

The source of sulfate in brachiopod calcite: Insights from μ -XRF imaging and XANES spectroscopy

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1 **Abstract**

2 Geochemical signatures preserved in sedimentary carbonate strata are often used as archives for
3 paleoenvironmental reconstructions. However, diagenetic overprinting and/or muting of primary
4 geochemical signatures complicates the interpretation of these data. To avoid this issue,
5 geochemical techniques strive to target unaltered (or minimally altered) carbonate components.
6 The multi-layer low-Mg calcite shell composition of articulate brachiopods are often the target in
7 such studies because they are commonly more robust to recrystallization than the shells of other
8 biomineralizers. Here, we have combined S K-edge μ -XRF imaging, XANES spectroscopy and
9 petrography to determine the source of sulfate in the calcite lattice (carbonate-associated sulfate;
10 CAS) of ancient and extant brachiopods, in order to establish their suitability for use in
11 reconstructing seawater sulfate $\delta^{34}\text{S}$ throughout the Phanerozoic. Both the extant brachiopod
12 *Terebratalia transversa* and fossil brachiopods display intra-specimen variability in sulfate
13 abundance parallel to the primary fabric, likely corresponding to variations in growth rate. XANES
14 spectroscopy identifies a majority of the sulfate as inorganic. Additionally, XANES spectroscopy
15 detected low abundances of both reduced and oxidized organic sulfur species (thiol, thioether,
16 sulfoxide and sulfate esters) in all *T. transversa* samples and lesser abundances in a few of the
17 fossil brachiopods. In *T. transversa*, inorganic sulfate and sulfate ester abundance increase towards
18 the hinge of the valves. Bulk $\delta^{34}\text{S}_{\text{CAS}}$ of the samples containing the fossil brachiopods are
19 consistently more positive than time-equivalent brachiopod-only values, likely reflecting a mixture
20 of CAS signals from homogenization of carbonate components differentially affected by
21 depositional environment and diagenesis. In contrast, bulk $\delta^{34}\text{S}_{\text{CAS}}$ of modern *T. transversa* is
22 approximately 1‰ more positive than coeval seawater. Although organic sulfate esters are found
23 within the brachiopod shells, they are only ever present as trace components. Our findings indicate
24 that the vast majority of sulfate in brachiopod shells is inorganic, sourced from coeval seawater.

25 This result supports the use of brachiopods as a potential archive for a faithful CAS record of
26 seawater sulfate throughout the Phanerozoic. The characterization of *in situ* organic sulfur
27 compounds in both extant and fossil brachiopods indicates the potential importance of various
28 organic sulfur compounds in mineralogical determination (and therefore fossil preservation) and
29 crystal orientation during brachiopod biomineralization throughout geologic time.

30

31 Keywords: carbonate-associated sulfate; CAS; XANES spectroscopy; μ -XRF imaging; sulfur
32 speciation; brachiopod

33

34 **1.0 Introduction**

35 The shells of biomineralizing organisms can leave behind in sediments a direct record of evolution,
36 ontogeny, and physiology and can passively record variations in local seawater chemistry,
37 particularly those composed of calcium carbonate minerals. Articulate brachiopods are an archive
38 commonly exploited for a range of geochemical proxies including $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$, and trace
39 element abundances (Brand et al., 2003; Kampschulte et al., 2001; Lowenstam, 1961; Popp et al.,
40 1986a; Present et al., 2015; Veizer et al., 1986). A large amount of research has focused on
41 protocols for the determination of minimally altered brachiopod fragments (e.g. Angiolini et al.,
42 2009; Brand et al., 2012; Casella et al., 2018a; 2018b; Popp et al., 1986a, 1986b; Rush and Chafetz,
43 1990) and their associated $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$ and carbonate clumped isotope records (e.g. Azmy et
44 al., 1998; Brand et al., 2015, 2013; Came et al., 2007; Cummins et al., 2014; Henkes et al., 2013;
45 Lowenstam, 1961; Qing and Veizer, 1994). The shells of articulate brachiopods are accepted to be
46 one of the most faithful archives of geochemical information, as the biomineralized shell is
47 typically constructed from two, sometimes three, layers (primary and secondary) of low-Mg

48 calcite; this makes brachiopod shells more resistant to recrystallization during diagenesis (Brand
49 and Veizer, 1980; Lowenstam, 1961). The original fabric of brachiopod shells is usually visible in
50 petrographic thin section as fibrous calcite, where calcite crystallites in the secondary layer are
51 oriented parallel or obliquely to the outer structure.

52 Similar to inorganic carbonate components, biogenic carbonates incorporate trace amounts
53 of sulfate into the crystal lattice, substituting for the carbonate ion, termed carbonate-associated
54 sulfate (CAS) (Burdett et al., 1989). Generally, biogenic carbonate components contain greater
55 abundances of sulfate than inorganic precipitates, such as early to late diagenetic cement (Staudt
56 and Schoonen, 1995; Present et al., 2015; Richardson et al., 2019a). In marine carbonates, the
57 stable isotopic signature of CAS ($\delta^{34}\text{S}_{\text{CAS}}$) is generally considered as a proxy for the isotopic value
58 of ancient seawater sulfate. Due to the temporal and spatial extent of marine carbonates, and the
59 other geochemical information they retain, bulk $\delta^{34}\text{S}_{\text{CAS}}$ records have been generated to constrain
60 the operation and evolution of the biogeochemical sulfur cycle over Earth history (Gill et al., 2011;
61 Hurtgen et al., 2009, 2005; Luo et al., 2010; Rennie and Turchyn, 2014). However, bulk $\delta^{34}\text{S}_{\text{CAS}}$
62 records often display large stratigraphic variability over timescales considered too short to reflect
63 changes to the global ocean sulfate reservoir (Jones and Fike, 2013; Kampschulte and Strauss,
64 2004; Osburn et al., 2015; Ries et al., 2009; Thompson and Kah, 2012) due to the expected ($\gg 1$
65 Myr) residence time of seawater sulfate, at least for much of the Phanerozoic (Berner, 2001;
66 Bottrell and Newton, 2006). It has been suggested that the characteristic variability in many deep-
67 time $\delta^{34}\text{S}_{\text{CAS}}$ datasets is caused by both local depositional and diagenetic processes (Fike et al.,
68 2015; Jones and Fike, 2013; Present et al., 2015; Richardson et al., 2019a; Richardson et al., 2019b;
69 Rose et al., 2019a). In order to use CAS to its fullest potential as a proxy, the source and
70 incorporation of sulfate in primary carbonate must be investigated.

71 In recent years, two different communities have been investigating sulfate in a variety of
72 carbonate components for different purposes: those measuring CAS abundance and $\delta^{34}\text{S}_{\text{CAS}}$ in the
73 rock record for paleoenvironmental and biogeochemical S-cycle reconstructions (e.g. Fike and
74 Grotzinger, 2008; Gill et al., 2011; Kampschulte and Strauss, 2004; Osburn et al., 2015; Present
75 et al., 2015; Rennie et al., 2018; Witts et al., 2018); and those investigating the role of sulfates
76 (potentially both organic and inorganic) in biomineralization and subsequent fossilization of
77 modern biomineralizers, as well as the suitability of biominerals for paleoenvironment
78 reconstructions (e.g., Cuif et al., 2003; Cusack et al., 2008; Perrin et al., 2017). It was first
79 recognized that CAS was lattice-bound sulfate, as opposed to micro-inclusions of sulfate minerals,
80 using Raman spectroscopy (Takano et al., 1980) and later by X-ray Absorption Near Edge
81 Structure (XANES) spectroscopy (Pingitore et al., 1995). This development resulted in an
82 increased number of studies utilizing $\delta^{34}\text{S}_{\text{CAS}}$ in the rock record, where ~ 40 g of homogenized
83 rock powder are typically used during sample preparation (e.g. Burdett et al., 1989; Wotte et al.,
84 2012). To decrease the amount of scatter in $\delta^{34}\text{S}_{\text{CAS}}$ sections, assumed to be sourced from
85 incorporating late-stage diagenetic carbonate components, studies have targeted specific
86 components such as micrite (Kampschulte and Strauss, 2004; Wotte et al., 2012) or fossils (Gill et
87 al., 2011; Kampschulte et al., 2001; Present et al., 2015) and/or reduced the sample size (Paris et
88 al., 2014; Rennie et al., 2018). Brachiopods frequently retain some of the highest abundances of
89 sulfate in biogenic calcite from the rock record (Staudt and Schoonen, 1995). Due to the robust
90 nature of brachiopod exoskeletons to recrystallization, some have suggested they may be a faithful
91 record for $\delta^{34}\text{S}_{\text{CAS}}$ (Kampschulte and Strauss, 2004; Present et al., 2015).

92 In addition to the potential as an archive for primary seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values, sulfate in
93 brachiopods may provide a platform to assess the evolution of biomineralization processes and

94 fossilization pathways. Previous work to determine the source of sulfate in biogenic calcite using
95 micro-X-ray Fluorescence (μ -XRF) imaging and XANES spectroscopy has focused on modern
96 corals (Cuif et al., 2003; Perrin et al., 2017; Tamenori et al., 2014), mollusks (Dauphin et al., 2005,
97 2003; Tamenori and Yoshimura, 2018; Yoshimura et al., 2013) and, to a lesser extent, brachiopods
98 (Cusack et al., 2008). These XANES studies have shown that sulfate is present within these
99 biogenic carbonates; however, the interpretations of these results has varied as to whether the
100 sulfate represents chondroitin sulfate (i.e., as sulfate esters; Cuif et al., 2003; Dauphin et al., 2003,
101 2005; Cusack et al 2008; Yoshimura et al., 2013; Tamenori and Yoshimura, 2018) or inorganic
102 sulfate as CAS (Tamenori et al., 2014; Perrin et al., 2017). Yet, none of these studies observed the
103 diagnostic fingerprint (lower energy shoulder; Almvist, 2010) of ester sulfate. As such, the
104 existence, relative abundance, and role of organic sulfates in biomineralization within biogenic
105 carbonates is relatively poorly constrained (Addadi et al., 1987; Cusack and Freer, 2008; de
106 Nooijer et al., 2014; Kitano and Hood, 1965). In addition to sulfate, organic sulfur species were
107 found in organic matrices, including thiols and sulfite (Dauphin et al., 2005; Tamenori et al., 2014;
108 Perrin et al., 2017; Tamenori and Yoshimura, 2018).

109 This study aims to answer questions pertinent to both communities investigating CAS by
110 determining if sulfate is predominantly organically (OSCs) or inorganically bonded within the
111 carbonate of brachiopod valves. Specifically, we report the spatial variation in sulfate abundance
112 within individual extant *Terebratalia transversa* (Sowerby, 1846) and within individual
113 Ordovician- and Silurian-aged fossil brachiopods using high resolution μ -XRF imaging and
114 XANES spectroscopy. Previous work has shown the first occurrences of organic sulfur compounds
115 (OSCs) preserved within a petrographic context in Ordovician and Silurian carbonates (including
116 sulfate esters, thioethers and sulfite) co-occurring with inorganic sulfate determined to represent

117 CAS (Richardson et al., 2019a; Rose et al., 2019b). This study aims to assess the reliability of
118 sulfate in brachiopods as a proxy for seawater sulfate by determining the abundance and role of
119 organic sulfur species present within modern and fossil brachiopod valves.

120

121 **2.0 Materials and Methods**

122 *2.1 Samples*

123 Living *T. transversa* samples were obtained by dredging around the San Juan Islands, Washington,
124 USA, by a research vessel from Friday Harbor Labs in March 2017. These samples were
125 subsequently left out of water to open and dry out. The brachiopods were sonicated and then
126 impregnated in an epoxy mold, cut along the plane of symmetry and mounted on a glass slide to
127 make a thin section. Sample TT01 is approximately 2.7 cm along the plane of symmetry with shell
128 thickness of 1 mm (Fig. 1A). Sample TT02 is smaller at 1.7 cm along the plane of symmetry and
129 has a shell thickness of ~ 0.3 mm (Fig. 1B). Additionally, the shell of TT02 is much darker in color
130 than TT01.

131 Fossil brachiopods analysed here are from Hirnantian-aged strata of Anticosti Island,
132 Canada, and Wenlock-aged strata of Gotland, Sweden. The fossil brachiopod thin sections from
133 Anticosti Island were taken from a sample of bioturbated packstone from the Fox Point Member
134 of the Becscie Formation (Fig. 1C) and a crinoidal wackestone from the Lousy Cove Member of
135 the Ellis Bay Formation (Fig 1D; Jones et al., 2011). Samples from Gotland are from a poorly
136 washed fossiliferous grainstone (Fig. 1E) and a brachiopodal grainstone (Fig. 1F) from the Upper
137 Visby Formation (Rose et al., 2019a). Calcite containing lattice-bound inorganic sulfate (acting as
138 CAS standards for XANES spectroscopy) were precipitated in the laboratory following the free
139 drift method (Gruzensky, 1967; Paquette and Reeder, 1990) as described in Rose et al., 2019b).

140 The CAS standard is a low Mg-calcite containing ~ 4000 ppm sulfate, determined by ion
141 chromatography.

142

143 2.2 SEM

144 Scanning Electron Microscopy (SEM) was performed using a FEI Nova Nano SEM at the Nano
145 Research Facility, Washington University. Extant *T. transversa* samples were gold coated with ~20
146 nm to create a conductive surface in order to reduce charging effects and improve the secondary
147 electron image. Analyses were performed with a voltage of 10 kV under high vacuum mode.

148

149 2.3 μ -XRF and XANES

150 Analyses were performed around the sulfur K-edge (2472 eV) at the GeoSoilEnviroCARS
151 microprobe beamline 13-ID-E, the Advanced Photon Source (APS), Argonne National
152 Laboratory, and beamline 14-3 at the Stanford Synchrotron Radiation Lightsource (SSRL),
153 Stanford Linear Accelerator Center. APS uses a liquid-N₂-cooled and SSRL uses a water-cooled
154 double Si (111) crystal monochromator to select the desired X-ray energy and Kirkpatrick-Baez
155 mirrors to focus to a ~2 to 5 μ m spot size. The sample environment is a helium-purged chamber
156 to reduce X-ray attenuation in air. For detailed descriptions of each beamline and measurement
157 approach see Rose et al. (2019b). At the APS, an anhydrite standard provides the white line for
158 sulfate (around 2481.5 eV) and maps were collected at the sulfide and sulfate excitation energies
159 (2472 and 2481.5 eV). At SSRL, a sodium thiosulfate powder calibrates the S K-edge to 2472.02
160 eV and maps were collected at the sulfide, sulfoxide, and multiple sulfate energies to detect
161 differences in organic and inorganic species (2472, 2476.3, 2482.1, 2482.3, 2482.6 and 2482.8
162 eV). μ -XRF maps were processed using the MicroAnalysis Toolkit (Webb et al., 2011) and

163 GSEMapView (Newville, 2013). At the sulfate excitation energy, reduced S-species contribute
164 to the fluorescence signal, complicating accurate reconstruction of sulfate abundances. To correct
165 for this, the fluorescence component from such species is subtracted from every sulfate excitation
166 map.

167 Locations for XANES analyses were determined based on the fluorescence maps. XANES
168 spectra from both the APS and SSRL were processed using the SIXPACK (Webb, 2005) XAS
169 software package. At the APS, S K-edge XANES spectroscopy was used to verify speciation. A
170 greater number of XANES spectra were collected at SSRL in order to perform a XANES fitting
171 of the map data. Spectra were corrected for detector deadtime and normalized using a background
172 subtraction of the linearized pre- and post-edge region (2165 and 2510 eV, respectively).
173 Subsequently, a principal component analysis (PCA) of the spectra for a given map region
174 generated components that were cross-plotted. ‘End-member’ spectra that are at the edge of the
175 cross-plot are the most dissimilar to one another. A least-squares fitting of these end-member
176 spectra to the original multi-energy maps creates spatial distribution maps of the species detected
177 as the end-members (Farfan et al., 2018; Mayhew et al., 2011; Richardson et al., 2019).
178 Comparisons of the XANES spectra of the standards at each beamline demonstrated that the SSRL
179 data were systematically shifted to higher energies by 0.5 eV due to calibration differences that
180 can be corrected by shifting the energy scale on one dataset. Therefore, for clarity in reporting the
181 results between the different beamlines, APS data were moved by + 0.5 eV to align with the SSRL
182 energy calibration before further analysis.

183

184 *2.4 Bulk Isotopes*

185 Samples for bulk $\delta^{34}\text{S}_{\text{CAS}}$ are prepared by the method described in Richardson et al., (2019a)
186 (adapted from Wotte et al., 2012). Briefly, CAS was extracted from samples by rinsing up to 60 g
187 of sample powder in a 10% brine for a minimum of three rinses. This step was followed by three
188 deionized (DI) water rinses, where the supernatant was checked for sulfate after the third rinse by
189 adding BaCl_2 . DI rinses were repeated until no precipitate formed in the supernatant on the addition
190 of BaCl_2 . Samples were then reacted with gradual addition of 6M HCl to reach a pH of 2 and
191 stirred for no longer than 3 hours. The supernatant was then filtered and left to react with BaCl_2
192 for up to 5 days to form BaSO_4 . *T. transversa* was prepared by homogenising 4 specimens,
193 generating 5.6 g of carbonate powder and followed the same extraction protocol outlined above.
194 Less sample for CAS extraction from *T. transversa* was required based on estimates of CAS
195 abundance from synchrotron data. Approximately 350 μg of the resulting barium sulfate was
196 combined with 1–3 mg of vanadium pentoxide and combusted using a Costech ECS 4010
197 elemental analyzer coupled to a Thermo Finnigan Delta V Plus isotope ratio mass spectrometer at
198 Washington University. S-isotopes ($\delta^{34}\text{S}$) are expressed in standard delta notation in per mil (‰)
199 as a deviation from V-CDT with an error of ± 0.3 ‰.

200

201 **3.0 RESULTS**

202 *3.1 Imaging of Calcite Textures*

203 SEM of TT02 depicts two distinct fabrics or textures (Fig. 2). The two textures are fibrous, bladed
204 calcite crystallites, generating layers (Figs. 2 A-C), and an indistinct texture that cannot be resolved
205 using the SEM protocol herein, but which is likely a different orientation of the calcite crystallite
206 fibers (Figs. 2B, D-E). A majority of the mapped region has this indistinct texture, with the fibrous
207 texture limited to the region below the socket.

208

209 3.2 μ -XRF and XANES of Extant Brachiopods

210 To observe differences between reduced and oxidized sulfur species, excitation maps for sample
211 TT01 are shown for 2476.3 eV and 2482.3 eV, corresponding to the sulfoxide and sulfate
212 excitation energy respectively (Almkvist et al., 2010) (Figs. 3A and 3B). Numerous reduced sulfur
213 species will fluoresce at 2476.3 eV, including sulfide. At the hinge line between the two
214 brachiopod valves, the highest abundance of reduced sulfur species is observed and co-occurs with
215 the highest abundance of inorganic sulfate and sulfate esters (Figs. 3A, 3B and 3C). Smaller, less
216 intense regions of increased reduced sulfur moieties occur along the edge of the shell (Fig. 3A).
217 Sulfate abundance is heterogeneous throughout the secondary layer, with the most abundant sulfate
218 occurring closer to the inner shell cavity (Fig. 3B). Reduced sulfur species that co-occur with
219 inorganic sulfate are common throughout the rest of the sample with no clear pattern as to where
220 they are present (yellow Fig. 3C). XANES spectra confirm the presence of thiol, sulfoxide (Fig.
221 3D, TT01_1 to TT01_3), sulfate esters (Fig. 3D, TT01_2) and inorganic sulfate (Fig. 3D, TT01_1,
222 TT01_2 and TT01_4). The organic S species have maximum intensities at 2473, 2476.3 and 2481
223 eV, and co-occur with sulfate peaks in a single region. The sulfate ester displays the shoulder at
224 2481 eV, but the energy of maximum intensity of the primary sulfate peak is shifted by 0.2 eV
225 relative to the other spectra (e.g. Farfan et al., 2018).

226 In contrast, due to the differences in experimental design and data collection at APS and
227 SSRL, the reduced-S excitation map obtained for TT02 corresponds to the sulfide energy at 2472
228 eV (Figure 4A). Around the brachiopod socket, sulfate abundance is high and co-occurs with a
229 low abundance of reduced-S species (Fig. 4A and 4B). Inorganic sulfate abundance is the greatest
230 along the top right edge of the shell. The sulfate abundance decreases towards the inner fibrous

231 calcite but there is an increase in the frequency of high abundance sulfate layers towards the inner
232 portion of the shell (Fig. 4B), which co-occurs with reduced-S species along one calcite layer
233 towards the inner shell (Fig. 4A). Additionally, in the fibrous calcite, sulfate abundance increases
234 around the edge of individual calcite crystallites. XANES spectra are indicative of inorganic
235 sulfate in a majority of the sample, with sulfate esters present around the socket (Fig. 4C, TT02_1
236 and TT02_5 respectively). In many locations, a low-intensity thiol peak of variable intensity co-
237 occurs with sulfate (Fig. 4C, TT02_2 to TT02_5).

238

239 *3.3 μ -XRF and XANES of Fossil Brachiopods*

240 Fossil brachiopods of Ordovician and Silurian age have some of the highest abundances of sulfate
241 compared to fossils of equivalent age such as bivalves, crinoids and corals (Present et al., 2015;
242 Richardson et al., 2019a). All fossil brachiopods analyzed contain intra-specimen variability in
243 sulfate abundance (Fig. 5). Within ORD1, sulfate abundance is variable along the original fibrous
244 fabric of the secondary shell layer (Fig. 5A). Within ORD2 (Fig. 5B), the original ribs are
245 preserved, indicating this cross-section is perpendicular to the plane of symmetry (unlike Fig. 5A
246 and 5C that are subparallel to symmetry), crosscutting fewer lines of growth than the other
247 samples. As such, variability is muted in ORD2 compared to other samples. Sample SIL1 is the
248 only fossil sample to preserve both valves of a single specimen (Fig. 5C). The two valves display
249 strong differences in sulfate abundance, while also recording variability along the original fabric
250 in the ventral valve (top valve Fig. 5C). Comparatively, SIL2 is an oblique cross-section. Again,
251 sulfate abundance follows the original fabric and is of comparable abundance to the sulfate zoning
252 within the surrounding abiotic calcite cement (Fig. 5D). Organic sulfur compounds are detected
253 only in ORD1, with a broadened sulfate peak, corresponding to the shoulder of a sulfate ester at

254 2481.1 eV at ORD1_1, and peaks at 2473.5 and 2478 eV corresponding to thiol and sulfite
255 respectively (Almkvist et al., 2010). The small sulfate shoulder represents a greater proportion of
256 inorganic sulfate mixed with a small abundance of esters sulfate. XANES spectra indicate that
257 inorganic, lattice-bound sulfate is the only species present in all other fossil brachiopods and is
258 directly comparable to the spectra within abiotic cement (Fig. 5E).

259

260 *3.4 Bulk Isotopes*

261 Bulk $\delta^{34}\text{S}_{\text{CAS}}$ for Anticosti Island samples ORD1 and ORD2 are +27.4‰ and +25‰ ($\pm 0.23\%$;
262 duplicate analyses), respectively (Jones and Fike, 2013). Bulk $\delta^{34}\text{S}_{\text{CAS}}$ for Gotland samples SIL1
263 and SIL2 are +33.6 and +29.6‰ ($\pm 0.2\%$; duplicate analyses), respectively (Rose et al., 2019a).
264 Bulk *T. transversa* have a $\delta^{34}\text{S}_{\text{CAS}}$ of +22.4‰ ($\pm 0.3\%$; triplicate analyses), while local seawater
265 from which they were sourced has a $\delta^{34}\text{S}_{\text{SO}_4}$ of +21.0‰ ($\pm 0.3\%$; Oduro et al., 2012).

266

267 **4.0 DISCUSSION**

268 *4.1 Characterization of Organic Sulfur Compounds (OSCs)*

269 The detection of co-occurring reduced and oxidized OSCs and the generation of spatially explicit
270 abundance maps of these species within a petrographic context can provide valuable new insights
271 into biomineralization in extant brachiopod exoskeletons and diagenetic processes in fossil
272 brachiopods. The presence of co-occurring reduced and putative oxidized OSCs has been reported
273 previously within modern coral calcite (Perrin et al., 2017), and within concentrated modern
274 brachiopod organic matrices (Cusack et al., 2008), specifically as thiols, sulfoxides, and presumed
275 esters. However, one outstanding question both in XAS and biomineralization studies of biogenic
276 carbonate is the nature of the lattice-bound sulfate (inorganic vs. organic ester; Cuif et al., 2003;

277 Dauphin et al., 2003; Cusack et al., 2008; Cusack and Freer 2008; Tamenori et al., 2014; Perrin et
278 al., 2017; Tamenori and Yoshimura, 2018). XANES spectra can differentiate between inorganic
279 and organic sulfate esters by an additional feature, a shoulder on the low-energy side of the main
280 sulfate peak that represents an organic sulfate ester (Almkvist et al., 2010; Rose et al., 2019b).
281 Although protamine sulfate has been compared to sulfate in red corals (Tamenori et al., 2014), we
282 limit the discussion of organic sulfate to sulfate esters (includes chondroitin sulfate). This is
283 because in protamine sulfate, a sulfate ion is bonded to a monovalent organic counter ion, as
284 opposed to an organic compound which is unlikely to form a major component of the
285 biomineralized skeleton. Additionally there is no clear evidence that protamine sulfate is important
286 in the biomineralization process. There are visible differences in the spectra obtained here,
287 indicative of organic sulfate esters with the characteristic shoulder (at 2481 eV; Fig. 3D, TT01_2)
288 versus those lacking a distinct shoulder (e.g. Fig. 3D, TT01_4). The spectra that do not have an
289 ester shoulder on the sulfate peak are akin to spectra within abiotic calcite (e.g. Fig. 5D and E,
290 SIL2_6) and are similar to S K-edge XANES of other carbonate components (Rose et al., 2019b;
291 Richardson et al., 2019a). This characteristic shoulder of an organic sulfate ester in XANES spectra
292 has seldom been observed within carbonates, suggesting that previous studies did not detect sulfate
293 esters using XANES spectroscopy (Cuif et al., 2003; Dauphin et al., 2003; Dauphin et al., 2005;
294 Yoshimura and Tamenori 2018).

295 To more definitively identify the nature of the sulfate that comprises a majority of the fossil
296 and extant brachiopods investigated (i.e., those with XANES spectra lacking an ester shoulder),
297 post-edge features can be used to further differentiate among sulfate species (Fig. 6; Fleet, 2005).
298 Many discrete sulfate minerals exhibit three fine-structure features at approximately 2484.9,
299 2491.3 and 2498 eV (Fleet et al., 2005) on top of the large, broad feature in all sulfate spectra

300 occurring between ~2490 and ~2505 eV. Such fine-structure features originate from photoelectron
301 scattering from ordered sulfur and cation neighbors, whereas the larger, broad feature originates
302 from the first tetrahedral oxygen shell. The majority of samples, including those from abiotic
303 carbonate cements, have a XANES spectrum that includes a post-edge feature at 2484.9 eV (Fig.
304 6, orange arrows). However, while some spectra also display higher-energy fine-structure features
305 in the post-edge region (e.g., TT02_1), these are weak or absent in the spectra of many samples.
306 All of the spectra have a large broad feature between 2490 and 2500 eV, yet in some samples the
307 peak of this feature is offset from what is observed in standard materials (Fig. 6, green arrows)

308 Previous work has interpreted the absence of features beyond 2485 eV to indicate that
309 organic sulfate compounds were present (Yoshimura and Tamenori, 2018). However, the synthetic
310 inorganic CAS sample presented here also shows no evidence of substantial fine-structure features
311 (Fig. 6). In addition, other oxyanions substituting in calcite (CrO_4^{2-} , AsO_4^{3-} , SeO_3^{2-} , and SeO_4^{2-})
312 have weak fine-structure features in the X-ray absorption spectra (Alexandratos et al., 2007; Aurelio
313 et al., 2010; Reeder et al., 1994; Tang et al., 2007). Both tetrahedral (CrO_4^{2-}) and trigonal pyramidal
314 (SeO_3^{2-} , AsO_3^{3-}) oxyanions have been shown using X-ray standing waves to occupy the carbonate
315 group site in calcite, but with the central atom of the oxyanion offset from the carbon position in
316 the structure (Bedzyk and Cheng, 2002; Cheng, 1998; Cheng et al., 1999, 1997). Such a shift
317 produces a distribution of oxyanion-Ca interatomic distances, creating a disordered Ca shell and
318 weak to negligible fine-structure features in the post-edge region of XANES spectra. The
319 consistent, systematic behavior of oxyanions in the calcite lattice suggests that sulfate will behave
320 similarly. The absence of fine-structure features above 2485 eV thus only indicates the absence of
321 crystalline/mineral sulfate salt (e.g., gypsum) and alone is not diagnostic of organic versus

322 inorganic sulfate. This conclusion is consistent with the original interpretation of the XANES
323 spectra of sulfate in natural calcium carbonates (Pisingitore et al., 1995).

324 Further evaluation of the XANES spectra, including the post-edge region, suggests that the
325 presence or absence of the features at 2484.9 eV does provide information regarding the form of
326 sulfate present. Post-edge features fall into different categories based on valency and crystallinity
327 (as seen in the standard XANES spectra Fig. 6). The shoulder at 2484.9 eV indicates divalency of
328 the sulfate ion and the two post-edge oscillations at 2491.3 and 2498 eV correspond to crystalline
329 structures. Using this, the sulfate can be classed as: gypsum-like (crystalline and divalent showing
330 all three features), monovalent sulfate minerals like Na_2SO_4 (crystalline and monovalent, lacking
331 the shoulder at 2484.9 eV), CAS (poorly crystalline and divalent, showing a feature at 2484.9 eV)
332 and organic sulfate esters (poorly crystalline and monovalent, showing one broad feature at 2498
333 eV). Samples TT01_2 (Fig. 3D) and ORD1_1 (Fig. 5E) that show the diagnostic ester sulfate
334 shoulder near 2481 eV have one main broad feature at 2495 to 2498 eV. In contrast, the features
335 diagnostic of inorganic sulfate in the form of CAS are no low-energy shoulder at 2481 eV, the
336 (variably muted) presence of a high-energy feature at 2484.9 eV feature, and a lack of fine-
337 structure features at energies about 2485 eV that would indicate crystalline sulfate minerals. This
338 set of spectral properties is thus indicative of inorganic sulfate contained in a calcite lattice.

339 The detection and characterization of reduced and oxidized organic S-species in small
340 regions of individual specimens is novel, especially within fossil brachiopods, due to the low
341 abundance of the organic matrix within brachiopods (< 3 wt. %; Cusack et al., 2008). It is clear,
342 however, that most of the sulfate in both extant and fossil brachiopods is predominantly inorganic,
343 as CAS. This observation does not rule out the possibility that some of this sulfate may originally
344 be sourced from organic compounds, through desulfurization of esters or oxidation of reduced

345 organic moieties. Some localized occurrences diagnostic of organic sulfate esters were observed,
346 albeit in trace amounts (e.g., Fig. 3C). However, considering the size of the sulfate reservoir has
347 been > 5 mM for most of the Phanerozoic (Lowenstein et al., 2003), the relatively high abundance
348 of sulfate in brachiopods and the relatively low abundance of OSCs in comparison, it is highly
349 likely that the vast majority of brachiopod-sourced CAS is inorganic and derived directly from
350 ambient seawater sulfate.

351

352 *4.2 Sulfate abundance and variability*

353 Each brachiopod displays internal variation in sulfate abundance that appears to follow the fabric
354 of the secondary layer. The source samples for the fossil brachiopods have not experienced broad-
355 scale post-depositional alteration (see Jones et al., 2011; Jones and Fike 2013; Rose et al., 2019a),
356 which is important in determining the fidelity of CAS to original marine sulfate. Diagenetic
357 recrystallization would result in homogenisation of sulfate abundance. Additionally, the
358 brachiopod shells are not visibly recrystallized. As such, we anticipate that this variation in sulfate
359 abundance does not reflect a diagenetic component. Further, since most articulate brachiopods are
360 epifaunal, sessile benthos (Ager, 1967) and therefore in good contact with overlying seawater, it
361 is not likely that changes in sulfate concentration, such as would be found within the sediment due
362 to microbial sulfate reduction, are the source of the observed sulfate variability in the brachiopods.

363 The rate of shell growth is not constant throughout the lifespan of a brachiopod. Growth
364 rate is faster in the juvenile stage and decreases after maturation (Buening and Carlson, 1992;
365 Pérez-Huerta et al., 2014). Additionally, growth rates may differ or shell may be resorbed (Carlson,
366 1989) between the ventral and dorsal valves (Buening and Carlson, 1992; Pérez-Huerta et al.,
367 2014). In abiotic carbonate precipitation, the likelihood of sulfate substitution into the carbonate

368 lattice is kinetically controlled and is anticipated to increase proportionally with crystal growth
369 rate (Busenberg and Plummer, 1985). Thus, sulfate abundance in brachiopods could be an
370 important recorder of growth rate (as has been suggested with Mg abundance; Garbelli et al., 2014)
371 irrespective of any local variation in seawater sulfate abundance. Based on the linear relationship
372 between length and width during brachiopod growth, and the size to shell thickness relationship,
373 TT01 is considered a fully mature sample while TT02 is not yet fully mature, but is developed
374 beyond the juvenile stage (Endo, 1987; Pérez-Huerta et al., 2014). The difference in total sulfate
375 abundance between TT01 and TT02 could be due to different juvenile growth rates (Fig. 3 and
376 Fig. 4). While ontogeny cannot be determined for the fossil brachiopod species, the preservation
377 of both valves, and difference in sulfate abundance between the valves, in SIL1 indicates that
378 growth rate was faster in the dorsal valve (Fig. 5C). Further, amorphous calcium carbonate (ACC)
379 is a common precursor to biomineral precipitation (Cusack and Freer, 2008) and has been detected
380 in modern Terebratulida as a precursor to calcite during shell repair, indicating it is likely a
381 precursor during original growth (Griesshaber et al., 2009). An ACC precursor may allow for
382 greater amounts of sulfate to substitute into the carbonate structure, since the ACC structure may
383 be more susceptible to incorporation of the larger sulfate ion.

384 Variation in sulfur abundance that appears as banding has been observed previously in
385 foraminifera and mollusks (Paris et al., 2014; Tamenori and Yoshimura, 2018; Tanaka et al.,
386 2019). These studies suggest that the increases in sulfate abundance are not associated with growth
387 rate but are coincident with enrichment in organic sulfur in the organic matrix (Paris et al., 2014;
388 Tanaka et al., 2019) or with disturbance lines in mollusks (false annual growth lines; Tamenori
389 and Yoshimura, 2018). Our data do not support the suggestion that banding is coincident with an
390 organic component (Fichtner et al., 2018; Guillaume Paris et al., 2014; Tanaka et al., 2019) and

391 are not comparable to annual/disturbance lines in mollusks (Tamenori and Yoshimura, 2018) as
392 brachiopod growth lines do not correspond to age (Paine, 1969). The appearance of bands of
393 increased sulfate abundance may reflect the growth process of brachiopods, where the fibers within
394 the secondary layer are individual crystals secreted by a moving array of epithelial cells. Each fiber
395 acts as a substrate, or nucleation point, for continued crystal growth, despite any shell curvature
396 (Griesshaber et al., 2007; Schmahl et al., 2004). Thus, the banding of sulfate likely follows
397 individual crystals throughout the brachiopod shell. The frequency of high sulfate bands increases
398 towards the inner shell margin, particularly within TT01 and TT02, where the crystallites are
399 younger (more recently formed) and therefore could have precipitated under different growth
400 regimes.

401 Comparisons of sulfate abundance and SEM images of TT02 (Fig. 2) indicate that sulfate
402 abundance increases on the outer edge of the oriented individual crystallites within the fibrous
403 calcite (oriented calcite that dominates the bottom left in Fig. 2C). It is important to consider
404 potential crystal orientation effects (i.e. calcite anisotropy) and/or changes in excitation volume
405 that may contribute to this apparent increase in abundance. It has been demonstrated that Sr and
406 Mg K-edge XANES spectroscopy can be affected by carbonate crystal orientation, due to calcite
407 anisotropy, based on both corals and brachiopods (Allison et al., 2005; Pérez-Huerta et al., 2008).
408 This orientation effect, however, results mostly in slightly variable pre- and post-edge features, as
409 opposed to differences in the normalised absorption intensity (Pérez-Huerta et al., 2008). There
410 are no differences in the sulfate absorption peaks in XANES spectra across TT02 (the only
411 difference is the variable abundance of the reduced S species). Due to this, we anticipate that calcite
412 orientation, has no appreciable effect on the observed sulfate abundance (fluorescence yield) in
413 the μ -XRF images of TT02. Comparisons of calcium and sulfate excitation maps indicate that

414 calcium abundance increases to the edge of some crystals in the region of oriented crystallites
415 (green box Fig. 7), meaning these increases in abundance could reflect surface topography of the
416 sample, where changes in excitation volume create an apparent abundance increase. It is important
417 to note that the difference in energy of fluorescence between calcium and sulfate can make it
418 difficult to deconvolve fluorescence response vs. surface roughness. However, there are increases
419 in sulfate abundance in this region (Fig. 7B) that show no associated increase in calcium abundance
420 (Fig. 7C), indicating that some of this variation in sulfate abundance at the edge of crystals may
421 be real.

422 If the increase in abundance around individual crystals is not an artefact caused by changes
423 in excitation volume, it may reflect the original organic template. Although the sulfate is not an
424 ester (Fig. 4C), it could be sourced from desulfurized esters or oxidation of reduced-S moieties
425 from the organic template, resulting in an apparent increase in CAS abundance around the fibrous
426 calcite. Intra-crystalline organic matrix (IOM) has been recognised as a template, or framework,
427 for carbonate nucleation in biomineralizers (Pérez-Huerta et al., 2018). IOM can include a protein
428 and polysaccharide-rich template or sheath that may often contain both reduced and oxidized sulfur
429 groups (Addadi et al., 1987; Cusack et al., 2008). A covariation of phosphorus and reduced OSCs
430 has been observed around individual calcite crystals in *T. retusa* that suggests this template can be
431 preserved (Cusack et al., 2008). The absence of any OSCs where sulfate abundance increases to
432 the edge of individual crystals in TT02 (Fig. 4B and 4C, spectrum TT02_1) suggests that the sulfate
433 would need to be sourced through the desulfurization of esters, oxidation of reduced OSCs, or
434 most likely directly from inorganic sulfate in seawater. Sulfate sourced from the oxidation of
435 reduced OSCs is possible due to the occurrence (yet low abundance) of thiol, sulfoxide and sulfite
436 throughout the extrant *T. transversa* samples (Figs. 3D and 4C). Micron-scale isotopic data using

437 secondary ion mass spectrometry (SIMS) will provide information on the original source of this
438 sulfate surrounding the crystallites, such that if the sulfate is sourced from the oxidation or
439 reduction of OSCs, it should have an isotopic signature offset from the $\delta^{34}\text{S}_{\text{SO}_4}$ of modern seawater.

440

441 *4.3 Implications for Biomineralization*

442 IOM takes part in numerous roles during biomineralization including nucleation, determination of
443 mineralogy, and crystal orientation (Pérez-Huerta et al., 2018). The interplay of IOM on the
444 resultant mineral composition and structure can affect the biomechanics of the exoskeletons and,
445 ultimately, how biominerals respond during diagenesis. However, IOM is not well preserved on
446 geologic timescales. In the absence of abundant IOM here, the presence (although in low
447 abundance) of similar OSCs in extant and fossil brachiopods is promising for understanding
448 brachiopod biomineralization, fossil preservation, and resistance to recrystallization. Sulfate
449 esters, in conjunction with carboxylates, can influence the orientation of calcite crystals (Addadi
450 et al., 1987; Nudelman et al., 2006). Within coccolithophorids, sulfated polysaccharides control
451 the outer shape of an individual coccolith (Marsh et al., 2002). Their presence in brachiopods could
452 give rise to the orientated fibrous calcite in the secondary layer that ultimately contributes to
453 brachiopod preservation potential. Additionally, the presence of chondroitin sulfate in solution
454 favors calcite precipitation (Kitano and Hood, 1965) and L-Cysteine, containing thiols, generates
455 hydrogen bonds between calcium or carbonate ions in solution, promoting calcite formation (Xie
456 et al., 2005). Together, one or both of these OSCs may play a role in the calcite mineralogy of
457 articulate brachiopods (low-Mg calcite) and are detected in extant and fossil brachiopods here
458 using XANES spectroscopy, a factor that further influences the unique preservation of brachiopods
459 over time. Overall, the similar OSCs between extant and fossil brachiopods points towards a

460 relatively conserved and deep-rooted biomineralization pathway for brachiopods throughout the
461 Phanerozoic (in agreement with transcriptomic and proteomic data of the extant brachiopod
462 *Magellania venosa*; Jackson et al., 2015). Similar observations of low abundances of reduced
463 OSCs corresponding to amino acids within IOM has been shown in modern mollusks, corals and
464 brachiopods (Dauphin et al., 2003; Cuif et al., 2003; Cusack et al., 2008), as well as within fossil
465 corals and micrite (Richardson et al., in review). However, the role that OSCs play in the
466 biomineralization pathway of genera may differ (e.g. nucleation vs. growth).

467

468 *4.4 Implications for Isotope Studies*

469 Global ocean chemistries have dramatically changed over the course of the Phanerozoic. For
470 example, the seawater sulfate reservoir has increased in size from approximately 5-12 mM to 28
471 mM (Horita et al., 2002; Lowenstein et al., 2003). Despite these changes, seawater sulfate has
472 remained the largest reservoir of sulfur in the biogeochemical sulfur cycle for the Phanerozoic and
473 the residence time of Phanerozoic seawater sulfate is on the multi-million-year time-scale (Berner,
474 2001). *T. transversa* are anticipated to live for approximately 10 years (Paine, 1969), growing
475 continually throughout their lifetime via accretionary growth, adding carbonate marginally to the
476 exoskeleton (Auclair et al., 2003; Baumgarten et al., 2014; Gaspard et al., 2018; Stricker and Reed,
477 1985). The lifespan of Ordovician and Silurian brachiopods is relatively unknown, since growth
478 lines of brachiopods do not necessarily correlate with age (Auclair et al., 2003; Paine, 1969).
479 However, it is not expected that fossil brachiopods would have had a lifespan wildly divergent
480 from those of extant brachiopods. If brachiopods are recording global or basinal $\delta^{34}\text{S}_{\text{SO}_4}$ then it is
481 unlikely that $\delta^{34}\text{S}_{\text{CAS}}$ of their shells should exhibit much, if any, variation, due to the magnitude of

482 difference between the lifespan of brachiopods and seawater sulfate residence time. Thus, if
483 variability does exist it is likely recording local $\delta^{34}\text{S}_{\text{SO}_4}$, as opposed to global ocean variability.

484 The bulk $\delta^{34}\text{S}_{\text{CAS}}$ value of *T. transversa* (+22.4‰) is more positive than local seawater
485 sulfate by ~ 1‰ (Puget Sound $\delta^{34}\text{S}_{\text{SO}_4}$ of +21 (± 0.3 ‰); (Oduro et al., 2012)). This value could be
486 accounted for by the small fractionation that can occur during sulfate incorporation and
487 substitution for the carbonate ion, which has been shown to be ≤ 1 ‰ in foraminifera (Burdett et
488 al., 1989; Paris et al., 2014; Rennie et al., 2018). Comparatively, bulk $\delta^{34}\text{S}_{\text{CAS}}$ value of the whole
489 rock from which the fossil samples were sourced are more positive than time-correlative
490 brachiopod-only samples for both the end-Ordovician and Silurian. Whole rock $\delta^{34}\text{S}_{\text{CAS}}$ values
491 from ORD1 (+27.4‰) and ORD2 (+25‰) (Jones & Fike 2013) are also more positive than
492 brachiopod-only values (+23 to +25‰; Present et al., 2015), while whole rock $\delta^{34}\text{S}_{\text{CAS}}$ values from
493 SIL1 (+33.6‰) and SIL2 (+29.6‰) (Rose et al., 2019a) are between 4.5 and 5.1 ‰ more positive
494 than brachiopod-only data (Present, 2018). We attribute this to the relatively low abundance of
495 brachiopods in these specific ancient carbonate samples relative to other carbonate components
496 that are more susceptible to early marine diagenesis (Richardson et al., 2019a). These other
497 components likely record a mixture of $\delta^{34}\text{S}_{\text{CAS}}$ signals from water column components, early syn-
498 sedimentary diagenesis, and post-depositional alteration (Present et al., 2015; Richardson et al.,
499 2019a; Richardson et al., 2019b). We anticipate that micron-scale analysis of $\delta^{34}\text{S}_{\text{CAS}}$ within the
500 fossil brachiopods (e.g., using SIMS or laser-ablation MC-ICP-MS) would agree more closely
501 with other temporal records (such as the nearest time-equivalent evaporite deposits), and any
502 variability will reflect local seawater (and potentially pore-water evolution for infaunal species)
503 chemistry during brachiopod growth.

504

505 **5.0 Conclusions**

506 We have demonstrated the differences between organic sulfate esters and inorganic sulfate in
507 extant and fossil brachiopod shells using XANES spectroscopy. Our results show that inorganic
508 sulfate is the dominant CAS signal in both extant and fossil brachiopods, and accounts for a
509 majority of the intra-specimen sulfate variability. Sulfate abundance maps of individual
510 brachiopods show variability parallel to the original fabric of the secondary layer. Sulfate
511 abundance likely changes with varying growth rate throughout the brachiopod lifespan. Organic
512 sulfate esters are present, albeit in low abundance, and often co-occur with reduced S-amino acids
513 where they appear to be preferentially located near the hinge line. The presence of oxidized and
514 reduced OSCs in both extant and fossil brachiopods suggests that these compounds may influence
515 mineralogy and crystal orientation during biomineralization. These findings are important for
516 researchers in paleoenvironmental reconstructions and biomineralization and we suggest (1)
517 brachiopods are likely a more faithful archive for seawater sulfate isotopic values and (2) the OSCs
518 may play a role in determining mineralogy and crystal orientation in brachiopods and therefore
519 influence the preservation of brachiopod shells throughout geologic time due to their low-Mg
520 calcite mineralogy.

521

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879

880 **FIGURES**

881 Figure 1 – images of extant and fossil brachiopods with outlined areas that correspond to mapped
882 regions in later figures. A) *T. transversa* sample TT01, B) *T. transversa* sample TT02, C) ORD1;
883 Bioturbated packstone from the Fox Point Member of the Becscie Formation, Anticosti Island, D)
884 ORD2; Crinoidal wackestone from the Lousy Cove Member of the Ellis Bay Formation, Anticosti
885 Island, E) SIL1; Poorly washed fossiliferous grainstone from the Upper Visby Formation, Gotland,
886 F) SIL2; Brachiopodal grainstone from the Upper Visby Formation, Gotland.
887

888 Figure 2 – SEM images of TT02. A) Large image corresponding to the mapped region in TT02,
889 with transmitted light image inset. Red box outlines the area mapped using μ -XRF. Areas outlined
890 and labelled in black correspond to the higher resolution images in B to E. B to E show varying
891 textures of crystallites.

892

893 Figure 3 – Sample TT0 A) sulfoxide excitation energy map at 2476.3 eV B) Sulfate excitation
894 energy map at 2482.3 eV with green boxes showing spot locations for representative XANES. The
895 color scale is the same for A and B. The gradient of the color scale corresponds to gradients in the
896 abundance of sulfur species; dark colours (blue, black, purple) correspond to low abundance and
897 brighter colours correspond to higher abundance (red, orange, yellow, white). C) tricolour plot
898 using data from XANES fitting where red corresponds to inorganic sulfate, blue is sulfate with an
899 ester and yellow is the location of sulfate combined with a reduced organic sulfur compound. D)
900 XANES of spot locations numbered in B. Dashed lines at 2473.2 eV, 2476.6 eV, 2481 eV and
901 2482.6 eV. Arrow points to sulfate ester shoulder in spectra TT01_2.

902

903 Figure 4 – Sample TT02 A) sulfide excitation energy map at 2472 eV. Color scale shown is the
904 same for A and B. Color gradients are as described in Fig. 3. B) sulfate excitation energy map at
905 2481.5 eV with green boxes showing spot locations for representative XANES. C) XANES of spot
906 locations in B. Dashed lines at 2473.5 eV and 2482.4 eV. Sample TT01 and fossil brachiopods are
907 all scaled to the same S (quantitative) counts for comparison. Sample TT02 (here), however,
908 contains higher sulfate abundance, thus, for variation within the shell structure to be visible, the
909 scale is 3 times that of TT01 and fossil brachiopods (i.e., sulfur counts corresponding to white on
910 TT02 map is three times greater than all other maps).

911

912 Figure 5 – Sulfate excitation energy maps of fossil brachiopods and XANES. Green boxes and
913 numbers correspond to a spectra number A) ORD1. Color scale shown is the same for A, B, C and
914 D. Color gradients are as described in Fig. 3. B) ORD2. C) SIL1. D) SIL2. E) XANES of spot
915 locations numbered on each map. SIL1_5 is located within abiotic cement as opposed to a
916 brachiopod, for comparison. Dashed lines at 2473.5 eV, 2478 eV and 2482.3 eV.

917

918 Figure 6 – XANES spectra post-edge features. Standards are outlined in black and sample points
919 are outlined in blue. Sample SIL5 is a spectrum obtained from abiotic cement that is not a sulfate
920 ester but represents inorganic, lattice-bound sulfate. Dashed lines at 2484.9, 2491.3 and 2498 that
921 correspond to features in sulfate mineral post-edge. Standard XANES of gypsum and sodium sulfate
922 in the S K-edge region obtained at BL 13-IDE. Chondroitin sulfate (ester) standard from the ESRF ID-21
923 S XANES spectra database (Cuif et al., 2003).

924

925 Figure 7 – Sample TT02 A) SEM image shown in Fig. 2 for crystal fabric context. B) sulfate
926 abundance map (also shown in Fig. 4) where the color scale is stretched for ease of comparison
927 with calcium. C) Calcium abundance map where the color scale is reduced in order to better
928 observe internal variation for comparisons with sulfate. Color scale shown is the same for B and
929 C. Color gradients are as described in Fig. 3. In each figure the green box outlines the region where
930 there are aligned fibrous calcite crystallites that show increases in the abundance of sulfate towards
931 the edge of the individual crystals.













