix.
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24 **FIGURE 7.** A) Depositional architecture of a SSE-NNW transect in the East Kirkton Limestone
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26 Quarry including logs (EK-1 and 2) and boreholes (BH-1, 2 and 3). Two large-scale cycles are
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28 identified composed up to 5 small-scale cycles. Metre-thick basalt layers occur on top of borehole
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30 BH-1. B) Location of logs and boreholes. Stereographic projection displaying slump fold polar axes
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32 grouped fairly parallel to the inferred paleo-slope strike polar projection [blue asterisk].
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38 **FIGURE 8.** Key symbols used in figures. Type section at East Kirkton succession (EK-1 and EK-2)
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40 integrating facies, small-scale cycles (SSC), large-scale cycles (LSC), sedimentary environment, lake
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42 level variations and distribution of spherulitic components.
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47 **FIGURE 9.** Spherulitic Coated Grains. A) Fibrous Calcite crystals [f] are fanning out from the
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49 carbonaceous cores [c]. Pervasive corrosion and later Subhedral Silica [Ss] obliterated the fibrous
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51 terminations. B) Spherulitic Calcite fabric is made of fibro-radial polycrystals growing upon Fibrous
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53 Calcite, and producing spheroidal grains (Type 1) (X-Nichols). C) Spherulitic Calcite growing on top
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55 of elongated substrates produced botryoidal fan-shaped coatings (Type 2 grains) in X-Nichols.
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57 Subhedral Silica [Ss] cementing decayed organic filaments as seen in a BSE image.. D) Spherulitic
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59 Calcite fans show corrosion scars (dotted lines) which act as nucleation surfaces from successive
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1 crystals (X-Nichols). E) Detail of D showing resumed Spherulitic growth upon dissolution surfaces
2 (dotted lines). Calcite growth directions shown in arrows (X-Nichols). F) Spherulitic ‘oncoids’ are
3 formed by concentric layers of crystals growing in optical and lattice continuity upon subtle previous
4 surfaces (yellow arrows) (X-Nichols). Deflection of fibres in the edges (red arrow) and corrosion
5 surfaces (dotted line) are common.
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13 **FIGURE 10.** Spherulitic Coated Grains. A) Spherulitic Calcite crystals commonly deflect in later
14 stages of growth [red arrows] (X-Nichols). B) Detail of A showing crystal deflection of spherules [red
15 arrow], and corrosion surfaces [yellow dotted line] overlaid by Spherulitic overgrowths (X-Nichols).
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17 C) Circular particles (Type 1) display Spherulitic Calcite fabrics growing in a spheroidal fashion,
18 whereas elongated particles (Type 2) show botryoidal fan overgrowths. Note the carbonaceous core
19 within the elongated coated grain (X-Nichols). D) Elongated algae fragments (top) or ash remains
20 (bottom) as precursor nuclei. Fibrous Calcite fringes (f) and Subhedral Silica (Ss) are seen in cores
21 (X-Nichols).
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33 **FIGURE 11.** Spherulitic Crusts. A) Spherulitic Crusts [SC] are buried by Mg-Si layers [S]. Note
34 sweeping extinction. X-Nichols image. B) Algae filaments with circular outlines (transversal) and
35 elongated and smooth outlines (longitudinal) are trapped in Spherulitic Calcite. C) Boundaries
36 between discrete Spherulitic Calcite bundles are corroded and filled by Mg-Si minerals [arrows]. D)
37 X-Nichols image of C with overlapping of crusts with sweeping extinction. Mg-Si minerals are
38 replaced by newer epitaxially grown spherulitic crusts. E) Moulds of decayed filaments are filled by
39 sparite (left) or Mg-Si minerals [S, arrow]. F) Spherulitic Crust fanning out from a Coated Grain.
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66 **FIGURE 12.** Spherulitic Intraclasts. A) Packstone of Type 1 Intraclasts formed by elongated
67 Spherulitic Calcite objects cemented by blocky calcite (c). X-Nichols image. B) Tubiform Type 2
68 Intraclasts made of laterally linked Spherulitic Calcite. Tubes are filled by peloids (Pel) and buried by
69 Mg-Si clays (S) replaced by calcite after dissolution (top). C) Panoramic view of a tubiform Type 2
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1 Intraclast (outlined in dotted line) filled with Spherulitic Crusts [SC]. D) Spherulitic Intraclast
2 corroded and filled with a Spherulitic Crust [SC]. E) X-Nichols image of D. F) Spherulitic Calcite
3 encapsulating filamentous algae. Deflection of calcite fibres is observed on top of the filament.
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8 **FIGURE 13.** Stacked Fans. A) Laterally and vertically-stacked ‘clotted’ forms. Dark patches are
9 kerogen. Breccias filled with silica cements [arrows]. B) Scalloped dissolution pits on top of the
10 Stacked Fans [arrows]. C) X-Nichols image of B. Note sweeping extinction and thin and continuous
11 silica rims outlining previous Stacked Fans [arrows]. D) Corroded Stacked Fans are successively
12 filled by turbid, pale brown Spherulitic Calcite growing in optical and lattice continuity [arrows]. E)
13 Chert filling corrosion cavities of fans. X-Nichols image. F) Detail in A. Interclast breccia voids (top)
14 are filled with microcrystalline to fibro-radial/spherulitic chalcedony. Spherulitic Calcite fans (bottom)
15 are stacked forming positive micro-reliefs. X-Nichols image.
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28 **FIGURE 14.** Formation of Spherulitic Coated Grains (top to bottom).
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33 **FIGURE 15.** Formation of Spherulitic Crusts (top to bottom).
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38 **FIGURE 16.** Formation of Spherulitic Intraclasts (top to bottom).
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42 **FIGURE 17.** Formation of Stacked Fans (top to bottom).
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46 **FIGURE 18.** Depositional model of the East Kirkton Limestone deposit, including sedimentary
47 features and the occurrence of processes, textures and small-scale cycles. Not to scale (See Fig. 8 for
48 symbols).
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55 **TABLE 1.** Summary of the facies types.
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60 **TABLE 2.** Summary of the petrographic features of spherulitic components.
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A depositional model for spherulitic carbonates associated with alkaline, volcanic lakes

Ramon Mercedes-Martín^{1*}, Alexander T. Brasier², Mike Rogerson¹, John J.G. Reijmer^{3,4}, Hubert
Vonhof⁵ and Martyn Pedley¹

1. School of Environmental Sciences, University of Hull, Cottingham Road, HU6 7RX, Hull, UK. (* Email:
r.mercedes@hull.ac.uk).

2. School of Geosciences, Meston Building, University of Aberdeen, Old Aberdeen, Scotland, UK. AB24 3UE.

3. Faculty of Earth and Life Sciences, VU University of Amsterdam, De Boelelaan 1085, 1081HV Amsterdam,
The Netherlands.

4. ~~Present at:~~ College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and
Minerals, Dhahran 31261, Saudi-Arabia

5. Max Planck Institut für Chemie, [Hahn-Meitnerweg 1](#), 55128 Mainz, Germany.

ABSTRACT

The South Atlantic Aptian ‘Pre-salt’ reservoirs are formed by a combination of spherulitic carbonates and Mg-rich clays accumulated in volcanic alkaline lake settings with exotic chemistries. So far, outcrop analogues characterised by metre-thick successions deposited in lacustrine scenarios are elusive so disentangling the genesis of spherulitic carbonates represents a major scientific challenge with business impact. Although the Cretaceous spherulitic lacustrine carbonates of the ‘Pre-Salt’ South Atlantic rift basins host remarkable hydrocarbon reserves, the controls on spatial distributions of spherulitic facies remain poorly constrained and hotly debated. In particular the controls on spatial distribution and the environment of spherulitic facies formation remain poorly constrained, little studied, and hotly debated. Although carbonate spherulites form in a wide range of environments, the

27 ~~processes by which metre-thick accumulations develop are little studied. Further complexity~~
28 ~~is added in the 'Pre-Salt' as the unusual carbonate fabrics occur in association with hydrated~~
29 ~~magnesium clays (stevensite), because interactions between clays and carbonates are poorly~~
30 ~~understood.~~ To shed light on this conundrum, a spherulitic carbonate-rich, alkaline ~~and~~
31 volcanic ~~rift~~ lacustrine succession has been analysed at outcrop scale: the Carboniferous East
32 Kirkton Limestone (Scotland). Despite clays being very scarce and limited to layers of
33 amorphous Mg-Si ~~phases~~ minerals, a diverse array of ~~carbonate~~ spherulitic calcitic
34 components were formed, including coated grains, crusts, and build-ups ~~with spherulitic~~
35 calcitic morphologies. This setting enables the mechanisms of spherulitic ~~fabrie~~ calcite
36 development and the patterns of sediment accumulation to be explored in a geobiological and
37 hydrochemical scenario similar to the 'Pre-Salt' subsurface occurrences, but divorced from
38 clay influence. The integration of ~~new~~ logs, borehole data, outcrop photomosaics and
39 petrographic observations collectively allowed the reconstruction of a ~~new~~ depositional
40 model for the East Kirkton lacustrine succession. In this model, calcite spherulite nucleation
41 took place at the sediment-water interface in the littoral zone, ~~stimulated~~ driven by the co-
42 occurrence of 1) high alkalinity, 2) ~~meta~~ Ca-Mg-rich hydrochemistry, and 3) microbial-
43 derived colloidal exopolymeric substances. These environmental conditions permitted the
44 coeval development of ~~shrubby spherulitic cementstone~~ carbonate build-ups and spherulitic
45 grainstone-packstone within the wave-agitated zone, and the accumulation of floatstones and
46 laminites of spherulitic grains in deeper lake regions by means of downslope reworking. This
47 ~~biogeochemical~~ model is consistent with the previously documented ~~bacterial-algal~~ microbial
48 bloom occurrences and highlights the need to better understand the complex 'microbe-
49 solution' interactions before any reliable facies model is envisaged.

51 **Keywords:** spherulite, ~~botryoidal~~spherulitic, calcite ~~shubby~~ calcite, alkaline, lacustrine,
52 volcanic, Carboniferous, [Pre-salt](#)

53 **Running title:** A depositional model for spherulitic [lacustrine](#) carbonates
54

55 1. INTRODUCTION

56 Spherulitic textures from alkaline and volcanic-influenced lacustrine environments have risen
57 to prominence following their discovery in abundance in the Cretaceous [subsurface](#) rift lake
58 [deposits](#) of the South Atlantic (Terra et al., 2010; Luiz-Dias, 1998; Rezende and Pope, 2015;
59 [Wright and Barnett, 2015](#); Saller et al., 2016). Spherulites are defined as components
60 formed by calcitic fibro-radial spherulitic polycrystals *sensu* Verrecchia et al., 1995. They are
61 well known from a wide variety of carbonate environments including soils, lakes, hyper-
62 saline lagoons, and marine tidal flat settings (Buczynski and Chafetz, 1993; Verrecchia et al.,
63 1995; Braissant et al., 2003; Spadafora et al., 2010; Pueyo et al., 2011; Arp et al., 2012;
64 Wanas 2012; Bahniuk et al., 2015). However they rarely contribute the most abundant
65 ~~allochem~~ [carbonate grain](#) in a deposit, and relevant outcrop examples of spherulitic limestone
66 are scarce meaning that the petrography of such carbonates is poorly constrained. Discoveries
67 of the South Atlantic ‘Pre-Salt’ hydrocarbon reservoirs of Brazil and Angola (Guardado et al.,
68 2000; Moreira et al., 2007; Carminatti et al., 2008; Cazier, et al., 2014) promoted interest in
69 deciphering the mechanisms capable of producing voluminous spherulitic carbonate
70 ~~sediments~~ [deposits](#) in volcanic and lacustrine settings (e.g., Mercedes-Martín et al., 2015;
71 Wright and Tosca, 2016), placing the need to build facies models for these systems beyond
72 the ability to understand their mode of formation.

73 Lacustrine depositional models have recently been proposed for the Aptian ‘Pre-Salt’
74 spherulite-bearing succession of the Angolan margin of the Kwanza Basin (Saller et al.,
75 2016), and the Brazilian margin of the Campos and Santos Basins ([Wright and Barnett, 2015](#);

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76 Sabato Ceraldi and Green, 2016). These models commonly display the occurrence of
77 spherulitic calcitic components intermingled within stevensite clays in deeper lake
78 environments. The ‘shrubby’ spherulitic boundstones generally occupied the shallow lake
79 settings where coeval clay minerals were less abundant (Sabato Ceraldi and Green, 2016;
80 Saller et al., 2016).

81 Calcite spherulite formation has previously been explained from both end-member
82 perspectives: a biotically-influenced origin (e.g., Verrecchia et al., 1995; Arp et al., 2012),
83 versus an abiotic mechanism (e.g., García-Ruiz, 2000; Wright and Barnett, 2015). In the case
84 of the ‘Pre-Salt’ deposits, the abiotic hypothesis has been built on the assumption that the
85 abundant smectite clays (stevensite) present in very alkaline lakes encouraged spherulitic
86 calcite particle generation in association with ‘clay-gel phases’ (Wright and Barnett, 2015;
87 Tosca and Wright, 2015).

88 To elucidate the mechanisms forming these carbonates a better understanding of the
89 biochemistry and the source of the carbonate-precipitating waters is required. In the case of
90 volcanic-influenced alkaline lakes, the chemical composition of these waters depends on at
91 least three factors: 1) the balance between runoff and evaporation, commonly related to
92 whether the basin is internally or externally draining; 2) the chemical composition of the
93 basement and recent-coeval extrusive rocks; and 3) the degree to which water can interact
94 with these rocks (Bertani and Carozzi, 1985; Rowe and Brantley, 1993; Romero and Melack,
95 1996; Carroll and Bohacs, 1999; Bohacs et al., 2000; Narcisi, 2001; Bowser and Jones, 2002;
96 Radke et al., 2002; Kebede et al., 2005; Ayenew, 2008; Bergner et al., 2009; Gierlowski-
97 Kordesch, 2010; Pecoraino et al., 2015; Rogerson et al., 2017). A recurrent issue for these
98 systems is how much carbonate can be deposited, given the mass flux of calcium and
99 magnesium being supplied to surface systems (Renaut and Jones, 1997; Guido and Campbell,
100 2011). In addition, alkaline lakes are favourable habitats for a broad assemblage of bacterial

101 | ~~and algal~~microbial communities, including both benthic and planktonic microbes. Biological
102 | productivity in these lakes can be extremely high (Melack, 1981; Galat et al., 1990; Jones et
103 | al., 1998; Grant and Jones, 2000; Stockner et al., 2000; Kandianis et al., 2008). The
104 | organisms in the lakes may control carbonate precipitation directly (Stabel, 1986, Chafetz and
105 | Buczynski, 1992, Arp et al., 2001; Dittrich and Obst, 2004; Dupraz et al., 2009; Pedley et al.,
106 | 2009), or indirectly by stimulating calcite crystal nucleation through the production and / or
107 | consumption of extracellular polymeric substances (hereafter EPS) (Trichet and Défarge,
108 | 1995; Arp et al., 1999; Dupraz et al., 2009; Decho, 2010). Several researchers have attempted
109 | to distinguish these bio-mediating processes from abiotic carbonate precipitating mechanisms
110 | (Burne and Moore, 1987; Kelts and Talbot, 1990; Kempe et al., 1991; Merz, 1992; Pedley,
111 | 1992; Jones and Renaut, 1995; Chafetz and Guidry, 1999; Schneider and Le Campion-
112 | Alsumard, 1999), but the division remains controversial.

113 |
114 | The present study examines a spherulite-rich carbonate deposit formed in a volcanic and
115 | comparatively clay-poor lacustrine setting: the Lower Carboniferous East Kirkton Limestone
116 | in Scotland (Rolfe et al., 1993; Walkden et al., 1993). The East Kirkton Limestone displays
117 | an abundant assemblage of spherulitic calcite fabrics. Thus, a detailed petrographic study of
118 | such components and the sedimentological analysis of the spherulite-bearing facies at East
119 | Kirkton can 1) help to better constrain the environmental conditions underpinning the
120 | formation and accumulation of these carbonates, and 2) provide an analogue case for other
121 | spherulitic carbonate occurrences like those in the Cretaceous ‘Pre-Salt’ lakes of the South
122 | Atlantic.

123 | 124 | **2. GEOLOGICAL BACKGROUND**

125 Half-grabens and intervening highs in the Midland Valley of Scotland were generated during
126 the Early Carboniferous by N-S oriented fault systems, with a right lateral strike-slip
127 component (Rippon et al., 1996). The Carboniferous strata are divided into the Inverclyde
128 (Tournasian) and Strathclyde (Viséan) Groups (Whyte, 1993; Read et al., 2002; FIG. 1). The
129 Strathclyde Group comprises a varied succession of sedimentary and volcanic rocks,
130 characterised by carbonaceous beds and coals. It is interpreted as largely fluvial and
131 lacustrine in origin but affected by sporadic marine incursions (Browne and Monro, 1989).
132 Basaltic volcanism ([basanite type](#)) increased during Strathclyde Group deposition (Whyte,
133 1993; FIG. 1) leaving the Midland Valley divided into a series of semi-enclosed continental
134 basins. They were filled by fluvial, deltaic and lacustrine-lagoonal deposits (Fig. 1, 2A; Read
135 [et al.](#), 2002). Sediments of the West Lothian Oil Shale Formation (Upper Viséan) were
136 deposited in a large stratified freshwater lake complex developed under a humid tropical
137 climate and collectively referred to as Lake Cadell (Greensmith, 1968) (Fig. 2B). The
138 accumulation of planktonic and benthic [micro](#)organisms gave rise to oil-shale deposits under
139 exorheic, meromictic, and deep (50 to 100m) conditions (Loftus and Greensmith, 1988;
140 Parnell, 1988). The East Kirkton Limestone formed within this lake complex (FIG. 2B, C),
141 comprising black shales, laminated limestones, tuffaceous [clastic](#) carbonates, and massive
142 limestones all yielding spherulitic calcite textures (Rolfe et al., 1993; Walkden et al., 1993;
143 Read [et al.](#), 2002, FIG. 2B). The East Kirkton Limestone displays well-exposed quarried
144 faces and relatively undisturbed depositional geometries. Exquisitely preserved skeletons of
145 amphibians, fishes, plants and ostracods have also been found at this locality (Smithson, 1989;
146 Clarkson et al., 1993; Rolfe et al., 1993; Scott et al., 1993; Walkden et al., 1993).
147 Palynological evidence shows that the East Kirkton lake was surrounded by an extensive
148 woodland dominated by gymnosperms, pteridosperms and, later on, by lycopods (Rolfe et al.,
149 1993; Scott et al., 1993).

150

151 ===== FIGURE. 1 and 2 HEREBOUTS =====

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153 3. MATERIAL AND METHODS

154 Fieldwork including ~~new~~ sedimentary logging (sections EK-1 and 2) and sampling at East
155 Kirkton Limestone Quarry was carried out in August 2014 (Fig. 2C; Fig. 3), with consent of
156 Scottish Natural Heritage and West Lothian Council. Thirty eight thin sections were
157 examined using Olympus BH2 and Nikon Microphot FX microscopes, and 45 polished slabs
158 were also optically studied. Seven of these specimens came from borehole cores s-named
159 BH-1, BH-2 and BH-3 stored at the British Geological Survey (BGS) at Keyworth, UK. Thin
160 sections were imaged with a flat-bed scanner, and textures were mapped. Eight cuttings were
161 carbon coated and imaged by Scanning Electron Microscopy (SEM) with a Zeiss EVO60 at
162 the University of Hull. False colour Back-Scattered Electron images (BSE) were taken on
163 thin-sections to obtain micro-scale resolution compositional maps enabling delineation of
164 different mineral phases (carbonate, clay, volcanic) and their featureelements (~~carbonate,~~
165 ~~clay, volcanic~~). An Oxford Instruments Peliter-cooled type X-Max 80 EDX system was used
166 to determine the abundance of specific elements through Energy Dispersive X-ray
167 Spectroscopy (EDX) in thin-sections and cuttings. X-ray powder diffraction data were
168 collected from ground samples mounted in stainless steel sample holders. A PANalytical
169 Empyrean diffractometer operating in Bragg-Brentano geometry with copper $K\alpha_1$ ($\lambda =$
170 1.54060 \AA) and a PIXEL detector was used for data collection. Sediment particle
171 morphologies were described following Blott and ~~Kenneth~~ Pye (2008). The term ‘oncoïd’ is
172 used *sensu* Flügel (2004): ‘unattached, rounded, calcareous nodules exhibiting concentric
173 layers and overlapping laminae around a core’.

174 Photograph-based outcrop panels were annotated to recognise the architectural relationships
175 within the sedimentary succession recorded from field (EK1, 2) and borehole core data (BH-1,
176 2 and 3). Existing BGS borehole log annotations were also integrated to complement the
177 absence of core record from BH-1, 2 and 3. Paleontological and sedimentological
178 descriptions from previous works (Clarkson et al. 1993; Rolfe et al., 1993), and other log
179 observations (illustrated in Goodacre, 1999) ~~are~~ were also combined with the new results in
180 this ~~manuscript~~ study.

182 ===== FIGURE. 3 HEREBOUTS =====

184 4. FACIES DESCRIPTIONS

185 Six facies have been identified and characterised on the basis of lithology and/or sedimentary
186 attributes. These facies are listed in Table 1, illustrated in Figs. 4, 5 and 6, and their outcrop
187 architecture shown in Fig. 7: (1) Laminites, (2) ~~Spherulitic g~~ Spherulitic Grainstone-packstone of
188 ~~spherulitic grains, intraclasts and crusts~~, (3) ~~Shrubby Spherulitic cementstone carbonate~~
189 ~~build-ups~~, (4) Volcanic and intraclastic calcareous tuffs, (5) ~~Layered carbonates~~ Intraclastic
190 wackestone-floatstone, and (6) Shales.

192 ===== TABLE. 1 HEREBOUTS =====

193 4.1. Facies 1: Laminites

194 Laminites are organised in 5 to 50 cm-thick, dark brown to yellowish, tabular and laterally
195 continuous beds. ~~Macroscopic evidence of soft sediment deformation (slumps) is present in~~
196 ~~the central portion of the quarry (Fig. 3B, C, D). Laminites yielded a diversity of fossils such~~
197 ~~as amphibians, scorpions, eurypterids, myriapods, ostracods, plant and wood remains (Wood~~
198 ~~et al., 1985; Clarkson et al. 1993; Rolfe et al. 1993; Ruta and Clack, 2006). Laminites are in~~

199 ~~tuff~~ made up of a sub-millimetre alternation of carbonate, organic and silica laminae (Fig. 3,
200 4; Table 1) packaged into couplets of up to 4 cm-thick carbonate-rich layers alternating with
201 up to 3 cm-thick organic or fine-grained silica-rich layers. Microscopic deformation of
202 laminae couplets (convoluted) and macroscopic evidence of soft-sediment deformation
203 (slumps) is common in the central region of the quarry, decreasing in abundance towards the
204 SSE (Fig. 3A to D). Laminites yielded a diversity of fossils such as amphibians, scorpions,
205 eurypterids, myriapods, ostracods, plant and wood remains (Wood et al., 1985; Clarkson et al.
206 1993; Rolfe et al. 1993; Ruta and Clack, 2006). Spherulitic components (see Section 6) were
207 recognised within organic laminae (Fig. 4D, E), the latter pinching out towards the edges of
208 the grains (Fig. 4E). Spherulitic grains were less commonly found in association with
209 carbonate laminae. ‘Spherulitic laminites’ are laminites notably rich in spherulitic
210 components (Fig. 4D, E). The laminite facies was recorded in boreholes BH-1 to 3 and in
211 EK-1 and 2 (Fig. 7). This facies is equivalent to the ‘Laminated limestones’ of Rolfe et al.
212 (1993).

213 *Carbonate laminae* (Fig. 4A, ~~B~~) are made of 30_μm to 1000_μm-thick pale to dark brown,
214 wrinkled to flat, continuous micritic to micro-sparitic calcite bands. Individual sparitic calcite
215 crystals can be up to 100 μm in diameter, having rhombohedral shapes and mosaic fabrics.
216 Remains of fish scales are present but scarce. Evidence of micro-faulting and micro-
217 disruption was also recognised in some intervals. Walkden et al. (1993) recorded average
218 element concentrations of 5920 ppm for Mg, 10962 ppm for Sr, 7585 ppm for Fe, and 387
219 ppm for Mn.

220 *Organic-rich laminae* (Fig. 4A, B, D, E) are made up of 7_μm to 1500_μm-thick dark brown,
221 wrinkled to undulated, continuous, particulate detritus-rich laminae. Backscatter electron
222 imaging revealed irregular darker patches of iron oxide minerals up to 50_μm in diameter,

223 euhedral pyrite crystals 5-6 μm in diameter, and framboidal pyrite aggregates of up to 20 μm
224 diameter (Fig. 4C). Ostracod carapaces and plant remains were also recorded.

225 *Silica laminae* (Fig. 4B, D) are composed of up to 350 μm -thick ~~cloudy-dark~~ brown, spatially
226 irregular ~~crystalline-amorphous vitreous~~ silica bands conformably interlayered with carbonate
227 and organic laminae. Silica is ~~isotropic-glassy~~ in cross-polarized light, and laminae show
228 inclusions of single euhedral and patchy subhedral calcite crystals and cracks filled by calcite
229 (Fig. 4B) (McGill, 1994).

231 ===== FIGURE. 4 HEREBOUTS =====

232
233 **4.2. Facies 2: Spherulitic grainstone-packstone ~~of spherulitic grains, intraclasts and~~**
234 **crusts**

235 This facies consists of 5 to 80 cm-thick, grey, spatially discontinuous layers of grainstone-
236 packstone exhibiting poorly to moderately ~~well~~-sorted spherulitic grains (FIG. 5A, see
237 Section 6), ranging from fine to coarse sand size, and well-rounded to angular texture (Fig.
238 5B). Sub-angular volcanic ~~litho~~intraclasts averaging 2 cm in diameter and rare fragments of
239 stacked fans (see Section 6) averaging 1 cm in diameter were also recognised. In some cases,
240 a finer sub-centimetre scale alternation of spherulitic grains (coated grains and intraclasts, see
241 Section 6) was observed. Packstone matrix is composed of red-brown, fine-grained
242 amorphous Mg-Si phase rich in Mg, Al and Fe, as determined by X-ray diffraction and EDX
243 spot analyses (see Facies 4). In some cases, millimetre-thick alternations of Spherulitic Crusts
244 (see section 6) and Mg-Si bands were recognised. Amorphous Mg-Si phases are commonly
245 replaced by ferroan blocky to granular calcite cements following vein-like structures (FIG.
246 5B). This facies was identified in the central part of the quarry (BH-2 and EK-1, Fig. 7) being
247 very rare in the SE part.

248

249 **4.3. Facies 3: ~~Shrubby carbonate build-ups~~Spherulitic cementstone**

250 This facies is represented by up to 2 m-thick and 3 m-wide, dark grey, un-fossiliferous
 251 carbonate units with distinctive dome-shaped to lenticular morphologies and limited lateral
 252 continuity towards the SSE of the quarry (FIG. 5C, D, E). According to Clarkson et al., (1993)
 253 this facies extended laterally at least 50 m to the west of BH-2 (Fig. 7). Two main metre-thick
 254 ~~shrubby~~ build-up intervals were identified in BH-2 and EK-1, although tiny centimetre-thick
 255 layers were reported interbedded within Facies 1 (EK-1). This facies is sandwiched between
 256 Facies 1 and 4 (FIG. 5C, D), and in some outcrops it passes laterally into Facies 2 (seen in
 257 BH-2 and EK-1, Fig. 7). ~~Shrubby-Spherulitic cementstone build-ups~~ encompass a ‘clotted’
 258 carbonate texture formed by calcite stacked fan ~~calcite~~ fabrics (see Section 6) ~~and developing~~
 259 millimetre to centimetre-sized, crackle to mosaic pack-breccias filled by pale white silica
 260 quartz/chalcedony cements (FIG. 5F). This facies was only recorded in the NW and central
 261 part of the quarry and it is equivalent to the ‘Massive limestones’ of Muir and Walton (1957)
 262 and Rolfe et al. (1993).

264 ===== FIGURE. 5 HEREBOUTS =====

266 **4.4. Facies 4: Volcanic tuffs and intraclastic calcareous tuffs**

267 This facies consists of 5 cm to 5 m-thick, green to yellow, nodular and discontinuous beds of
 268 epiclastic tuffs interbedded throughout the entire succession, though more abundant and
 269 thicker units were identified at the top of the sequence (Fig. 7). These deposits can reach up
 270 to 7 m-thick in BH-1 and 3.3 m-thick in BH-2. Volcanic tuffs display a fabric of coarse-
 271 grained lapilli clasts (up to 15 mm in diameter) floating in poorly sorted fine-grained
 272 vesicular or amygdaloidal ash with shards (FIG. 6A left). Lapilli clasts exhibit a porphyritic

273 fabric of plagioclase, augite, olivine and magnetite phenocrysts (Fig. 6B). Calcite
274 pseudomorphs after olivine are also present. EDX spot analyses of lapilli show ~~an~~ abundance
275 of Al, Ti and Ca, and minor amounts of K, Mg and Fe (FIG. 6D). Petrographic and chemical
276 analysis points to a basaltic to basanitic composition. Furthermore, centimetre to decimetre-
277 thick (averaging 20 cm in thickness), greenish to dark grey, heterogeneous layers of
278 intraclastic calcareous tuffs were systematically recorded ~~systematically~~ intercalated within
279 Facies 1 in EK-1 and 2, and BH-1, 2 and 3 (Fig. 6A right; Fig. 7). These layers display sharp
280 and erosive basal contacts, normal grading and load casts. ~~Coarse-grained intervals~~ Intraclastic
281 calcareous tuffs comprise moderately sorted, poorly rounded, coarse sand to coarse pebble-
282 sized fragments of volcanic tuffs, coarse sand-sized spherulitic grains and intraclastic
283 carbonate laminae (Facies 1) embedded in, ~~and~~ submillimetre-thick patches of irregularly
284 banded amorphous Mg-Si minerals (kaolinite-serpentine group) as indicated by X-ray
285 diffraction analyses (Fig. 6C). Fine grained intervals are normally made up of well sorted,
286 very fine to medium sand-sized, dark black volcanic ash. Up to 6 m-thick basaltic bodies are
287 reported at the top of BH-1 (~~borehole annotations are reprinted in Fig. 7~~) though such rocks
288 were not stored at Keyworth (borehole annotations are reprinted in Fig. 7). Overall, this
289 facies is equivalent to the Geikie Tuff unit of Rolfe et al. (1993).

4.5. Facies 5: ~~Layered carbonates~~ Intraclastic wackestone-floatstone

292 This facies comprises centimetre to decimetre-thick (up to 15 cm-~~thick~~) continuous, nodular
293 to tabular wackestone to floatstone layers (Fig. 6E, F) commonly observed in the upper parts
294 of EK-2 and BH-3, but decreasing in abundance towards the NW of the quarry (FIG. 7). In
295 some cases normal graded beds (wackestone grading to floatstone), and macroscopic and
296 microscopic evidence of soft-sediment deformation was identified (slumps and convolute
297 beds). Carbonate allochems comprise millimetre-sized contorted laminae intraclasts (Facies

1) peloids, fish scales, ostracod shells, and very rare spherulitic components floating in a micritic matrix. SEM BSE analyses reveal abundant euhedral pyrite framboids (up to 6 µm in diameter), and kerogenous matter both within laminae intraclasts and the carbonate matrix. This facies is partially equivalent to the Little Cliff Shale of Rolfe *et al.* (1993).

4.6. Facies 6: Shales

This facies is constituted by up to 6 m-thick, blue-grey, laterally variable, organic-rich shales (Fig. 5E). They were recognised in the upper parts of BH-1, BH-3 and EK-2, thinning laterally northwards (Fig. 7). ~~This facies~~It contains sporadic [thin continuous horizons of centimetre-thick ironstone bands and concretions forming thin continuous horizons](#), and a wide array of fossiliferous remains such as bivalves (*Curvirimula scotica*), fish scales and skeletons (actinopterygians, acanthodians, and sharks), ostracod shells (*Carbonita*), arthropod cuticles, spores, lycopsids (*Lepidodendron*), and other foliage remains (Rolfe *et al.*, 1993; Clarkson *et al.*, 1993). Shales alternate with Facies 5 as seen in EK-2 (Fig. ~~6E5F~~) though Facies 4 can also be sporadically interbedded within shales (e.g. BH-1). This facies is comparable to the ‘Little Cliff Shale’ described by Rolfe *et al.* (1993).

===== FIGURE. 6 HEREBOUTS =====

5. FACIES SUCCESSIONS

At outcrop and borehole scale, lithofacies are stacked repeatedly, forming metre-thick small-scale, usually asymmetrical cycles (Fig. 7, 8). ~~These elementary cycles can be viewed as parasequences (sensu Spence and Tucker, 2007). The East Kirkton sedimentary succession is built by~~ The stacking of these ~~basic units~~[cycles build up the East Kirkton sedimentary succession. Parasequences which](#) were distinguished on the basis of their bounding surfaces

323 | and/or abrupt facies changes. ~~F~~, and four types were recognised across the carbonate system
1
2 324 | studied (labelled A, B, C, and D).
3
4

5 325

7 326 | **5.1. Type-A ~~Parasequence Cycle~~**

9 327 | The thickness of this asymmetrical cycle varies between 1 and 3_m. It is composed of

11 328 | millimetre to centimetre-thick shaly layers (Facies 6) (FIG. 7, 8), followed by up to 2.5_m-

13 329 | thick ~~shrubby carbonatespherulitic cementstone~~ build-ups (Facies 3) which is sharply

15 330 | overlain by up to 1 m-thick beds of grainstone-packstone of spherulitic grains (Facies 2).

17 331 | Evidence for paleosols or paleokarst horizons is lacking, despite this ~~parasequence cycle~~ was

19 332 | appearing to locally develop on top of an erosional surface ~~ve-uneconformity~~ (as seen in EK-1).

21 333 | This type of ~~parasequence cycle~~ can contain up to 15 cm-thick intraclastic calcareous tuff

23 334 | layers (Facies 4) intercalated within Facies 2, centimetre-thick levels of grainstone-packstone

25 335 | of spherulitic grains (Facies 2) and rare centimetre-thick spherulitic-shaly limestone beds

27 336 | (Facies 6) intermingled within Facies 3. Type-A ~~parasequences cycles~~ were exclusively

29 337 | recorded in the NW part of the quarry (EK-1 and BH-2, Fig. 7).
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34 338

36 339 | **5.2. Type-B ~~parasequence Cycle~~**

38 340 | This type of ~~cycle parasequence~~ is constituted by up to 1.5_m-thick strata bounded by sharp

40 341 | surfaces and forming asymmetrical ~~eyessequences~~ (Fig. 7, 8). They are constituted by a

42 342 | lower part of up to 1.1m-thick spherulitic laminite beds (Facies 1) grading upwards towards

44 343 | up to 40 cm-thick of grainstone-packstone of spherulitic grains (Facies 2). Type-B

46 344 | ~~parasequences cycles~~ were only recognised in the central part of the quarry (EK-1) (Fig. 7).
48
49
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51 345

53 346 | **5.3. Type-C ~~parasequence Cycle~~**

347 These basic accretional units are made up of 1 to 3_m-thick packages bounded by sharp
348 flooding surfaces. This asymmetrical [parasequence-cycle](#) is composed by a lower portion of
349 up to 1_m-thick (typically <25 cm-thick) organic-rich shales (Facies 6) commonly overlain by
350 up to 2_m-thick upper portion constituted by coarse-grained calcareous tuffs (Facies 4)
351 grading to spherulitic laminites (Facies 1) (Type-C1, Fig. 7, 8). Facies 4 tend to show basal
352 sharp erosional surfaces or undulating contacts due to plastic buckling on top of shale beds.
353 In some cycles, laminites are notably devoid of spherulitic grains defining Type-C2
354 [cyclesparasequences](#). Type-C1 [parasequences-cycles](#) were recognised in the NW part of the
355 quarry (BH-2, EK-1 and BH-1) while Type-C2 were identified in the SE region (BH-3 and
356 EK-2) (Fig. 7).

5.4. Type-D [parasequence-Cycle](#)

359 These elemental cycles are constituted by up to 6_m-thick strata bounded by sharp facies
360 contrasts or flooding surfaces (Fig. 7, 8). They are organised by a metre-thick lower shale-
361 rich package (Facies 6) or laminites with absence of spherulitic grains (Facies 1) occasionally
362 alternating with centimetre-thick intraclastic calcareous tuff levels (Facies 4), and an upper
363 interval formed by an alternation of [intraclastic wackestone-floatstone layered carbonates](#)
364 (Facies 5) and shales (Facies 6). Type-D [cycles parasequences](#) were preferentially recorded in
365 the upper and SSE part of the quarry (EK-2 and BH-3) (Fig. 7).

367 ===== FIGURE. 7 and 8 HEREBOUTS =====

6. PETROGRAPHY OF SPHERULITIC COMPONENTS

370 Spherulitic components are characterised by a recurrent combination of several crystal fabrics:
371 Fibrous Calcite, Spherulitic Calcite, [Botryoidal Calcite](#), and Subhedral Silica (Table 2).

372 The Fibrous Calcite (*sensu* Schroeder, 1972; Longman, 1980, or Mazzullo, 1980) (FIG. 9A)
373 consists of needle-like and radially divergent crystals with length-to-width ratio of ~9.2:1
374 (>6:1 according to Folk, 1965) and typically average lengths and widths of ~83 μm and ~9
375 μm respectively. In some cases, pervasive corrosion ~~followed by silica replacement~~
376 obliterated the characteristic fibrous terminations (FIG. 9A).

377 Spherulitic Calcite (*sensu* Schroeder, 1972; Davies, 1977, or Verrecchia et al., 1985) is
378 made up of dense spheroidal ~~to botryoidal~~ coatings constituted by elongated, rectilinear fibro-
379 radial calcite polycrystals with their *c* axes radiating from a previous substrate, and exhibiting
380 sweeping extinction (FIG. 9B, C, D; 10A, C). A characteristic feature of Spherulitic Calcite
381 crystals is their epitaxial growth on top of Fibrous Calcite, or ~~other~~ Spherulitic Calcite ~~bodies~~
382 (Fig. 9A, 9F). ~~Polycrystals in~~ Spherulitic ~~C~~calcite ~~polycrystals~~ are between ~~80 μm to 2 mm-~~
383 ~~length 100 μm to 1mm-~~length and up to ~10 μm -width. ~~Trace element analyses indicate a~~
384 ~~low-Mg ferroan composition (average Mg content of 14345ppm), and Sr, Fe and Mn~~
385 ~~concentrations averaging 11500, 3400 and 390ppm respectively (Walkden et al., 1993).~~

386 ~~Botryoidal Calcite (*sensu* Davies, 1977; Ginsburg and James, 1976) is comprised by~~
387 ~~elongated and radially divergent calcite polycrystals (80 μm to 2mm length, and up to 10~~
388 ~~μm width in average) generating botryoidal fans with sweeping extinction (FIG. 9C).~~

389 ~~Botryoidal fans are nucleated upon previous surfaces and competitive crystal growth between~~
390 ~~fans is observed (FIG. 9C).~~ Spherulitic Calcite ~~and Botryoidal Calcite~~ coatings exhibit
391 corrosion scars characterised by dentate or irregular surfaces (FIG. 9D, E). Younger
392 generations of these fabrics were nucleated on previous surfaces, and sometimes they grew in
393 optical and lattice continuity with the older crystals. In so doing they left subtle concentric
394 lines between each growth stage (FIG. 9F). ~~Trace element data shows a low-Mg ferroan~~
395 ~~calcite composition (average Mg content of 10550ppm), and Sr, Fe and Mn concentrations~~
396 ~~averaging 8690, 5097, and 600ppm respectively according to Walkden et al. (1993).~~ Trace

397 element analyses indicate a low-Mg ferroan composition (average Mg content of 14345ppm),
398 and Sr, Fe and Mn concentrations averaging 11500, 3400 and 390ppm respectively (Walkden
399 et al., 1993).

400 Subhedral Silica is recognised as up to 40 µm diameter crystals that exhibit single-crystal and
401 undulose extinction (FIG. 9A, C; 10D up) and partially ~~seen~~ replac~~ing~~ Fibrous Calcite, and
402 less commonly replac~~ing~~ Spherulitic ~~or Botryoidal~~ Calcite.

404 ===== TABLE 2. HEREBOUTS =====

406 **6.1. Petrography of Spherulitic Coated Grains**

407 In two-dimensional sections, these grains display diverse sizes and morphologies (Table 2).

408 Two types of particles were recognised according to their outlines. Around 85% are Type 1
409 Coated Grains, described as circular to sub-circular (50 to 700 µm-diameter) with rounded to
410 sub-rounded corners and edges, and irregular and/or abraded outlines (FIG. 9B, 10A, C). The
411 remaining 15% are Type 2 Coated Grains, which have elongated outlines (up to 4 mm length)
412 and similar roundness and irregularities to Type 1 (FIG. 9C, 10C, D). Most grains have
413 allochthonous particles in their cores, commonly lycopsids, ferns, gymnosperms or algal
414 fragments, and less frequently volcanic grains and peloids (FIG. 10D). Core dimensions
415 average between 50µm to 3 mm in length and their shape are curled, elongated or sub-
416 circular.

417 Physical characteristics of cores are closely linked to the final external morphology of these
418 grains. Type 1 exhibit arcuate to spheroidal cores such as foliage particles and ash fragments
419 of 50µm to 700µm in length, and length to width (L:W) ratios of 2:1 (Fig. 4E; 9B). Type 2
420 have elongated and non-spheroidal cores such as plant debris with lengths up to 4mm, and
421 L:W ratios >2:1 (Fig 9C, 10D). Although some grains appear to lack cores, this likely reflects

422 that the plane of the thin-section did not cut through the particle core, or that core size was
423 very small (e.g. Fig. 9B, 10C).

425 ===== FIGURE. 9 and 10 HEREBOUTS =====

426
427 Spherulitic Coated Grains are composed of Fibrous Calcite, ~~Subhedral Silica, and~~ Spherulitic
428 Calcite ~~or Botryoidal Calcite fabrics~~. Microscopy including SEM—EDX analyses revealed
429 the absence of Mg-Si mineral inclusions within Spherulitic ~~and Botryoidal~~ Calcite. Fibrous
430 Calcite formed widespread calcite fringe coatings that nucleated on and grew normal to the
431 core surface (FIG. 9A and 10D). Spherulitic Calcite ~~or Botryoidal Calcite~~ was epitaxially
432 nucleated upon Fibrous Calcite templates or on antecedent Spherulitic Calcite coatings. In
433 some cases, pervasive corrosion of these crystals is later filled by Subhedral Silica. This
434 adversely affected the continuity and terminations of fibrous crystals (FIG. 9A, ~~C~~ and 10D).
435 Type 1 grains were dominated by Spherulitic Calcite adopting spheroidal coatings, whereas
436 non-spheroidal, elongated Type 2 grains were normally made of Spherulitic Botryoidal
437 Calcite displaying botryoidal fan-shaped coatings. ‘Oncoidal’ forms were represented by the
438 <5% of studied grains where concentric generations of Spherulitic Calcite grew in optical
439 and lattice continuity around a core (FIG. 9F).
440 Some Spherulitic Calcite fibres experienced deflection during later stages of growth, and this
441 is visible where crystals reached >1mm in length (FIG. 10A, B). These deviations imparted
442 arcuate crystal terminations to the spherules. Some other grains have polished, and irregularly
443 dentate outlines (FIG. 10C).

445 6.2. Petrography of Spherulitic Crusts

446 These crusts (FIG. 11; Table 2) are made up of a first generation of Fibrous Calcite fabrics
447 nucleating from core nuclei, and a second phase constituted by Spherulitic Calcite.
448 Spherulitic Calcite encapsulated carbonaceous filaments (mono-specific, dark brown, double
449 walled filamentous structures and their fragments) (FIG. 11A to D). Preserved carbonaceous
450 filaments displayed circular to prismatic outlines in transverse cross-sections (~50_μm in
451 diameter) and elongated, parallel and smooth outlines in longitudinal cross-sections (at least 4
452 mm in length). Outer boundaries of Spherulitic Calcite bundles overlap and are fused together,
453 defining distinct planes (FIG. 11D). These planes display dissolution cavities filled by Mg-Si
454 phases-minerals that in turn were replaced by younger Spherulitic Calcite (FIG. 11C, D).
455 Spherulitic Crusts were overlain by filament-free Mg-Si-rich layers (FIG. 11A).
456 Circular to sub-circular abraded fragments of Spherulitic Crusts were found in Facies 1 and 4.
457 In these cases, the tubular moulds left by the decay of the filamentous inclusions became
458 filled by sparite (FIG. 11E, left) or amorphous Mg-Si minerals (FIG. 11E, right). Crusts were
459 also seen growing around nuclei made of coated grains (FIG. 11F). Deflection of calcite
460 fibres around algae objects was common-observed (Fig. 11F, inset)

===== FIGURE. 11 HEREBOUTS =====

6.3. Petrography of Spherulitic Intraclasts

465 Two types of Spherulitic Intraclasts were recognised: Type 1 (90% in abundance), sub-
466 millimetre-sized individual objects, and Type 2 (10% in abundance), millimetre-sized
467 tubiform objects (FIG. 12; Table 2).

468 Type 1 comprised elongated particles (100 to 500_μm long) constituted by laterally stacked
469 Botryoidal-Spherulitic Calcite fans. Each intraclast measured up to 20-30 μm in width and
470 most exhibited flat and smooth bases (Fig. 12A). Some bases had slightly irregular and

1 471 corroded boundaries. Type 2 comprised individual tubiform particles reached 4 mm in length,
2 472 and up to 2 mm in width, each exhibiting an outer layer of laterally and vertically-stacked
3
4 473 Spherulitic Botryoidal Calcite. The latter have dimensions of 100 to 500 µm in width (Fig.
5
6
7 474 12B, C). In some cases, corrosion cavities within Spherulitic Intraclasts were filled by
8
9
10 475 Spherulitic Crusts (FIG. 12C, D, E). Spherulitic Botryoidal Calcite fans can rarely
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12 476 incorporate fragments of carbonaceous filaments. In such cases, calcite fibres around
13
14 477 filaments displayed deflected growth trajectories (FIG. 12F).
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17 478
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19 479 ===== FIGURE. 12 HEREBOUTS =====
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24 481 **6.4. Petrography of Stacked Fans**

25
26 482 Carbonate ‘clots’ of Facies 3 (Spherulitic cementstones) are constituted by ‘~~shrub~~botryoidal-
27
28 483 like’ growths of laterally and vertically-stacked Spherulitic Botryoidal Calcite. Individual
29
30 484 fans reach 100 to 1000 µm thick, and 100 to 3000 µm in width (FIG. 13; Table 2).
31
32

33
34 485 Composites of laterally-aligned fans have lengths of several centimetres. Some Spherulitic
35
36 486 Coated Grains served as initiation points for these fans. Scalloped solution pits and vertical
37
38 487 cracks up to 200 µm deep were observed on top surfaces (Fig. 13B, C). These corroded areas
39
40
41 488 were successively epitaxially covered by lighter and turbid and pale brown Spherulitic
42
43 489 Botryoidal Calcite (FIG. 13D). In some cases, chert replaced corroded fans (FIG. 13E). 10 to
44
45 490 50µm-thick continuous silica laminae separates some of the Spherulitic Botryoidal Calcite
46
47 491 fans (FIG. 13C). Centimetre-sized crackle to mosaic pack-breccia interclast voids were filled
48
49 492 with fibro-radial ~~chert~~ chalcedony cement (FIG. 13F).
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51

52
53 493 Though Goodacre (1999) identified filamentous carbonaceous inclusions within stacked fans
54
55 494 ~~that were~~ attributed to cyanobacterial remains, none were found in our samples, resulting in
56
57 495 similar calcitic ‘shrubby’ textures to those illustrated in ‘Pre-Salt’ Campos Basin (Herlinger,
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2016). However, intra-crystalline micro-porosity filled by kerogenous matter was observed in the calcite fans as suggested by EDX and BSE analyses (FIG. 13A).

===== FIGURE. 13 HEREABOUTS =====

7. DISCUSSION

7.1. Geochemical considerations

The occurrence of amorphous magnesium-silicate minerals in association with intraclastic calcareous tuffs (Facies 4) is not surprising. Alteration of Mg-rich silicates (e.g., pyroxene or olivine) from alkaline and ultramafic igneous rocks can have generated a range of Mg/-Si-rich phyllosilicate phases such those ~~observed-recorded~~ in East Kirkton and probably in the 'Pre-salt' lacustrine basins (Rogerson et al., 2017). According to XRD and EDX analyses such Mg-Si phases are compositionally similar to minerals of the kaolinite-(a-'serpentine group-like', --product according to XRD analyses[(Mg,Fe)₃ Si₂O₅ (OH)₄]. Climatic-influenced wWeathering by infiltrating waterprocesses may have ~~favoured-triggered~~ the hydrolysis of basaltic lavas favours the formation of of the Bathgate Hills volcanic formationhydrous magnesium iron phyllosilicates (see Rogerson et al., 2017Smith et al., 1993; Whyte 1993). A tropical and humid climate is supported by the abundant lycopod and fern vegetation surrounding the lake margins (Clarkson et al., 1993; Scott et al., 1993). Furthermore, water-rock ~~weathering~~ interactions can have raised the pH and increased the alkalinity of the aqueous solutions sourcing the East Kirkton lake (Pecoraino et al., 2015; Deocampo and Renaut, 2016;). ~~The abundance of permeable tuffaceous volcanics and volcanic ash may have~~ Enhanced the surface area available forsubstrate hydrolysis ~~and canthe~~ release ~~of~~ alkali cations in solution (Ca, Mg, Sr) encouraging elevated CaCO₃ supersaturation in the lake waters (Rogerson et al., 2017). Moreover, the East Kirkton

521 carbonates (laminites and spherulitic components) showed ~~high trace element contents (Sr, Fe~~
522 ~~and Mn), and also~~ $\delta^{18}\text{O}_{\text{calcite}}$ ~~values of (-11 to -2‰)~~ and $\delta^{13}\text{C}_{\text{calcite}}$ ~~values of (0 to 4‰)~~ values
523 globally indicating precipitation in a meteoric-sourced, dysaerobic to anoxic, volcanic lake
524 (Walkden et al., 1993). The lack of evaporite minerals and the depleted $\delta^{18}\text{O}_{\text{calcite}}$ values
525 questions whether the lake had persistent salinity departures.

527 7.2. Diagenesis and trace element concentrations

528 Subhedral Silica is usually replacing early Fibrous Calcite in those spherules encapsulating
529 carbonaceous filaments. Filament decay may have generated favourable conduits for the
530 circulation of silica fluids into the permeable organic cores producing enhanced silicification
531 within and around Fibrous Calcite crystals soon after spherule formation (Fig. 14). In
532 addition, amorphous silica lamina in laminite facies was interpreted as primary in origin via
533 formation of silica gels because: 1) plastic deformation of slumped silica laminae show no
534 evidence of fracturing, 2) silica laminae is cut by tiny perpendicular cracks leaving the
535 overlying laminae unaffected (*sensu* McGill, 1994) (Fig. 4B).

536
537 Furthermore, the Spherulitic Calcite textures show no evidence of an original aragonite
538 precursor neither the presence of neomorphic calcite fabrics selectively replacing aragonite.
539 Strikingly, spherulitic fabrics contain high Mg and Sr concentrations as occur in the ‘Pre-salt’
540 shrubby carbonates where calcite was hypothesised to be directly precipitated from alkaline
541 lake waters (Saller et al., 2016). Enhanced strontium uptake into calcite minerals originally
542 precipitated in low-temperature alkaline experiments has been reported via initial formation
543 of amorphous calcium carbonate (ACC) precursor phases (Littlewood, et al., 2017). The
544 presence of dissolved Mg^{2+} ions can further stabilise ACC phases thus promoting Sr^{2+}
545 incorporation (Rodríguez-Blanco et al., 2012) and favouring the direct transformation of

546 [ACC into calcite crystals \(Loste et al., 2003; Rodríguez-Blanco et al., 2012\) with high-](#)
1
2 547 [magnesium contents \(Raz et al., 2000; Wang et al., 2012\). The initial formation of ACC can](#)
3
4 548 [be achieved in moderate to high alkalinity environments with concomitant high Mg:Ca](#)
5
6 549 [contents \(Wang et al., 2012\) turning alkaline lake chemistries suitable for potential primary](#)
7
8 550 [precipitation of high-Mg calcites.](#)
9
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11

551 12 551 13 14 552 **7.23. Sedimentology of spherulitic components**

15
16 553 The isopachous calcite rims of Fibrous Calcite grew upon organic cores in conditions
17
18 554 favourable for crystal nucleation. Such conditions may have included elevated pH and high
19
20 555 alkalinity linked to high CaCO₃ supersaturation, perhaps coupled with active water agitation
21
22 556 (e.g. Schroeder, 1972; Longman, 1980) and ~~an~~ abundance of loose carbonaceous material to
23
24 557 form cores (Fig. 14). ~~Both-The epitaxial growth of Spherulitic and Botryoidal Calcite grew on~~
25
26 558 ~~top of epitaxially on~~ Fibrous Calcite indicating that the crystalline substrate played a role in
27
28 559 the development of these fabrics (Fig. 14). Indeed, the shape of the cores in Spherulitic
29
30 560 Coated Grains (Type 1 and Type 2) seemingly dictated the final external morphology (FIG.
31
32 561 10C). Absence of evidence for clay or volcanoclastic inclusions within Spherulitic ~~and~~
33
34 562 ~~Botryoidal~~ Calcite suggest that Spherulitic Coated Grains developed at the sediment-water
35
36 563 interface rather than within the sediment. Absence of conspicuous biological inclusions
37
38 564 further suggests that the type of microbial communities thriving at the time of spherule
39
40 565 formation did not leave noticeable organic remains. Evidence of clay cavity-filling textures
41
42 566 within spherules is here consistent with late corrosion processes. All of this evidence points
43
44 567 to a depositional environment capable of forming packstone, grainstone and floatstone of
45
46 568 Spherulitic Coated Grains regularly agitated by currents and supplied by plant debris
47
48
49 (common nuclei) at or above the sediment-water interface.
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571 ===== FIGURE. 14 HEREBOUTS =====

572
573 | Conversely, Spherulitic Crusts ~~were characterised by their~~ tendency to incorporate
574 | filamentous components into their crystal structure. Petrographic analysis suggests that
575 | Spherulitic Crusts grew within an intertwined framework of filamentous green algae
576 | (*Cladophora*-like) (FIG. 11C, 15). Deviation of the Spherulitic Calcite growth trajectories in
577 | proximity to algal fragments further suggests that crystallite trajectories were affected by the
578 | presence of these objects (Fig. 11F). Overlapping of crystal fans is compatible with
579 | competitive growth of Spherulitic Calcite bundles that ceased when remaining space was
580 | filled. Lack of sediment inclusions indicates that growth occurred above the sediment-water
581 | interface (Fig. 15). In the East Kirkton Lake, very rare Mg-Si mineral occurrences were
582 | recognised and these were found overlaying spherulitic crusts (Fig. 10A). Such phyllosilicate
583 | layers were largely devoid of carbonaceous filaments, consistent with a cessation of algal
584 | production during Mg-Si presence (Fig. 11A; 15).

585 ===== FIGURE. 15 HEREBOUTS =====

586
587 | The ~~Botryoidal-Spherulitic~~ Calcite forming Spherulitic Intraclasts are likely calcite
588 | encrustations on the external surfaces of subaquatic plants and algae or within internal
589 | cavities producing laterally-linked botryoids (Type 1) (FIG. 16). Similarly, tubular spherulitic
590 | aggregates may have originally encrusted macro-algal thallae (Type 2). Subsequent
591 | reworking of the organic templates may have generated intraclastic textures seen in thin
592 | sections (FIG. 12, 16). The predominance of packstone-grainstone textures supports the
593 | contention that water agitation was a factor in their accumulation. Similar fibro-radial crystals
594 | have been reported as forming attached to the trichomes of freshwater cyanobacterium
595 | *Nostoc parmelioides* (Freytet and Verrecchia, 1993), filling the axial voids of the freshwater

596 algae *Zarramenella minorica* (Freytet *et al.*, 1999), or the lysed cells of the green-alga
597 *Cladophoropsis* (Arp *et al.*, 2003).

598

599 ===== FIGURE. 16 HEREBOUTS =====

600

601 Stacked Fan nucleation and growth likely required a static substrate (FIG. 17), and these
602 facies may be partially analogous to stacked botryoidal micro-stromatolitic crusts (20 to
603 60µm-thick) and globular aragonitic fans of Satonda Lake, Indonesia (Arp *et al.*, 2003). The
604 crusts of Arp *et al.* (2003) veneered the outer moulds of green algal filaments and were
605 terminated by smooth, undulating surfaces. East Kirkton Stacked Fans, however, lacked
606 noticeable organic filaments (although these are ~~reported~~ mentioned by Goodacre, 1999),
607 which raises questions over the spatial organisation of active calcite growth and the microbes
608 that will inevitably have been present within this site.

609 Petrography shows epitaxial ~~Botryoidal-Spherulitic~~ Calcite nucleated on previously corroded
610 fans (Fig. 13D), indicating that corrosion occurred during growth ~~of Botryoidal Calcite~~
611 ~~fabrics~~stages, and that sustainable conditions for ~~Botryoidal-Spherulitic~~ Calcite growth re-
612 emerged after short-lived dissolution events (FIG. 17). Lack of clay or volcanoclastic
613 materials within Stacked Fans suggests that they may ~~have~~ formed in an agitated ~~sub~~aqueous
614 environment.

615

616 ===== FIGURE. 17 HEREBOUTS =====

617

618 ~~7.34. Parasequence-Cyclostratigraphy architecture~~ and depositional model

619 ~~Parasequence-Cycle~~ data was integrated with the sedimentological observations of spherulite-
620 bearing lithofacies (Fig. 7) and spherulitic components (Fig. 14 to 17). ~~This~~ allowed ~~ing~~ the

621 reconstruction of ~~the refined~~-depositional model for the East Kirkton sedimentary
622 succession (Fig. 18) ~~and comparisons with the 'Pre-salt' cyclostratigraphic data.~~

623

624 *7.43.1. Littoral environment*

625 Type-A ~~cycles parasequences~~ characterise the shallower lake environments where carbonate
626 production took place in moderate to high energy conditions, perhaps in the littoral to

627 proximal sublittoral setting towards the lake centre. This environment was located on the

628 NNW side of the quarry (Fig 7). Type-A ~~cycles parasequences~~ reflect an initial transgressive
629 phase (Facies 6) overlain by a regressive spherulite-dominated stage (Facies 2 and 3) (Fig 7).

630 The sporadic occurrence of poorly sorted spherulitic grainstone to packstone on top of these
631 cycles points to intermittent low-energy periods enabling co-occurrence with Mg-Si minerals.

632 Spherulitic Coated Grains, Spherulitic Crusts, and Spherulitic Intraclasts were

633 penecontemporaneously nucleated in this setting, which hosted the optimal conditions for

634 nucleation and growth of ~~S~~spherulitic ~~C~~calcite (Fig. 18). Moreover, the fact that Facies 2 and

635 3 are laterally linked or intermingled suggest that they formed in close temporal association.

636 The local erosional truncation underlying Type-A ~~cycles parasequences~~ likely reflects a

637 phase of lake contraction followed by the development of ~~shrubby spherulitic cementstone~~

638 ~~carbonate~~ build-ups during a resumed lake re-flooding (Fig. 7, 8). Intermittent input of

639 undersaturated waters into the lake (*sensu* Driscoll and Newton, 1985; Reuss et al., 1987)

640 could explain some early dissolution features in spherulitic textures. McGill (1994) and

641 Walkden et al. (1993) documented cathodoluminescence banding in spherulitic components

642 that would be coherent with E_H -pH variations of the fluids forming these grains. The shallow

643 water, high energy setting and simultaneous development of ~~shrubby and~~ spherulitic

644 ~~cementstones growths~~ of East Kirkton compares well with ~~similar the~~ 'Pre-Salt' shrubby

645 microbial boundstones from Brazil and Angola, (Saller et al., 2016; Sabato Ceraldi and Green,

646 2016). In East Kirkton, Type-A cycles are similar to those described for the ‘Pre-salt’ by
647 Wright and Barnett (2015), and Sabato Ceraldi and Green (2016). In the latter cases, the
648 laminated argillaceous mudstone is placed at the beginning of the cyclothems (Wright and
649 Barnett, 2015) and considered as formed during transgressive pulses (*sensu* Sabato Ceraldi
650 and Green, 2016) as similarly occur with Facies 6 in this work. In some ‘Pre-salt’ cycles the
651 occurrence of thin spherulitic grainstone with intraclastic shrub material has been reported
652 underlying the laminated mudstone indicating potentially active reworking events before
653 deposition of muddy facies. In the Scottish cycles spherulitic grainstone to packstone
654 represents the most regressive parts accumulated on top of spherulitic cementstone packages
655 or even occurring intermingled within them suggesting a close origin for both facies.

659 *7.43.2. Sublittoral to shallow profundal environment*

660 Type-B and C ~~cycles parasequences~~ define the littoral to sublittoral settings respectively,
661 which were located in the central part of the quarry (Fig 7). Type-B ~~cycles parasequences~~
662 show an initial deepening phase (Facies 1), and a subsequent shallowing phase (Facies 2).
663 More distal Type-C ~~cycles parasequences~~ (C1 and C2) display a transgressive pulse (Facies
664 6), and a regressive stage formed by the stacking of Facies 1 and 4. Normal graded beds with
665 erosive bases are best interpreted as pulses of downslope sediment gravity transport triggered
666 by slumping processes (e.g., Lowe, 1979) generated during regressive intervals (Fig 7, 8).
667 The fold axes of slumps and convolute beds are similarly grouped sub-parallel to one another
668 and parallel to the inferred paleo-slope strike suggesting that soft-sediment deformation
669 (slumping and convolute laminae) was likely triggered by slope gradients to the WNW
670 (Woodcock, 1979; Strachan and Alsop, 2006) (Fig. 7B, Fig. 18).

671 Sub-millimetre scale continuous laminae formed under low energy depositional conditions
672 with limited siliciclastic input. Carbonate laminae are 2 to 4 times thicker than organic
673 laminae, suggesting ~~either~~ brief intervals of carbonate-free sedimentation interrupting
674 ongoing calcite production triggered by photosynthesis in the water column (*sensu* Dittrich
675 and Obst, 2004)~~or else organic sedimentation being slow relative to carbonate accumulation~~
676 ~~in this setting~~. Evidence of chipped and polished spherulitic grains, and abraded spherulitic
677 crust fragments within Type-B and C1 ~~cycles parasequences~~ points to reworking of these
678 components from the shallow lake factory areas (Fig. 18). Likewise, in the ‘Pre-Salt’ sag
679 lakes clay-rich spherulitic facies tend to occur in deeper environments below the platform
680 margin where lower energy enabled the deposition of finer-grained sediments (Saller et al.,
681 2016; Sabato Ceraldi and Green, 2016). Thus ‘Pre-salt’ cycles show spherule-stevensite
682 floatstone packages capped by calcite shrubs framestone beds (Wright and Barnett, 2015) or
683 microbial crusts-reworked spherules in an upward regressive trend (*sensu* Sabato Ceraldi and
684 Green, 2016). Type-B cycles in East Kirkton show similar stratal arrangement though low
685 energy intervals are here dominated by laminites instead of substantial clay beds.
686 Pinching out of organic laminae against spherulitic grains further indicates that East Kirkton
687 grains were systematically buried by muddy sediments (Fig. 4E). Type-C2 cycles
688 ~~parasequences~~ are apparently devoid of spherulitic grains indicating deposition of laminites
689 in deeper environments than Type-C1 (Fig 7). The occurrence of pyrite framboids, preserved
690 biota, absence of bioturbation, and trace element geochemistry (Clarkson et al., 1993; Rolfe
691 et al., 1993; Scott et al., 1993) is consistent with low oxygen conditions.

693 7.43.3. Profundal environment

694 Type-D ~~cycles parasequences~~ indicate sedimentation in a profundal lake setting under low
695 energy conditions found predominantly in the SE part of the quarry (Fig. 7, 18). These ~~cycles~~

696 ~~parasequences~~ display an initial shale-rich deepening interval (Facies 6) followed by
697 carbonate-rich shallowing intervals (Facies 5) (Fig 7). Graded and convolute beds are
698 evidence for gravity flows and reworking of semi-consolidated layers from lake margins to
699 depocentres. Preservation of pyrite framboids and fauna and flora indicates conditions of
700 water stagnation and oxygen depletion. These features imply the bottom was well below lake
701 wave base, which is reliable with earlier suggestions that the lake was of sufficient water
702 depth to sustain sporadic meromictic conditions and support nektonic vertebrate life (Parnell,
703 1988; Loftus and Greensmith, 1988; Clarkson et al., 1993). Similar anoxic conditions were
704 reported in the 'Pre-salt' lakes during the sag 2 microbial interval when organic-rich shales
705 and marls were deposited in the deeper parts (Sabato Ceraldi and Green, 2016).

707 ===== FIGURE. 18 HEREBOUTS =====

709 **7.54. Origin of Spherulitic ~~and Botryoidal~~ Calcite: microbes versus stevensite**

710 Nucleation of Spherulitic ~~and Botryoidal~~ Calcite is a phenomenon that has been linked to
711 bacterial and cyanobacterial activity, as demonstrated through laboratory experimentation
712 (Buczynski and Chafetz, 1993; Verrecchia et al., 1995; González-Muñoz et al., 2000;
713 Braissant et al., 2003; Ercole et al., 2007; Rodríguez-Navarro et al., 2007; Sánchez-Navas et
714 al., 2009; Pedley et al., 2009). Microbial physiological processes (see Arp et al., 2003;
715 Dupraz et al., 2009; Decho 2010) can alter the subaqueous carbonate equilibrium to
716 effectively promote calcium carbonate precipitation that in some cases exhibits spherulitic
717 morphologies (Verrecchia et al., 1995; Rodríguez-Navarro et al., 2007; Arp et al., 2012).
718 However, in hyper-~~saline and calcium limited~~ alkaline systems these metabolic activities are
719 less likely to stimulate substantial calcification (Arp et al., 2001; 2012). In these settings
720 bacterial degradation of the biofilm EPS significantly increases supersaturation and promote

721 calcification (Arp et al., 1999; Dupraz, et al., 2009; Decho, 2010). Indeed, fibrous and
722 radially-divergent aragonite layers are interpreted from lysed green algal structures in
723 Satonda Lake (Arp et al., 2003). Similarly, millimetre-sized aragonite spherulites grew and
724 accumulated within deeper parts of cyanobacterial mats in the Recent Kiritimati Lake where
725 progressive EPS degradation was attributed to spherulite formation (Arp et al., 2012). In all
726 these cases, calcite precipitation will be occurring in environments rich in dissolved EPS,
727 which have been demonstrated to promote spherulite formation (Braissant et al., 2003,
728 Wolthers et al., 2008; Mercedes-Martín et al., 2016). This mechanism is highly likely to be
729 responsible for the abundant spherulitic carbonates at East Kirkton, and the absence of
730 fossilised bacteria suggesting that calcite mineralisation is forming within degrading EPS gels
731 rather than within actively photosynthesising biofilms (*sensu* Trichet and Défarge, 1995; Arp
732 et al., 2003; 2012) and in alkaline lakes (Walkden et al., 1993; Rogerson et al., 2017).
733 Whether EPS molecules are produced from lake bottom-benthic biofilms or being sedimented
734 as polymer gels from planktic-colloidal planktonic material onto the lake bottom (Decho,
735 1990; Hoagland et al., 1993; Passow et al., 2001; Passow, 2002) is unclear, but likely only
736 relevant as an indicator of the water depth at which Spherulitic Calcite formation took place.
737 This mechanism is supported by the abundance of bacterial and micro-algal planktonic
738 organisms known from the Midland Valley Carboniferous oil-shale lakes (Loftus and
739 Greensmith, 1988; Parnell, 1988; Raymond, 1991).

In the ‘Pre-salt’ lakes, stevensite clay was invoked to participate in the growth of calcitic
spherules (Tosca and Wright, 2015; Wright and Barnett, 2015). In East Kirkton, amorphous
clay is limited to tiny occurrences in the sublittoral slope settings where chemical (pH,
alkalinity, saturation index) and physical (low energy) conditions enabled its formation and
accumulation. At the same time, stevensite mineral formation is favoured at high pH, high
salinity and high Mg/Si ratios (Tosca and Masterson, 2014) suggesting that the East Kirkton

746 [lake did not undergo such conditions in low energy zones. Interestingly, the occurrence of](#)
747 [authigenic sparite in laminites \(Fig. 4A\) suggest that the sublittoral region was characterised](#)
748 [by lower pH/ saturation indexes than the littoral zone probably explaining why clay minerals](#)
749 [were volumetrically rare. Nevertheless, examples such as the East Kirkton Limestone](#)
750 [demonstrate that the formation of abundant spherulitic carbonates can be decoupled from clay](#)
751 [influence in alkaline lakes and that ‘microbial-solution’ interactions warrant further research.](#)

753 **7.65. Further hydrological implications**

754 The sedimentary record of the East Kirkton lake displays two incomplete, large-scale
755 deepening-shallowing cycles bounded by an erosional surface [interpreted as an](#)
756 ~~(unconformity) interpreted to have~~ formed in the littoral lake portion (Fig. 7, 8). These larger-
757 scale cycles may reflect a broad deepening pulse, as Type-C2 and D ~~cycles parasequences~~ are
758 progressively more abundant upwards in the sedimentary sequence (Fig 7). A change towards
759 a more humid climate is recorded by the transition from gymnosperm to lycopsid vegetation
760 in the lake margin (Scott et al., 1993), and from tetrapods-arthropods to fishes-ostracods
761 within the lake water (Clarkson et al., 1993), thus the overall deepening trend of the lake
762 appears to reflect increasing ~~fresh~~water incursion. Variable ~~fresh~~water input is also reflected
763 in the wide spectrum of $\delta^{18}\text{O}_{\text{calcite}}$ reported from the ‘Pre-Salt’ spherulitic carbonates of Brazil
764 (-6 to 5‰) and Angola (-2 to 3‰), which fall within a broad range between fresher and more
765 evaporative lake water conditions (Saller et al., 2016; Sabato Ceraldi and Green, 2016).

766 Although the unusual carbonate phases of East Kirkton and the ‘Pre-Salt’ are certainly
767 dependent on sufficiently high calcite supersaturation to form, this is apparently decoupled
768 from evaporation. The lack of sulphates, chlorides, or their calcite/silica pseudomorphs even
769 in the most regressive facies further indicates that the lake was not truly endorheic. It

770 therefore seems unlikely that hydrological closure ~~is~~ was a pivotal precondition for the
771 development of calcitic spherulites (Saller et al., 2016; Sabato Ceraldi and Green, 2016)

773 8. CONCLUSIONS

774 1) A widespread assemblage of calcite spherulitic components (Coated Grains, Intraclasts,
775 Crusts, and Stacked Fans) were formed in a clay-poor, volcanic and alkaline lacustrine
776 system.

777 2) The carbonate factory of spherulitic components was located in the littoral lake region (Fig.
778 18). This setting experienced a combination of high alkalinity, metal-rich hydrochemistry,
779 and microbe-derived organic acid interference with the mineral formation process. These
780 conditions collectively encouraged widespread Spherulitic ~~and Botryoidal~~ Calcite nucleation
781 at the sediment-water interface.

782 3) *Spherulitic Coated Grains* were nucleated at the sediment-water interface on loose organic
783 cores in an agitated environment (Fig. 14). Initial isopachous rims of Fibrous Calcite coated
784 these cores. Spherulitic ~~and Botryoidal~~ Calcite grew epitaxially upon Fibrous Calcite giving
785 the characteristic spheroidal shape to the grains. *Spherulitic Crusts* grew at the sediment-
786 water interface within an intertwined framework of filamentous green algae subsequently
787 buried by amorphous Mg-Si matrices (Fig. 15). *Spherulitic Intraclasts* may have first formed
788 as ~~Botryoidal-Spherulitic~~ Calcite bodies laterally encrusted to organic templates. Later
789 reworking produced the intraclastic accumulations texture (Fig. 16). *Stacked Fans* grew as
790 laterally-stacked, ~~Botryoidal-Spherulitic~~ Calcite nucleated upon static substrates building
791 metre-thick lenticular ~~shrubby-spherulitic cementstones~~ carbonates (Fig. 17). Spherulitic
792 nucleation resumed upon corroded surfaces indicating that conditions of calcite
793 supersaturation alternated with periods of undersaturation. Corrosive events are linked to
794 input of fresher waters into the lake.

795 4) Three lacustrine depositional settings were recognised: littoral, sublittoral, and profundal
796 (Fig. 18). The *littoral* zone was characterised by coeval ~~shrubby-spherulitic~~
797 ~~cementstone~~carbonate build-ups and grainstone-packstone of spherulitic components formed
798 in well-agitated, shallow environment. The *sublittoral* zone was define by metric scale,
799 slumped beds, and sediment gravity deposition triggered by slope gradients. Significant
800 down-slope re-sedimentation of spherulitic grains allowed spherulitic laminites to form in the
801 sublittoral to profundal region. The *profundal* setting was constituted by abundant carbonate-
802 shale alternations with highly preserved fossiliferous remains recording sporadic conditions
803 of water stagnation, oxygen depletion and shedding episodes into lake depocentres.

804

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24 1166 FIGURE CAPTIONS

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27 1167

28
29 1168 **FIGURE 1.** Litho- and chronostratigraphical divisions of the Carboniferous in the Midland Valley of
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31 1169 Scotland. The East Kirkton Limestone area is located in the red square. Modified from Read et al.,
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33 1170 (2002). Ages from Gradstein et al., (2012).
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35 1171

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38 1172 **FIGURE 2.** A) The Midland Valley isopachs during Strathclyde Group deposition ([modified from](#)
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40 1173 [Read et al., 2002](#)). B) Paleogeographic map of the Lake Cadell in the West Lothian Oil Shale
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42 1174 Formation (~~Bathgate Group~~). Extensive volcanic piles divided the Midland Valley into a series of
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44 1175 semi-enclosed lacustrine-lagoonal basins (modified from Parnell, 1988). Marine incursions were
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46 1176 intermittent. C) Geological map of the East Kirkton Limestone area, [modified from Cameron et al.,](#)
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49 1177 [\(1998\)](#).
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51 1178

52
53 1179 **FIGURE 3.** The East Kirkton Limestone Quarry area. A) Photomosaic of the studied quarry and
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55 1180 location of boreholes BH-1, BH-2 and BH-3, and logs EK-1 and EK-2 (inset) (reprinted from McGill,
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57
58 1181 1994). ~~Person for scale.~~ B) [Detail of m](#)Metric-scale slumped beds inclined towards the WNW. C)
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1182 Detail of B showing distorted slumped ~~Facies~~ Laminites. D) Internal soft-sediment deformation
1 within a flat-bounded bed.

1184
1185 **FIGURE 4.** Laminites. A) Left: Flat tabular beds ~~in outcrop showing millimetre thick alternation of~~
1186 ~~carbonate rich layers with organic rich layers.~~ Right: -B)-Internal structure shows (Thicker yellowish
1187 carbonate laminae [C] alternating with thinner darker organic laminae [O] or milky-silica laminae [Si]
1188 in ~~cross~~X-Nichols. B) Composite image of alternating organic laminae [O] with primary silica
1189 laminae [Si] seen vitreous in X-Nichols (left) and milky in plane light (right). Cracks in silica laminae
1190 are filled by calcite (arrow). C) BSE image of pyrite framboids ~~al aggregates~~-(EDX pattern, ~~bottom~~
1191 ~~left inset~~)-embedded in carbonate or organic laminae. D) Spherulitic laminites ~~contain with~~ Spherulitic
1192 Coated Grains [SG] displaying ~~isolated,~~ loosely packed textures ~~mainly~~-within organic laminae. E)
1193 Organic laminae pinches out towards the edges of grains [arrows] displaying thickness variations
1194 across them. ~~Carbonaceous/algal remains constitute the core of some grains (centre)~~-(~~cross~~X-Nichols
1195 image).

1196
1197 **FIGURE 5.** Spherulitic grainstone-packstone and ~~Spherulitic cementstone~~Shrubby carbonate build-
1198 ~~ups.~~ A) Laminated gGrainstone-packstone ~~displaying a laminated fabric made of with~~ spherulitic
1199 grains alternating with thin amorphous Mg-Si ~~layers clays~~ [arrow]. B) Detail of Moderately-sorted
1200 and well-rounded grainstone-packstone of ~~well sorted and well rounded~~-spherulitic grains embedded
1201 in an amorphous Mg-Si matrix [arrow] locally replaced by blocky calcite, in ~~cross~~X-Nichols. C)
1202 Dome-shaped ~~to lenticular~~ spherulitic cementstone shrubby carbonate-build-ups (F3) tilted on top of
1203 slumped layers ~~composed made~~ of laminites (F1), volcanic tuffs (F4) and shales (F6). Original
1204 depositional angles beds are ~~preserved over a steep margin transition~~-inclined towards the left over the
1205 margin. D) An incised surface [dotted line] on top of laminites (F1) is filled by volcanic and
1206 intraclastic tuffs (F4), and overlaid by spherulitic cementstone shrubby carbonates-(F3). E) Detail on
1207 C showing laminites (F1) overlaid by tiny shrubby ‘clotted’ fabrics [arrow] giving rise vertically
1208 evolving to to decimetre thick bodies of spherulitic cementstone shrubby carbonate-build-ups (F3). F)

1209 Polished slab of the spherulitic cementstone ~~shrubby carbonate build-ups~~ displaying ‘clotted’ clast-
1 supported breccias ~~with interclast voids~~ filled with silica cements [red arrow].

4 1211
5
6 1212 **FIGURE 6.** Volcanic and intraclastic calcareous tuffs, Intraclastic wackestone-floatstone layered
7 ~~carbonates~~ and Sshales. A) Volcanic tuffs ~~as they appear~~ in core (BH-2) and intraclastic calcareous
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9 1213 tuffs (~~arrowed in BH-3~~). B) Volcanic tuff ~~in thin section show displaying a~~ porphyritic texture with of
10
11 1214 phenocrysts floating in a cryptocrystalline glassy matrix. Plagioclase (Pg), Clinopyroxene (Cpx) and
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13 1215 Olivine (Ol). C) Floatstone of spherulitic components (Spherulitic Coated Grains, (SG) in a red ~~brown~~
14
15 1216 Mg-Si clay matrix [S]. Lapilli intraclasts [Lap] ~~with show~~ vesicular textures ~~are observed~~.
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17 1217 SerpentineClay-like XRD pattern at the bottom (red spot). D) BSE image of a ~~similar~~ floatstone with
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19 1218 Spherulitic Coated Grains [SG], and lapilli fragments [Lap] ~~embedded~~ in a Mg-Si matrix [S]. EDX
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21 1219 analyses of amorphous Mg-Si phases (~~now serpentine~~, red spots) and volcanic minerals (blue spots).
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23 1220 E) Intraclastic wackestone-floatstone Layered carbonates alternating with ~~dark S~~shales ~~in outcrop~~
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25 1221 (left). ~~Cores from BH-3~~ Cores on the right displaying showing laminites (F1) on top of shales (F6) and
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27 1222 volcanic tuffs (F4) ~~on the right~~ (arrow ~~points~~ to base). F) Detail of E showing Intraclastic wackestone-
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29 1223 floatstone the internal fabric of the layered carbonates. Wackestone floatstone of intraclastic contorted
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31 1224 carbonate laminae ~~are floating~~ in a muddy matrix.

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38 1226
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40 1227 **FIGURE 7.** A) Depositional architecture of a SSE-NNW transect in the East Kirkton Limestone
41
42 1228 Quarry including ~~data from~~ logs (EK-1 and 2) and boreholes (BH-1, 2 and 3). Two large-scale cycles
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44 1229 are identified (~~Cycle 1 and 2~~) and they are in turn composed up to 5 small-scale cycles. Note that
45
46 1230 mMetre-thick basalt layers occur on top of borehole BH-1. B) Location of logs and boreholes ~~over the~~
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48 1231 quarry face. Stereographic projection displaying slump fold polar axes grouped fairly parallel between
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50 1232 ~~one another and~~ to the inferred paleo-slope strike polar projection [blue asterisk].

53 1233
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55 1234 **FIGURE 8.** Key symbols used in figures. Type section at East Kirkton succession (EK-1 and EK-2)
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57 1235 integrating facies, small-scale cycles (SSC), large-scale cycles (LSC), sedimentary environment, lake
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59 1236 level variations and distribution of spherulitic components.

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FIGURE 9. Spherulitic Coated Grains. A) Fibrous Calcite crystals [f] are ~~bordering-fanning out from~~ the carbonaceous cores [c]. Pervasive corrosion and later Subhedral Silica [Ss] obliterated the fibrous terminations. B) Spherulitic Calcite fabric is made of fibro-radial polycrystals growing upon Fibrous Calcite, and producing spheroidal grains (Type 1) (~~erossX~~-Nichols). C) ~~Botryoidal-Spherulitic~~ Calcite ~~consist-growing on top of elongated substrates produced botryoidal fan-shaped coatings on radially divergent polycrystals generating botryoidal fans, and producing non-spheroidal, elongated grains~~ (Type 2 ~~grains~~) in X-Nichols. Subhedral Silica [Ss] cementing decayed organic filaments as seen in a ~~BSE image. Competition for growth space between fans is common.~~ D) Spherulitic Calcite ~~fans and Botryoidal Calcite exhibit show~~ corrosion scars (dotted lines) ~~which acting~~ as nucleation surfaces ~~of renewed generations offrom successive~~ crystals (~~erossX~~-Nichols). E) Detail of D showing resumed ~~Botryoidal-Spherulitic Calcite~~ growth upon dissolution surfaces (dotted lines). Calcite growth directions shown in arrows (~~erossX~~-Nichols). F) Spherulitic ‘oncoids’ are formed by concentric layers of crystals growing in optical and lattice continuity upon subtle previous surfaces (yellow arrows) (~~erossX~~-Nichols). Deflection of ~~calcite~~-fibres in the edges (red arrow) and corrosion surfaces (dotted line) are ~~present~~common.

FIGURE 10. Spherulitic Coated Grains. A) Spherulitic Calcite crystals commonly deflect in later stages of growth [red arrows] (~~erossX~~-Nichols). B) Detail of A showing crystal deflection of spherules [red arrow], and corrosion surfaces [yellow dotted line] overlaid by ~~Botryoidal-Spherulitic Calcite~~ overgrowths (~~erossX~~-Nichols). C) Circular particles (Type 1) display Spherulitic Calcite fabrics ~~growing in a spheroidal fashion~~, whereas elongated particles (Type 2) ~~display show Botryoidal Calcite fabrics botryoidal fan overgrowths~~. Note the carbonaceous core within the elongated coated grain (~~erossX~~-Nichols). D) Elongated algae fragments (top) or ash remains (bottom) ~~can serve as~~ precursor nuclei. Fibrous Calcite fringes (f) and Subhedral Silica (Ss) are ~~observed coating cores seen~~ in cores (~~erossX~~-Nichols).

1264 **FIGURE 11.** Spherulitic Crusts. A) Spherulitic Crusts [SC] are buried by Mg-Si layers [S]. Note
1 sweeping extinction. ~~CrossX-Nichols~~ image. B) Algae filaments ~~display with~~ circular ~~to prismatic~~
2 1265 outlines ~~in (transversal) cross-sections~~ and elongated and smooth outlines ~~in (longitudinal) cross-~~
3 1266 ~~sections and~~ are ~~embedded-trapped within~~ Spherulitic Calcite. C) Boundaries between discrete
4 1267 Spherulitic Calcite bundles are corroded and filled by Mg-Si minerals [arrows]. D) ~~CrossX-Nichols~~
5 1268 image of C ~~displaying with~~ overlapping of crusts ~~showing with~~ sweeping extinction. Mg-Si minerals
6 1269 are replaced by ~~new generations of newer epitaxially grown~~ spherulitic crusts ~~growing on top of older~~
7 1270 ~~crusts~~. E) ~~Algae inclusions~~ ~~Moulds of decayed filaments within spherules can be~~ ~~replaced filled~~ by
8 1271 sparite (left) or ~~filled with~~ Mg-Si minerals [S, arrow]. F) Spherulitic Crust ~~enveloping fanning out~~
9 1272 ~~from~~ a Coated Grain. ~~Calcite-Crystal~~ fibres ~~are~~ deflected around algae inclusions (bottom left, arrow).
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1275 **FIGURE 12.** Spherulitic Intraclasts. A) Packstone of Type 1 Intraclasts formed by elongated
1276 ~~Spherulitic Botryoidal~~ Calcite objects cemented by blocky calcite (c). ~~CrossX-Nichols~~ image. B)
1277 Tubiform Type 2 Intraclasts made of laterally linked ~~Spherulitic Botryoidal~~ Calcite. Tubes are filled
1278 by peloids (Pel) and buried by Mg-Si ~~matrices-clays~~ (S) ~~often~~ replaced by calcite ~~pseudomorphs~~ after
1279 dissolution (top). C) Panoramic view of a tubiform Type 2 Intraclast (outlined in dotted line) filled
1280 with Spherulitic Crusts [SC]. D) ~~Surface of a~~ Spherulitic Intraclast corroded and filled with a
1281 Spherulitic Crust [SC]. E) ~~CrossX-Nichols~~ image of D. F) ~~Spherulitic Botryoidal~~ Calcite ~~incorporated~~
1282 ~~encapsulating~~ filamentous algae. Deflection of calcite fibres is observed on top of the filament.
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1284 **FIGURE 13.** Stacked Fans. A) Laterally and vertically-stacked ~~shrubby 'clotted'~~ forms. Dark patches
1285 are ~~kerogenous organic matter~~. ~~Micro-scale brecciation features~~ filled with silica cements ~~are~~
1286 ~~common~~ [arrows]. B) Scalloped dissolution pits ~~and vertical cracks~~ on top of the Stacked Fans
1287 [arrows]. C) ~~CrossX-Nichols~~ image of B. Note sweeping extinction and thin and continuous silica
1288 ~~laminae-rims~~ outlining previous Stacked Fans [arrows]. D) Corroded Stacked Fans are successively
1289 filled by turbid, pale brown ~~Spherulitic Botryoidal~~ Calcite growing in optical and lattice continuity
1290 [arrows]. E) Chert filling corrosion cavities of ~~individual~~ fans. ~~CrossX-Nichols~~ image. F) Detail in A.
1291 Interclast breccia voids (top) are filled with microcrystalline to fibro-radial/spherulitic

1292 | ~~silicachalcedony. Spherulitic Botryoidal~~ Calcite fans (bottom) are stacked forming positive micro-
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2 1293 | reliefs. ~~Cross~~X-Nichols image.
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7 1295 | **FIGURE 14.** Formation of Spherulitic Coated Grains (top to bottom).
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11 1297 | **FIGURE 15.** Formation of Spherulitic Crusts (top to bottom).
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15 1299 | **FIGURE 16.** Formation of Spherulitic Intraclasts (top to bottom).
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18 1300
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20 1301 | **FIGURE 17.** Formation of Stacked Fans (top to bottom).
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22 1302
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24 1303 | **FIGURE 18.** Depositional model of the East Kirkton Limestone deposit, including sedimentary
25
26 1304 | features and the occurrence of processes, textures and small-scale cycles. Not to scale (See Fig. 8 for
27
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29 1305 | symbols).
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31 1306
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33 1307 | **TABLE 1.** Summary of the facies types.
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38 1309 | **TABLE 2.** Summary of the petrographic features of spherulitic components.
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Figure 1
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Period	Series	Group	Midland Valley					
			Ayrshire & Fife	W Lothian	E Lothian			
Carboniferous	Serpukhovian	Clackmannan Group	Passage Fm. mostly fluvial					
			Bathgate Group	Upper Limestone Fm.	Major marine limestone & incised fluvial sandstones			
				Limestone Coal Fm.	Fluviodeltaic coal-bearing cycles & sandstones			
				Lower Limestone Fm.	Marine to fluviodeltaic			
			Viséan	Strathclyde Group	Bathgate Group	Lawmuir Fm.	West Lothian Oil-shale Fm.	Aberlady Fm.
	Kirkwood Fm.							
	Clyde Plateau Volcanic Fm.	Fluvial & lacustrine: oil-shales in deep, stratified lakes						
	Subaerial basalts from vents & volcanoes	Gullane Fm.				Arthur's Seat Volcanic Fm.	Garleton Hills Volcanic Fm.	
		Fluvial & lacustrine, rare marine incursions						
	Tournasian	Inverclyde group		Clyde Sandstone Fm.				
			Ballagan Fm.					
			Kinnesswood Fm.					

Figure 2

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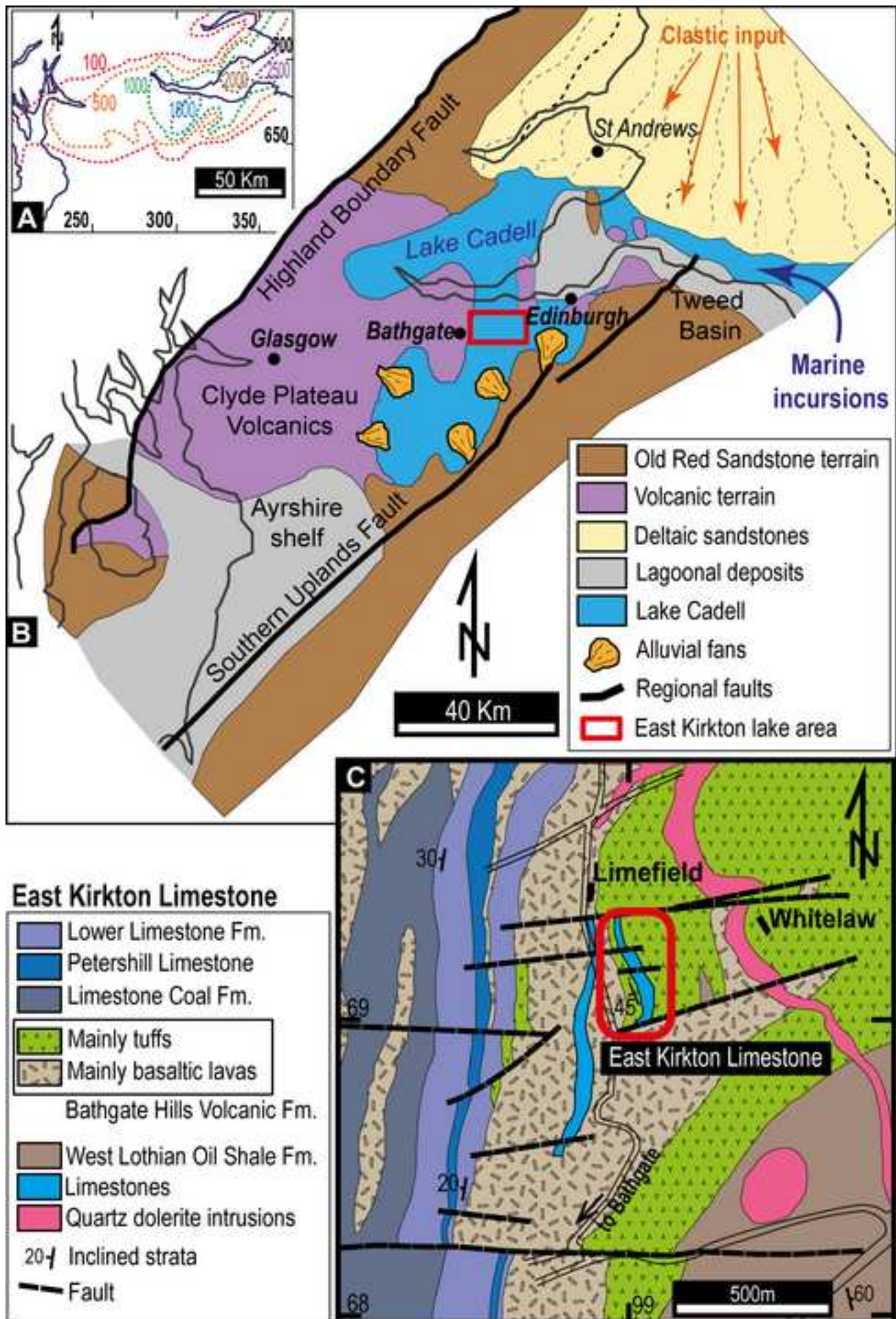


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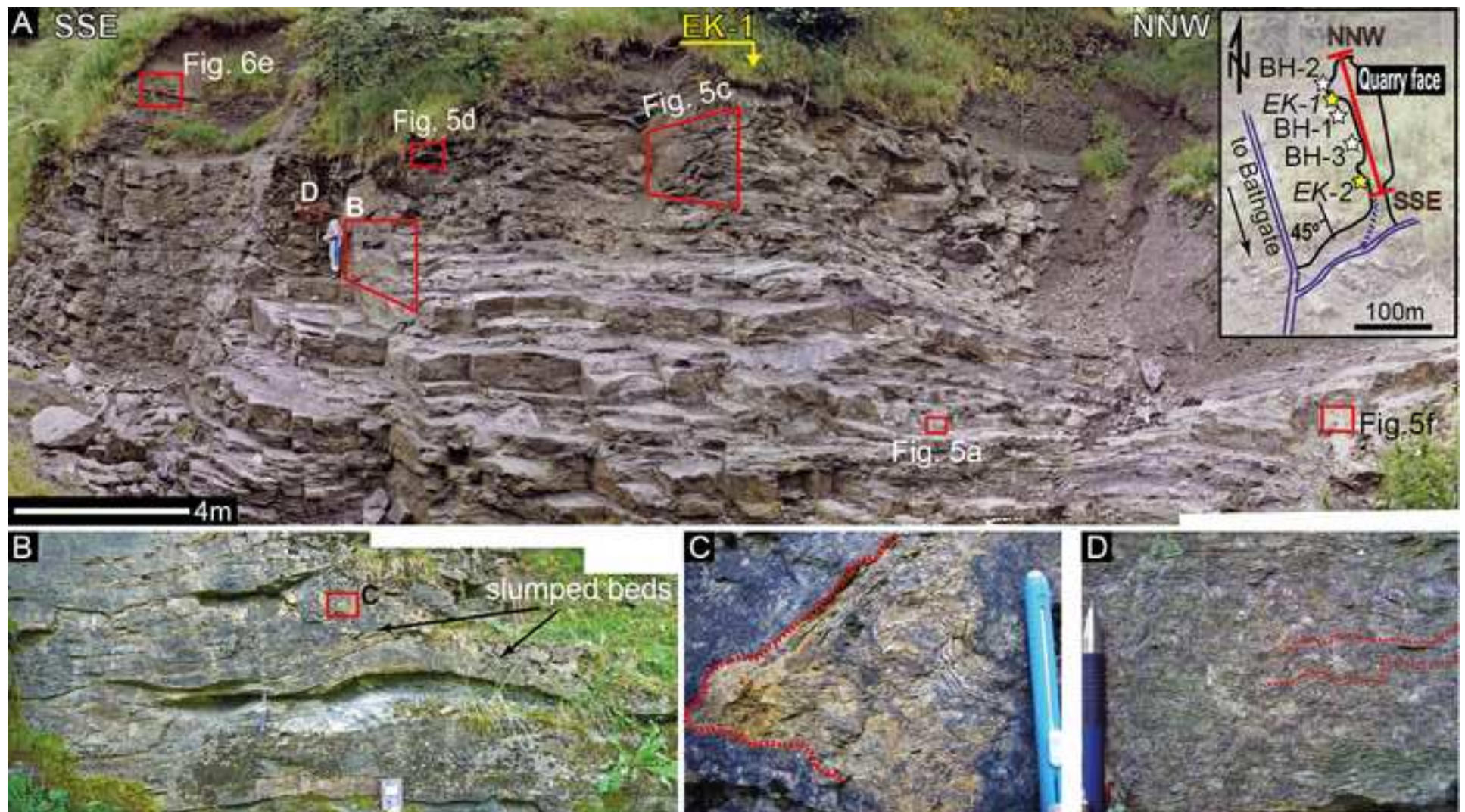


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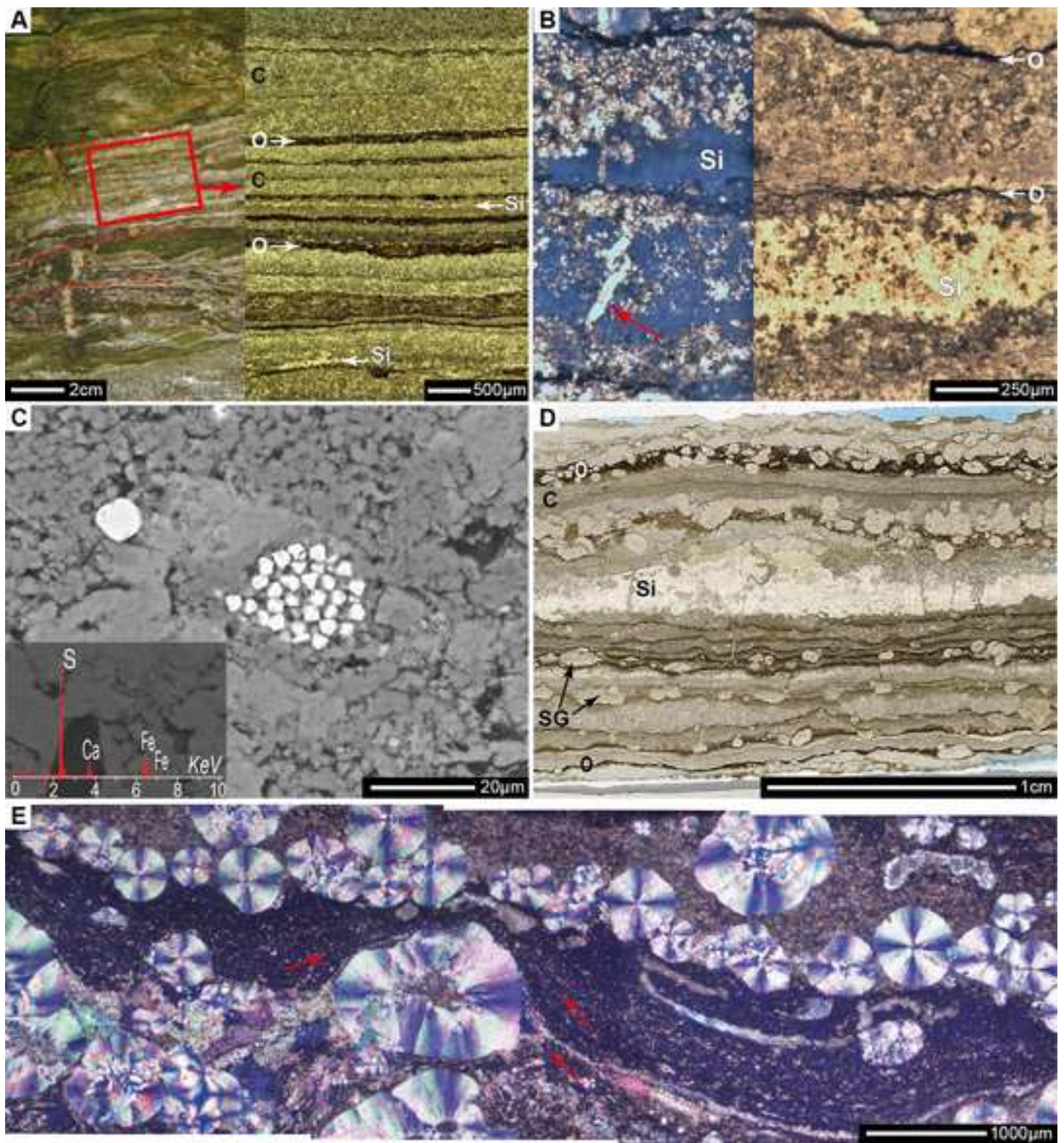


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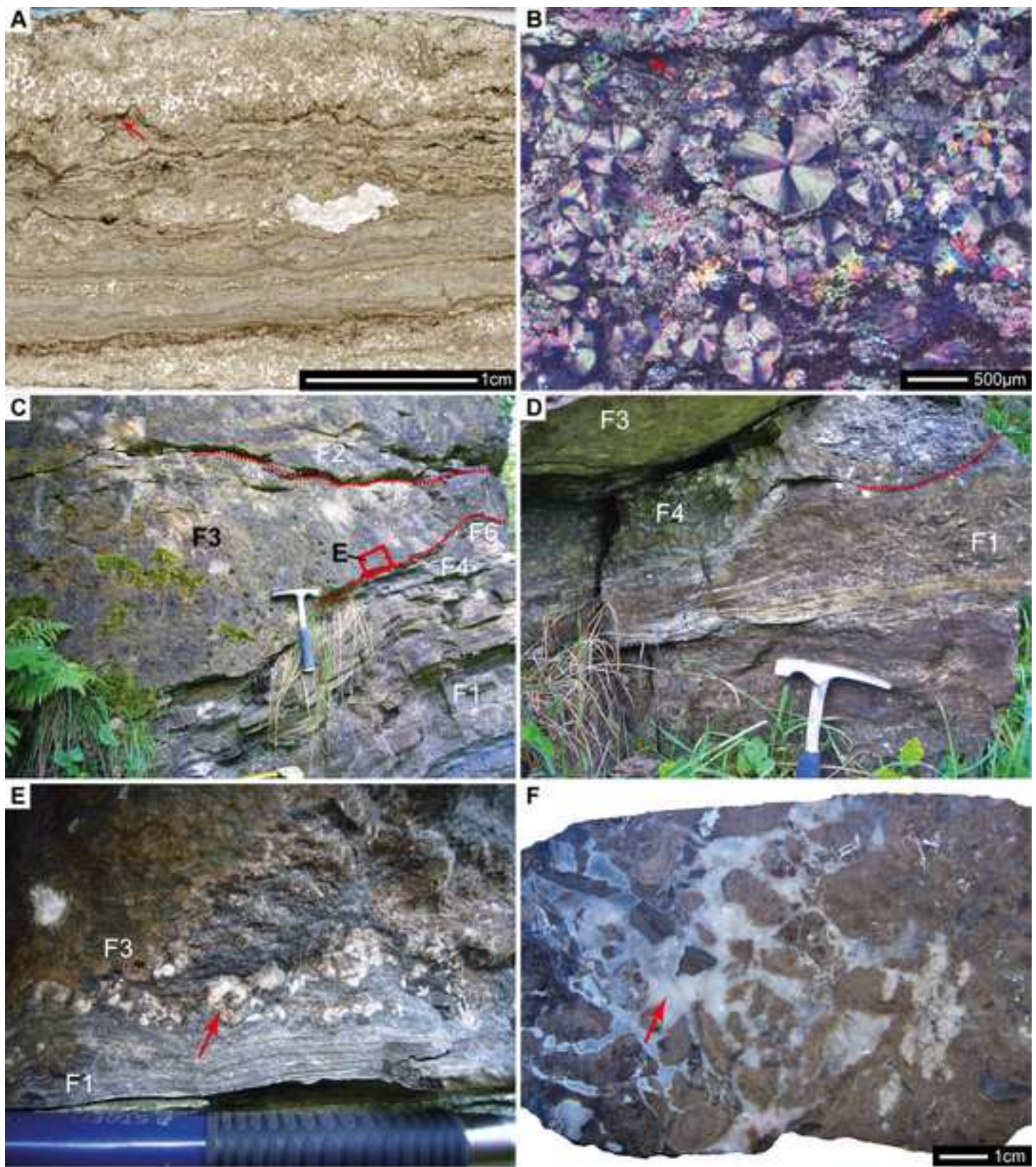


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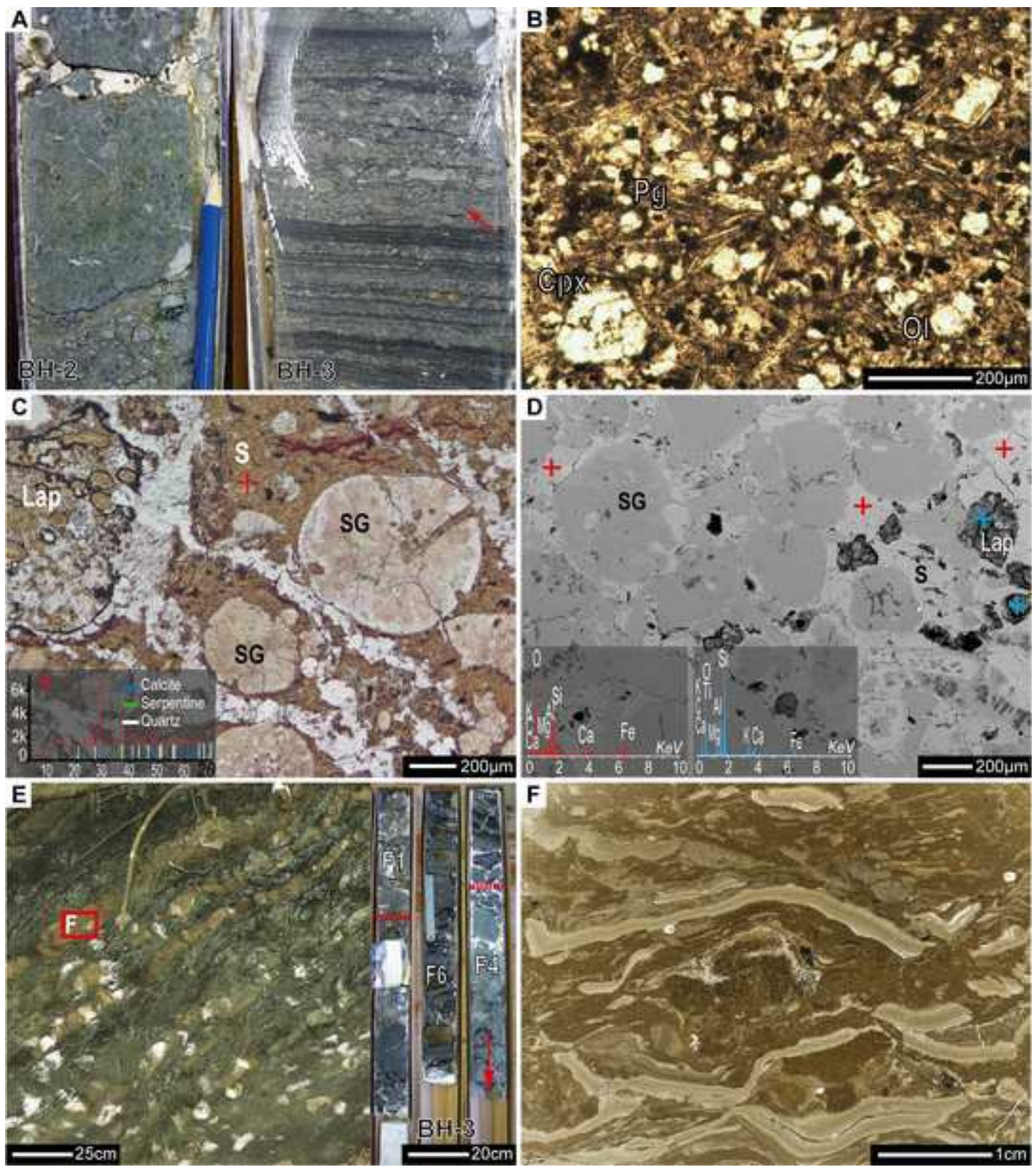


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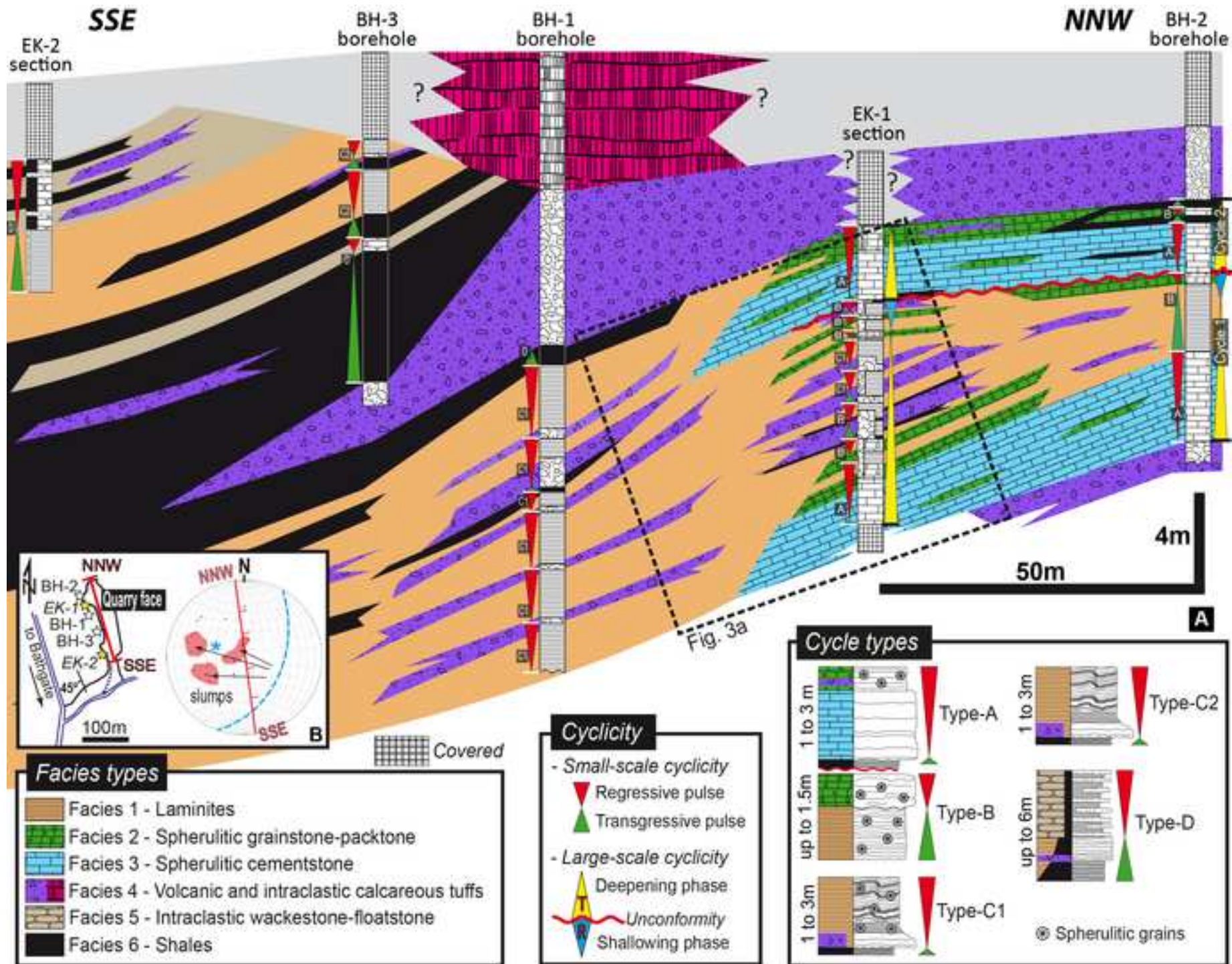


Figure 8a








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Symbols used in Figures

Sedimentary features and fossil content

-  Slumps
-  Laminated fabrics
-  Creeping and micro-sliding
-  Silica nodules
-  Ostracods (*Carbonita*)
-  Plant remains
-  Clotted fabrics
-  Shale, Mud-, Wacke-, Pack-, Grainstone
Cementstone

Spherulitic components and related textures

-  Stacked Fans
-  Cavity-filling silica cements
-  Coated Grains
-  Oncoids
-  Crusts
-  Intraclasts
-  Algae/plants incrustated with Spherulitic Calcite

Distribution and abundance of components



-  Allochthonous grains
-  Autochthonous grains
- 0, 1, 2, 3** Scarce, Common, Abundant, Very abundant

Figure 8b
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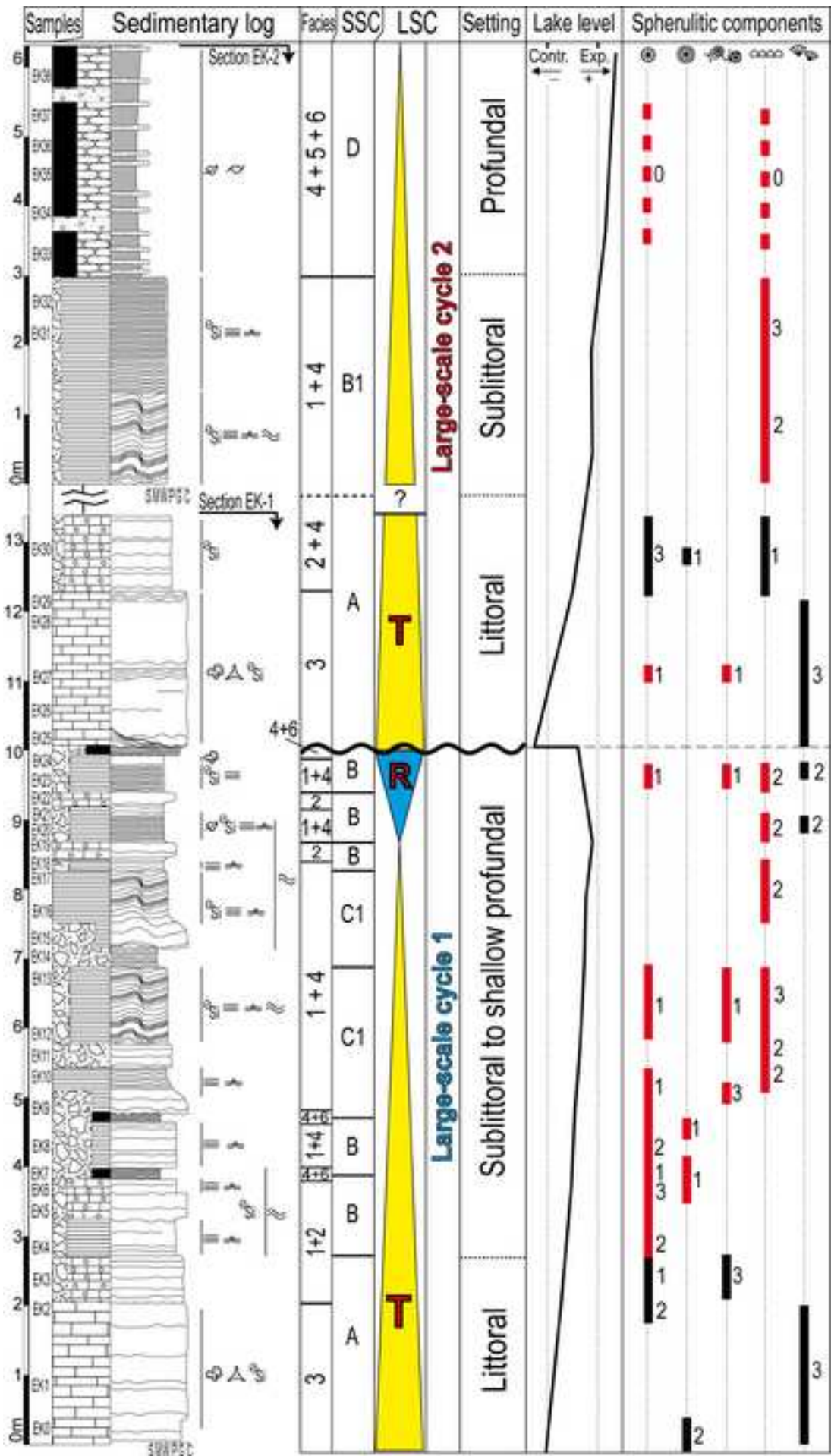


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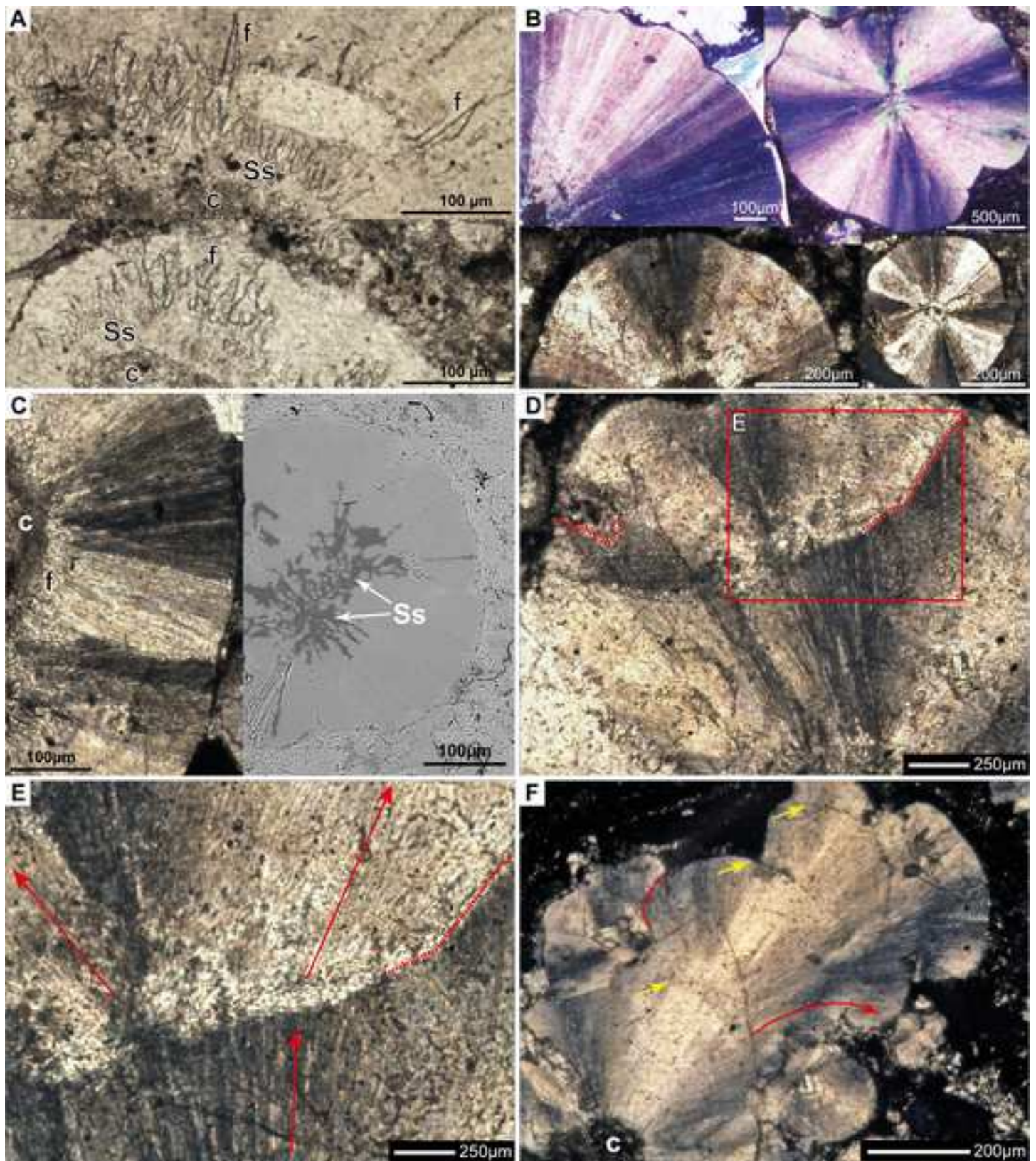


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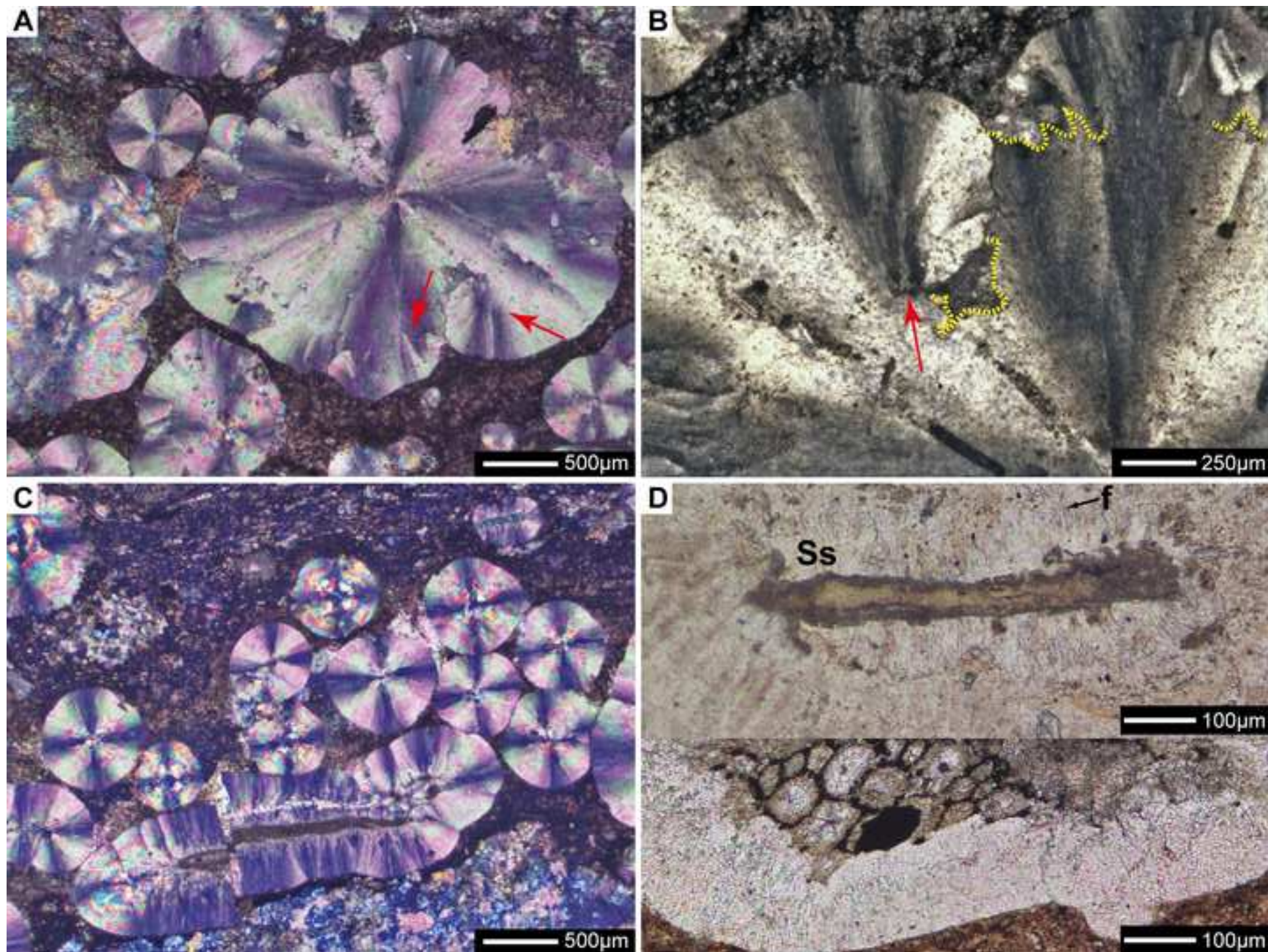


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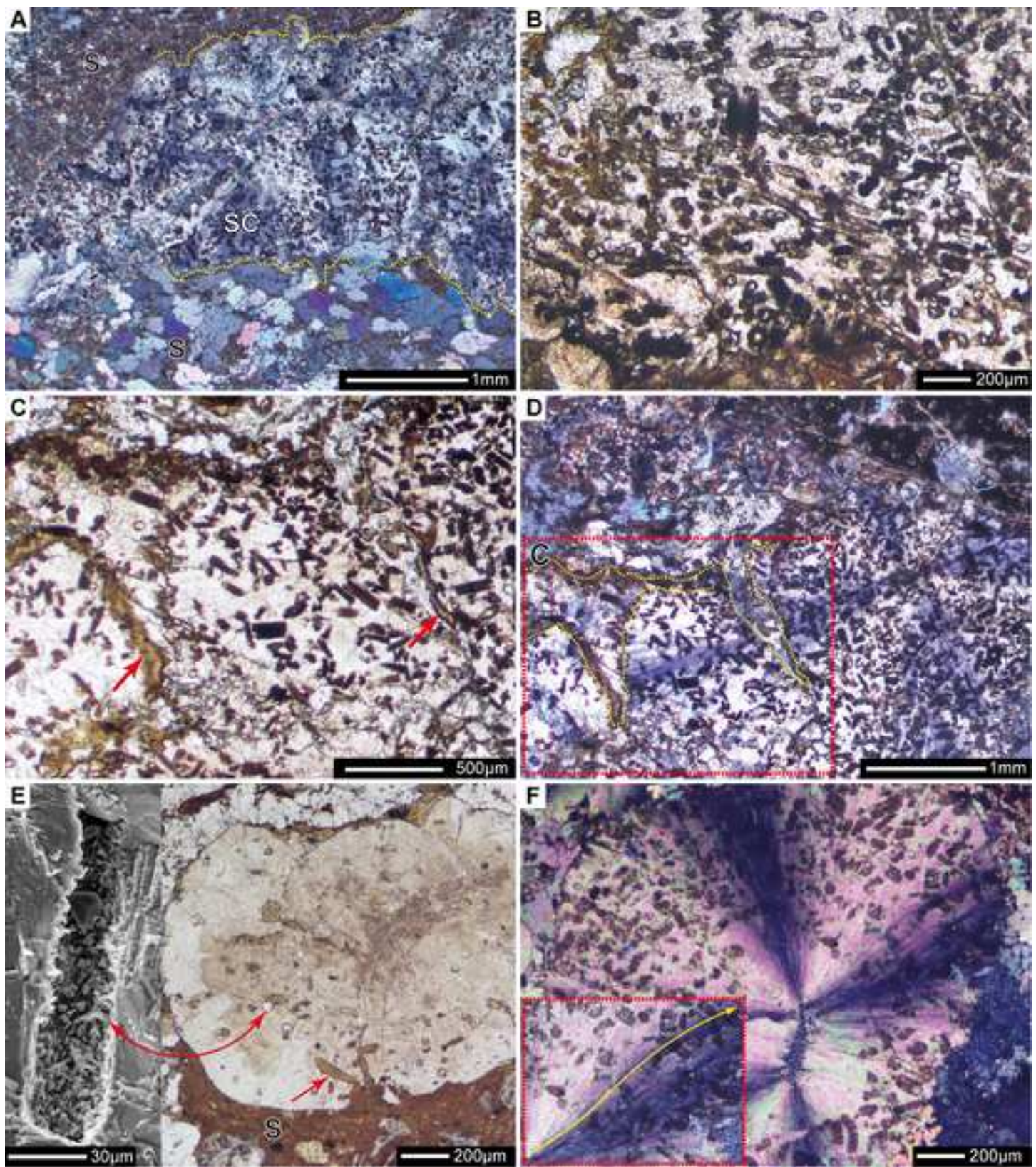


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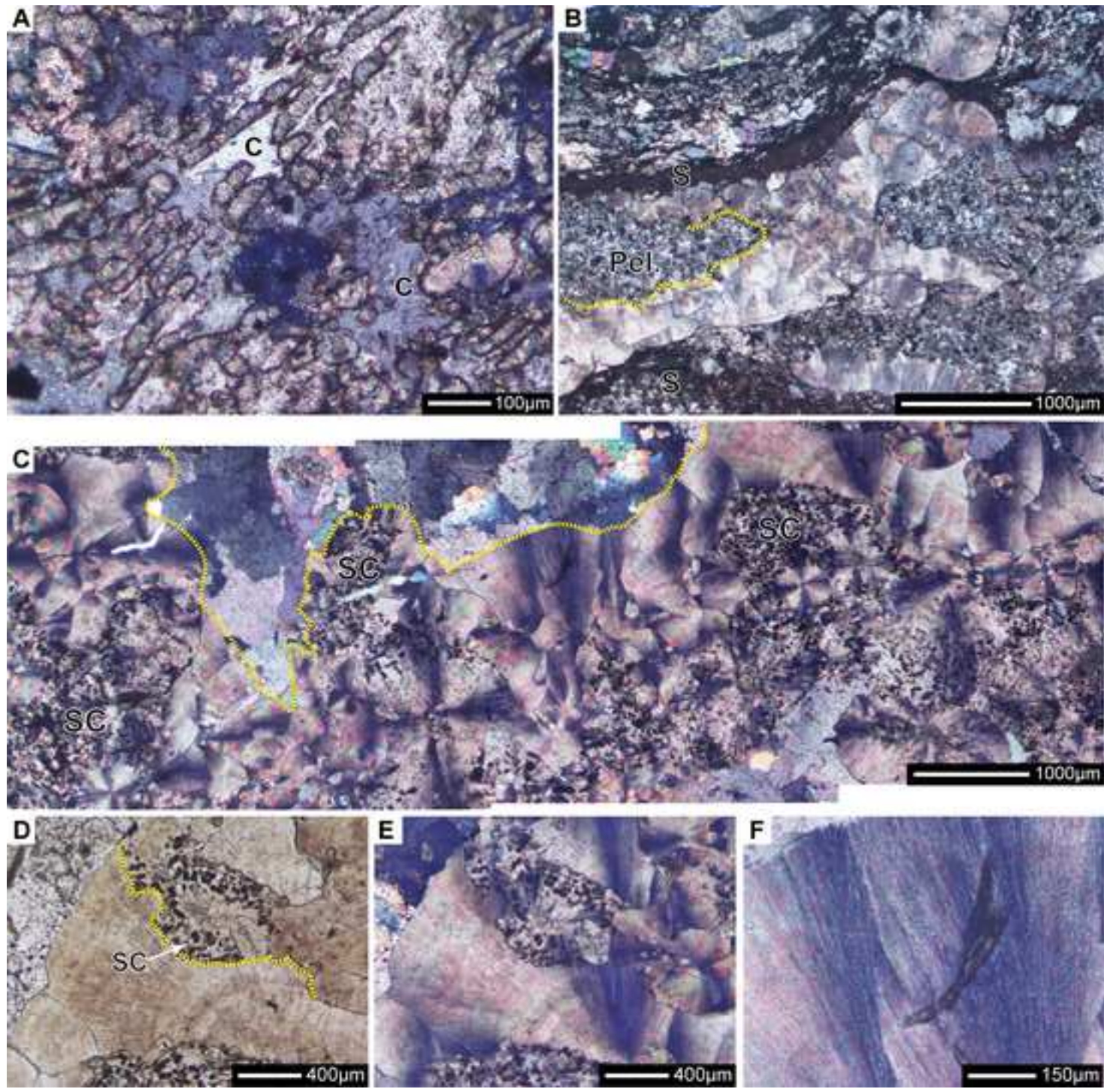


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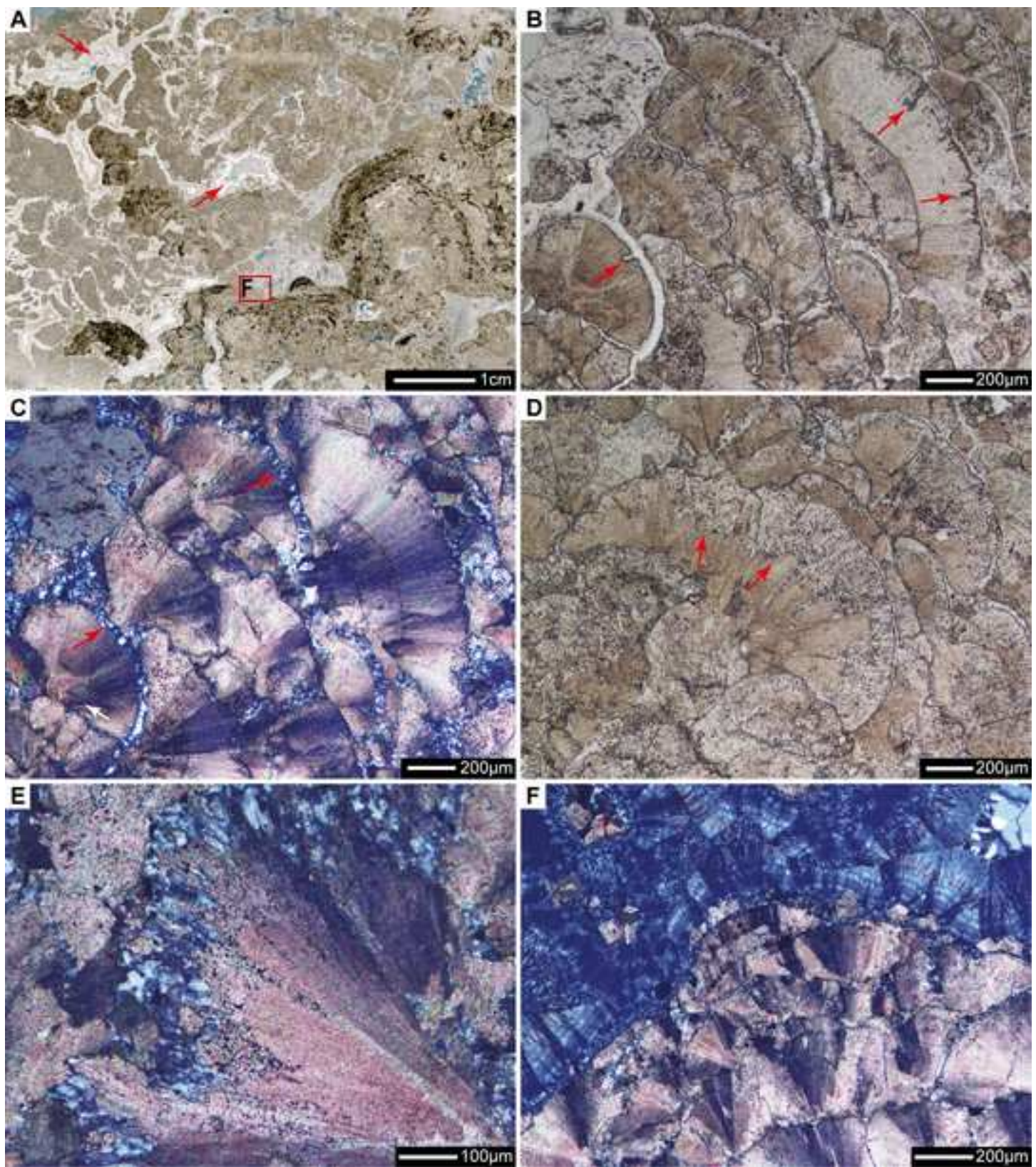


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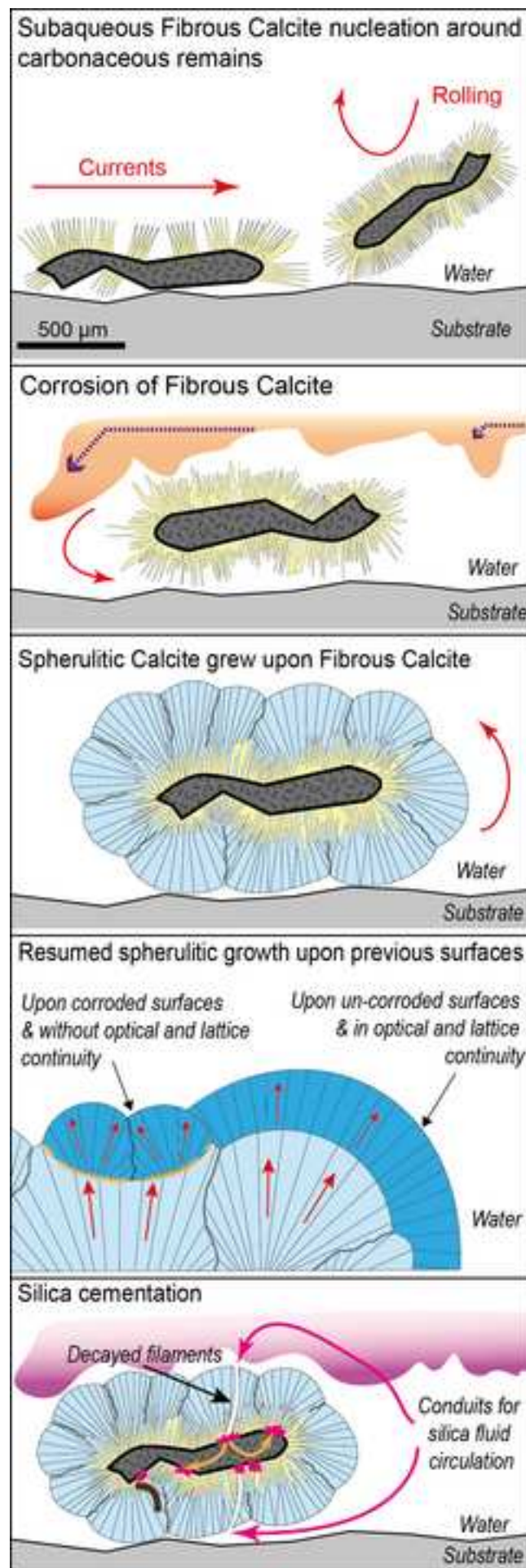


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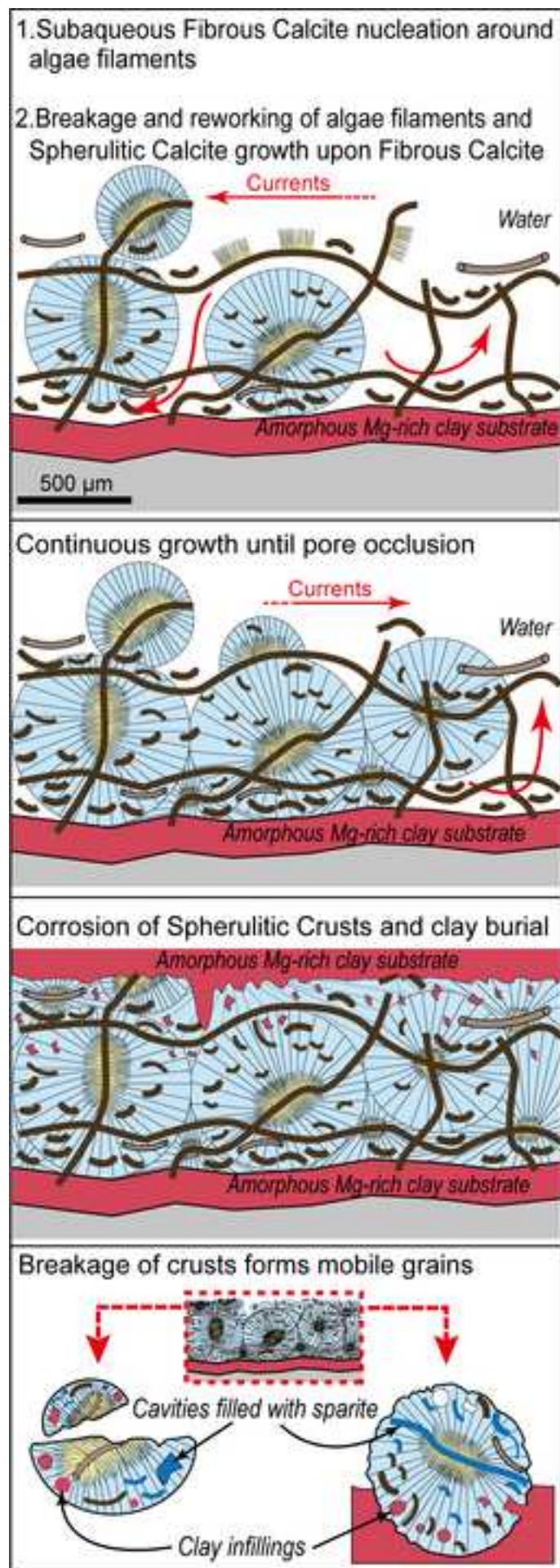


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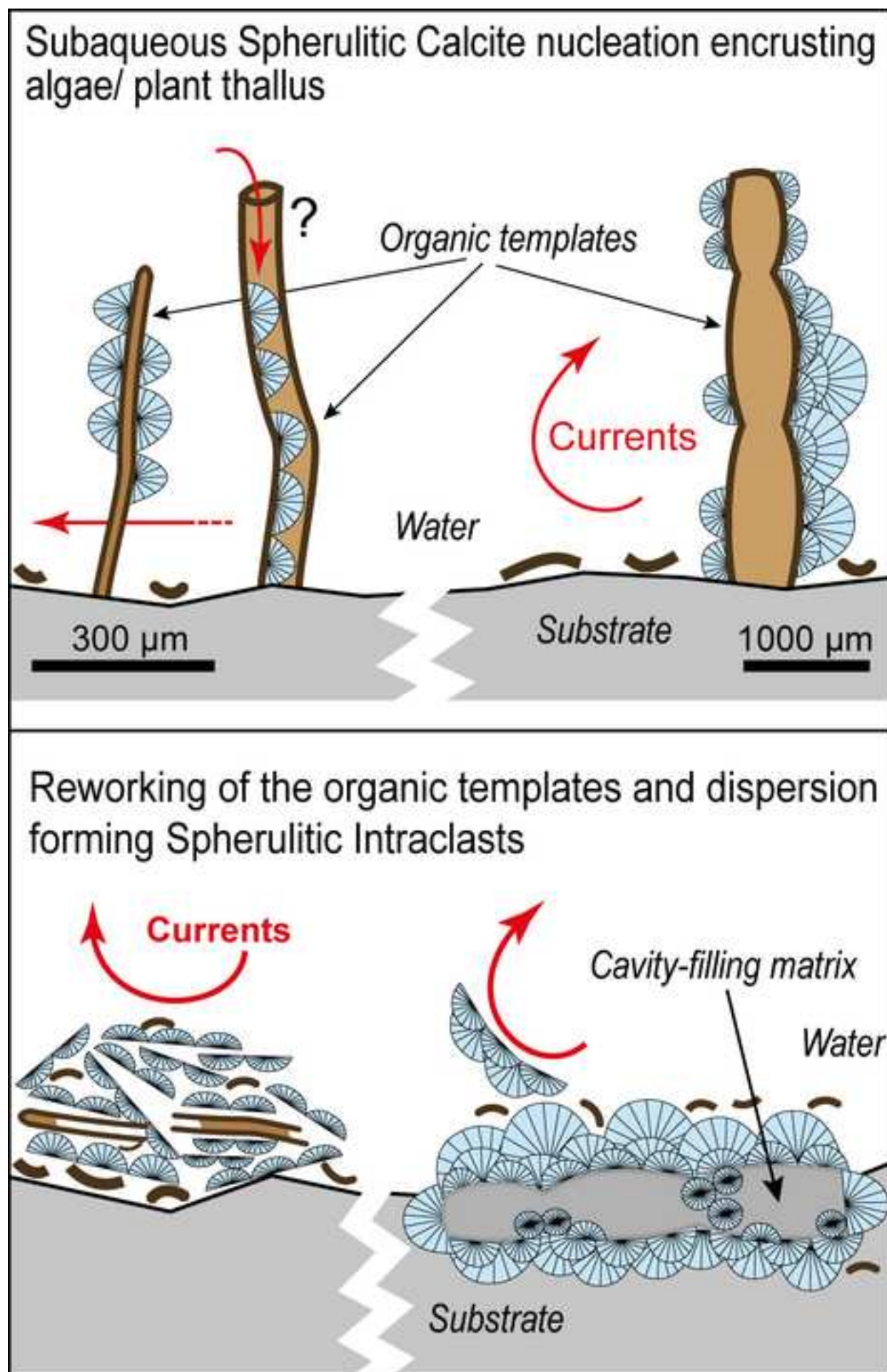


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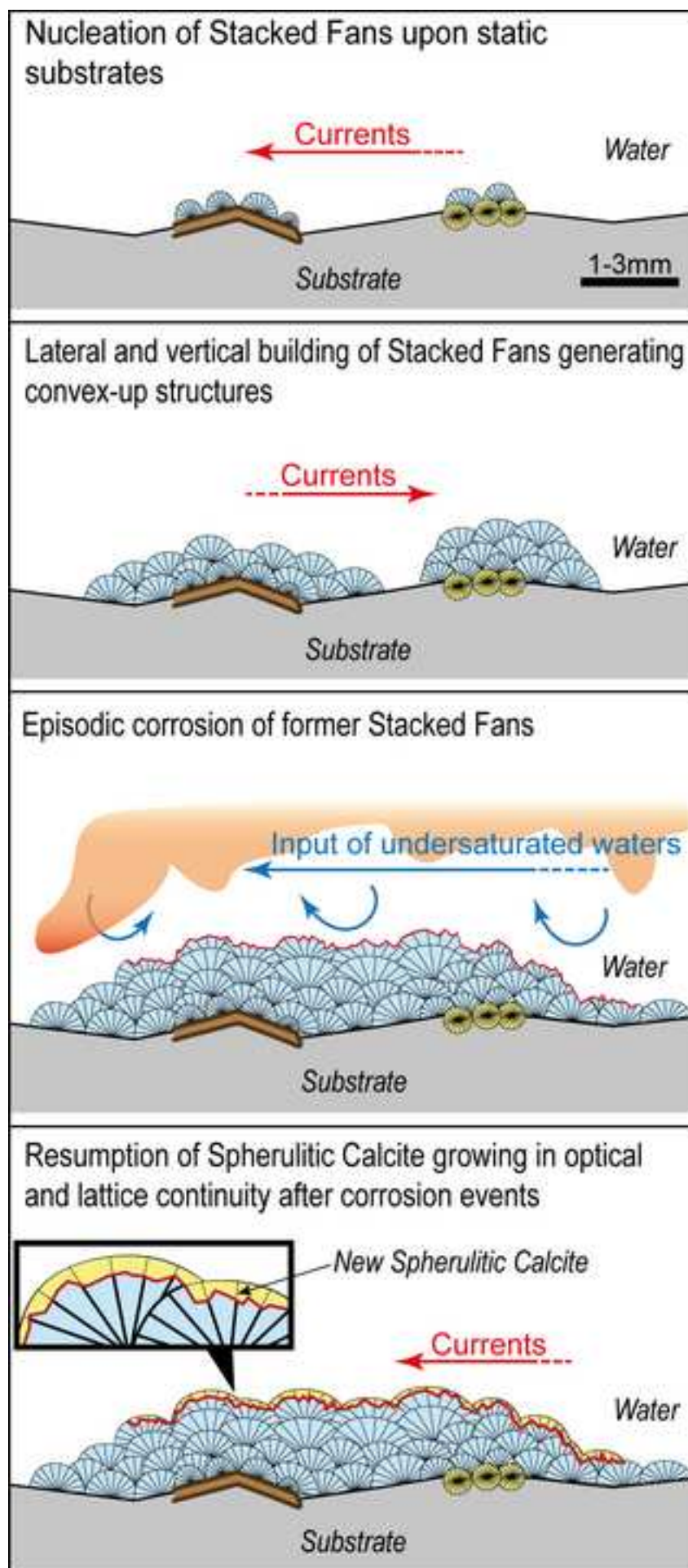


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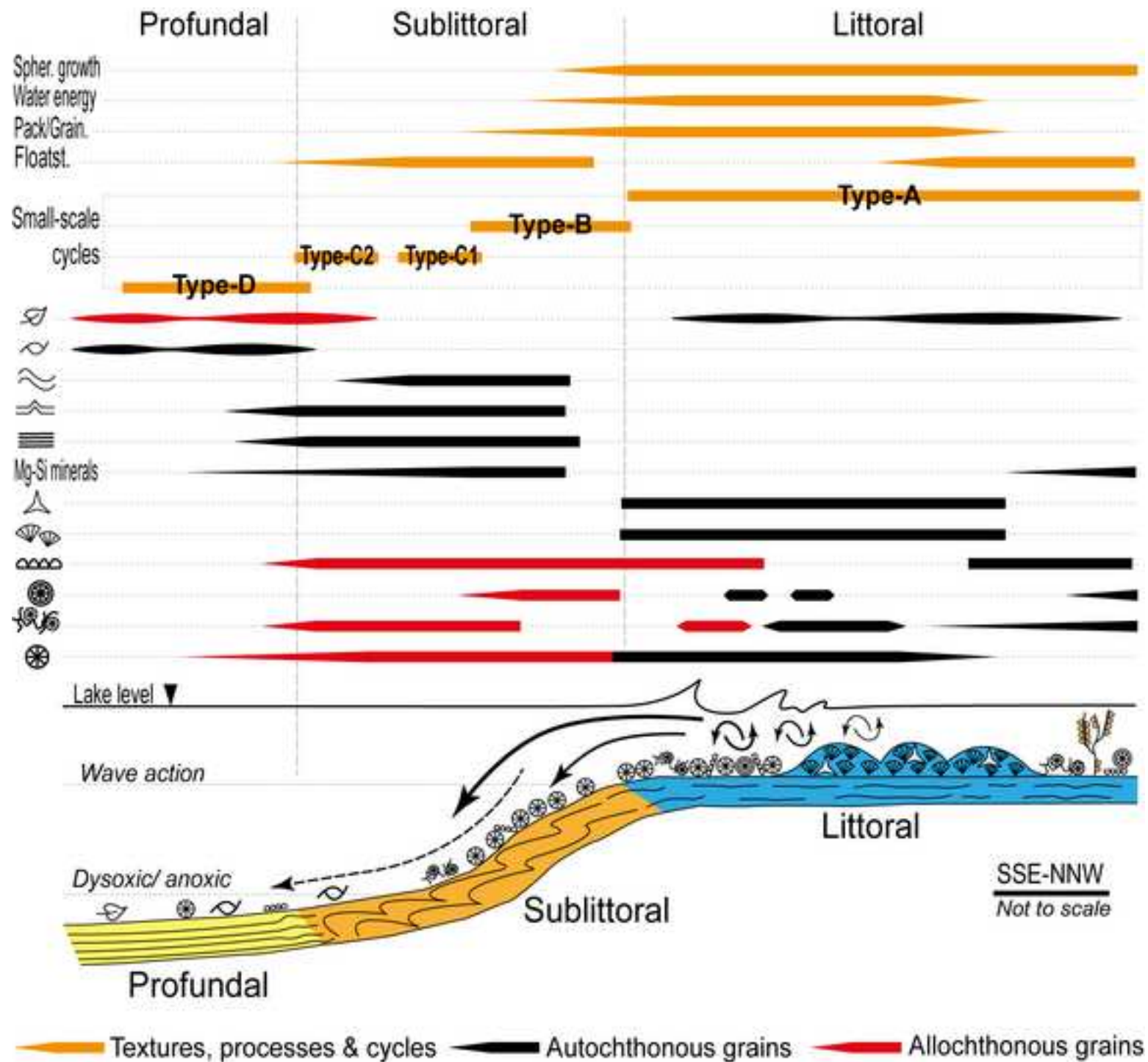


Table 1

Facies	Outcrop features	Mesoscopic features	Microscopic features	Petrography	Allochems	Textures
Laminites <i>Fig. 4</i>	Flat and tabular beds with high lateral continuity (5 to 50 cm-thick, decametric lateral extension)	Repetitive alternation of carbonate-rich layers (up to 4 cm-thick) and organic/ fine-grained silica-rich layers (up to 3 cm-thick)	Alternation of carbonate, organic and silica laminae	Carbonate laminae : wrinkled to slightly flat, continuous, pale to dark brown micrite to microspar (30µm to 1000µm-thick) Organic laminae : Wrinkled to undulated, continuous, dark brown, detritus-rich (7µm to 1500µm-thick) Silica laminae : irregular, continuous, cloudy brown microcrystalline-vitreous silica (up to 350µm thick)	Plant/ Algae remains, Fish scales, pellets, Spherulitic Coated Grains Organic matter, Pellets, Fish scales, Spherulitic Coated Grains, Pyrite framboids	Laminites Spherulitic Laminites
Grainstone-packstone Spherulitic grainstone-packstone grains, intraclasts and crusts <i>Fig.5a, b</i>	Discontinuous layers, restricted continuity (5 to 80 cm-thick, decimetric lateral extension)	Sub-cm layers	- -	Poorly to moderately sorted spherulitic grainstone-packstone. Fine to coarse sand size, well-rounded to angular grains. Matrix of red-brown amorphous Mg-Si matrices-clay (kaolinite-serpentine group) occasionally replaced by ferroan blocky to granular calcite cements	Spherulitic Coated Grains, Spherulitic Intraclasts, Spherulitic Crusts, Volcanic clasts -	Grainstone-packstone;
Shrubby Spherulitic cementstone carbonate build-ups <i>Fig.5c to f</i>	Dome-shaped to lenticular bodies (up to 2 m-thick and 3 m-wide, decametric lateral extension)	Massive and indurated 'clotted' bodies	Pale white coloured irregular cavities filled with silica cements (mm- to cm-sized)	See Stacked Fans (Table 2)	-	Boundstone-Cementstone
Volcanic and intraclastic calcareous tuffs <i>Fig.6a to d</i>	Layered bodies (5cm- to 5m-thick, decametric lateral extension)	-	Pyroclastic texture (lapilli) surrounded by a chaotic shard groundmass	Lapilli: Porphyritic texture with phenocrysts floating in a cryptocrystalline glassy matrix. Plagioclase, Clinopyroxene (augite), Olivine, Magnetite. Red-brown amorphous Mg-Si minerals are common	-	Basalt/ Basanite
Layered carbonates Intraclastic wackestone-floatstone <i>Fig.6e,f</i>	Continuous and slightly nodular to tabular layers (up to 15 cm thick, decametric lateral extension)	Slumps and convolute beds, graded beds	-	Wackestone-floatstone of contorted laminae intraclasts	Intraclastic laminae, peloids, ostracods, minor Spherulitic Coated Grains, pyrite framboids	Wackestone - floatstone
Shales <i>Fig. 6e</i>	Dark blue-grey, organic-rich shale/clay (up to 6m-thick, decametric lateral extension)	Ironstone bands and concretions in thin horizons	-	-	Bivalves, Ostracods, Arthropod cuticles, Foliage remains, Trunks, Fish scales, Vertebrates	Shale

Table 2

Components	Occurrence	Crystal Fabrics	Petrographic characteristics
Spherulitic Coated Grains <i>Fig. 4, 5, 9, 10</i>	Facies 1, 2, 4 and 5	Fibrous Calcite	Vegetated remains (lycopsids, ferns or gymnosperms), algae, volcanic remains, and peloids acting as cores
		Subhedral Silica	<i>Type 1</i> (85%) – Circular and spheroidal grain morphologies, rounded to sub-rounded corners and edges, and irregular and/or abraded outlines. Build upon arcuate and spheroidal nucleus (50 to 700 µm-length). Spherulitic Calcite fabrics common (sweeping extinction)
		Spherulitic Calcite Subhedral Silica Botryoidal Calcite	<i>Type 2</i> (15%) – Elongated and non-spheroidal grain morphologies, and similar roundness and irregularities. Build upon irregular and elongated nucleus (up to 4 mm-length). Spherulitic Botryoidal Calcite fabrics common (sweeping extinction) Spherulitic and Botryoidal Calcite crystals experience deflection in later stages of growth. Corrosion features are common
Spherulitic Crusts <i>Fig. 11</i>	Facies 1, 2 and 4	Fibrous Calcite	Spherulitic Calcite encapsulating fragments (~50µm in diameter) and whole specimens (at least 4 mm in length) of green algae filaments and sporadic plant remains . Sweeping extinction
		Subhedral Silica	Fragments of Spherulitic Crusts display polished outlines and <u>decayed</u> filament inclusions are now filled by <u>amorphous</u> Mg-Si phases-minerals or calcite cements
		Spherulitic Calcite Subhedral Silica	Corrosion features are common. Resultant cavities can be filled by clay or blocky calcite cement
Spherulitic Intraclasts <i>Fig. 12</i>	Facies 1, 2 and 4	Spherulitic Botryoidal Calcite	<i>Type 1</i> (90%) – Laterally stacked Spherulitic Botryoidal Calcite (up to 20-30 µm in width) with flat and smooth bases (100 to 500 µm long). Sweeping extinction
			<i>Type 2</i> (10%) – Tubiform objects (4mm in length, 2 mm in width) with outer layers made of composite laterally and vertically stacked Spherulitic Botryoidal Calcite (100 to 500 µm in width). Sweeping extinction
			Spherulitic Botryoidal Calcite may have grown upon the external surface of plant/ algae thallus Corrosion cavities are common and can be filled by Spherulitic Crusts
Stacked fans <i>Fig. 13</i>	Facies 3	Spherulitic Botryoidal Calcite	Laterally and vertically-stacked ‘shrub-like’ Spherulitic Botryoidal Calcite (100 to 1000µm thick, and 100 to 3000µm width). Sweeping extinction Spherulitic Botryoidal Calcite have scalloped dissolution pits and vertical cracks (up to 200 µm-length) and are outlined by thin and continuous silica laminae (10 to 50µm-thick)