

1 **Micro-Scale Isotopic Analysis of Ice Facies Frozen from Supercooled**
2 **Water**

3
4 Connor J. Shiggins^{a1*}, Matthew R. P. Harris^a, Peter G. Knight^{a*},
5 Christopher J. Fogwill^a.

6 *^aSchool of Geography, Geology and the Environment, Keele University, Staffordshire,*
7 *ST5 5BG, United Kingdom.*

8 *Correspondence to: Connor Shiggins (Connor.Shiggins@liverpool.ac.uk).

9 Connor J. Shiggins: PhD student at University of Liverpool. Twitter handle:
10 @glacialicon

11 Matthew R. P. Harris: PhD student at Keele University. Twitter handle:
12 @Organic_Matters

13 Peter G. Knight: Reader in Geography, Head of Geography Programmes and Physical
14 Geography Course Director at Keele University. Twitter handle: @PKGeog

15 Christopher J. Fogwill: Professor of Glaciology and Palaeoclimatology and Head of
16 School at Keele University.

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¹ Connor Shiggins has changed affiliation during the peer review process from Keele University to the University of Liverpool. The new address is: Department of Geography and Planning, School of Environmental Sciences, University of Liverpool, Liverpool, L69 7ZT, United Kingdom.

19 **Micro-Scale Isotopic Analysis of Ice Facies Frozen from Supercooled** 20 **Water**

21 ABSTRACT. Subglacial glaciohydraulic supercooling can form basal ice and
22 affect glacier dynamics, sediment transfer and geomorphology. Whilst isotopic
23 analysis ($\delta^{18}\text{O}$ - δD) of basal ice has demonstrated the significance of
24 supercooling, questions remain as to what extent the identification of
25 supercooling depends on sampling resolution. We conducted laboratory
26 experiments in which ice was frozen from supercooled water and sampled at a
27 micro-scale (1.5 millilitre) to identify highly localised variations in isotopic
28 compositions that might be lost in bulk-scale sampling. Three distinctive ice
29 facies produced by the freezing process demonstrated diagnostic isotopic
30 signatures that were distinguished when the facies were sampled independently.
31 However, their respective isotopic signatures were lost when bulk-scale sampling
32 combined the two facies, demonstrating the requirement of micro-scale sampling
33 when identifying supercooling in basal ice facies. These findings indicate that
34 sampling for isotopic compositions of ice facies frozen from supercooled water
35 should be conducted at a scale that prevents the amalgamation of different facies
36 to highlight a detailed isotopic signature. We conclude that micro-scale sampling
37 is imperative to understanding and quantifying this subglacial process.

38 Keywords: supercooling, isotopes, sample size, freezing slopes.

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44 **1.0 Introduction**

45 Glaciohydraulic supercooling occurs when basal water at, or below the pressure melting
46 point ascends from a subglacial overdeepening and the water temperature rises quicker
47 than the water which is heated by viscous dissipation (Alley et al. 1998; Lawson et al.
48 1998). Where it occurs, supercooling can lead to the accretion of ice at the base of
49 glaciers even where the basal thermal regime is temperate, and provides a mechanism
50 for the creation of debris-rich basal ice in those temperate settings. Supercooling was
51 found to be the primary formational process of stratified basal ice at the Matanuska
52 Glacier, Alaska (Alley et al. 1998; Lawson et al. 1998; Evenson et al. 1999; Ensminger
53 et al. 2001; Larson et al. 2010; Larson et al. 2016). At other temperate glaciers which
54 could support supercooling, the Matanuska-type model has been shown to be less
55 efficient with regards to basal ice formation elsewhere (Spedding and Evans, 2002;
56 Swift et al. 2006; Cook et al. 2007; 2010; Swift et al. 2018). For example, Cook et al.
57 (2010) determined supercooling only formed 42% of the stratified basal ice facies at
58 Svínafellsjökull, Iceland.

59 Ice formed from supercooled water is known to be isotopically ($\delta^{18}\text{O}$ - δD) lighter
60 relative to the parent water, but the extent to which this occurs is unknown (Lawson et
61 al. 1998; Ensminger et al. 2001; Cook et al. 2010; Larson et al. 2010). Cook et al.
62 (2010) found at Svínafellsjökull that the isotopic composition of anchor ice frozen from
63 supercooled water was lighter by $\sim 2.4\text{‰}$ in $\delta^{18}\text{O}$ and 15.2‰ in δD relative to the
64 subglacial upwelling. Larson et al. (2010) concluded that supercooling at Vatnajökull
65 and Öräfajökull, Iceland was the primary formational process for the stratified basal ice
66 facies because it was lighter by $\sim 2.4\text{‰}$ in $\delta^{18}\text{O}$ and 12‰ in δD relative to the vent
67 water. Thus, whilst we understand the isotopically light nature of stratified basal ice

68 formed from supercooling, a lack of detailed knowledge remains surrounding the
69 specific mechanisms and levels to which this occurs.

70 Methods used to quantify supercooling consist of visual, sedimentological,
71 stable isotope and radionuclide analysis (e.g. Alley et al. 1998; Lawson et al. 1998;
72 Evenson et al. 1999; Titus et al. 1999; Ensminger et al. 2001; Roberts et al. 2002;
73 Spedding and Evans. 2002; Swift et al. 2006; Cook et al. 2007; 2010; Larson et al.
74 2010; Cook et al. 2011; Swift et al. 2018). Here, we focus on the importance of sample
75 scale for stable water isotope analysis of ice facies frozen from supercooled water.
76 Water isotope analysis has frequently been used as a quantification method when
77 evaluating the significance of glaciohydraulic supercooling (e.g. Lawson et al. 1998;
78 Titus et al. 1999; Ensminger et al. 2001; Swift et al. 2006; Cook et al. 2010; Larson et
79 al. 2010). Sample sizes of basal ice formed from supercooling collected at glaciers for
80 isotopic analysis range from 25-300 mL (Titus et al. 1999; Ensminger et al. 2001; Swift
81 et al. 2006; Cook et al. 2010; Larson et al. 2010). However, due to their large sizes,
82 these basal ice samples could contain ice facies formed from multiple alternative
83 processes. This amalgamation of different ice facies could dilute the isotopic fingerprint
84 of supercooling, potentially leading to an inaccurate diagnosis of basal ice formation.
85 This study develops on comments from Cook et al. (2010) suggesting the scale in which
86 basal ice samples are collected will be important as bulk-scale sampling could
87 homogenise the isotopic signatures of formational processes.

88 Basal ice investigations separate from supercooling have also considered their
89 sample sizes. Hubbard and Sharp (1993) illustrated if the basal ice layer is sampled with
90 a cylindrical sampler that has a diameter of 2 cm, it could incorporate several layers of
91 laminated facies, instead of a single layer of ice. Souchez and De Groot (1985)
92 sampled basal ice samples at the base of Grubengletscher that were placed in 30 mL

93 glass bottles. Souchez et al. (1998) revised a sampling strategy developed by Souchez
94 and DeGroot (1985), collecting samples at a resolution of 1 mL instead of 30 mL from
95 five Arctic glaciers. A fractional melting experiment was applied from Russell Glacier
96 and demonstrated the lack of fractionation by sampling 25 mL of melt water. The
97 clustering of samples on co-isotopic plots ($\delta^{18}\text{O}$ - δD) suggested there was no
98 fractionation during basal ice formation by regelation, or the scale of the sample had
99 homogenised the isotopic compositions (Souchez et al. 1988).

100 This study takes a laboratory-based approach to investigate whether field studies
101 of basal ice evaluating glaciohydraulic supercooling should consider a micro-scale
102 approach to sample size collection at glaciers. Replicating supercooling conditions
103 under laboratory conditions has been performed in three studies to date (Knight PG and
104 Knight DA, 2005; 2006; Cook et al. 2012). The overarching similarity found by the
105 studies was a distinct ‘herringbone’ crystal structure associated with supercooling
106 (Figure 1). This diagnostic crystal structure forms as a result of multi-directional ice
107 growth during freezing from supercooled water (Knight PG and Knight DA, 2005).
108 Thus, ice frozen from supercooled water will henceforth be referred to as ‘herringbone
109 ice’. In order to determine whether bulk-scale sampling of ice frozen from supercooled
110 water yields the same isotopic composition as a micro-scale sampling approach, four
111 laboratory experiments were performed in a closed-system.

112 [Figure 1 near here]

113 **2.0 Methodology**

114 We sampled and melted ice frozen from supercooled water on a 1.5 mL scale to identify
115 any micro-scale isotopic differences in basal ice facies. Our aim was to determine
116 whether bulk-scale sampling resolves the same isotopic composition for the ice facies
117 frozen from supercooled water as the micro-scale sampling technique. Four laboratory

118 experiments were conducted, with the sampled ice isotopically and statistically
119 analysed.

120 ***2.1 Replicating Supercooling Conditions***

121 We followed previous methodologies which have replicated supercooling conditions
122 (Knight PG and Knight DA 2005, 2006; Cook et al. 2012), where a small recirculating
123 pump (flow-rate 1400 litres per hour) was clamped to the side of an open, plastic
124 container (16x36x27 cm) half filled with tap water to a depth of 8 cm in a cold
125 laboratory at -12 °C. The tap water had a temperature of 11 °C at the beginning of each
126 experiment before being placed in the cold laboratory. This setup stimulated
127 supercooling, keeping the water turbulent and allowing it to drop below 0 °C without
128 freezing. The pump was switched on and the experiment was left for five days. On the
129 fifth day, the pump was switched off to allow the remaining supercooled water to freeze
130 (Figure 2). After the seventh day, the ice block was removed from the container and
131 separated into its respective facies. The experiment was conducted four times across a
132 four-week period, accumulating 84 samples in total. 28 samples of each facies (clear,
133 herringbone and mixed) were sampled and analysed (Figure 3).

134 [Figure 2 near here]

135 [Figure 3 near here]

136 ***2.2 Micro-Scale Sampling***

137 We applied a biased sampling strategy where the facies were sampled based on their
138 crystal structure. Once the ice types had been categorised into their facies, they were
139 carefully cut by a bandsaw to allow for micro-scale sampling. The samples were placed
140 on the bandsaw in the cold laboratory at -12 °C and were pushed through the blade to

141 create the thin sections in preparation for melting. The facies were visually identified
142 and separated precisely using the bandsaw, ensuring that the ‘supercooled’ sample only
143 contained the herringbone crystal structure. The mixed ice facies was sampled to
144 combine both the herringbone and clear ice, in order to determine whether this
145 amalgamation of facies would homogenise the isotopic composition of the herringbone
146 ice. After thin-sectioning, samples were immediately placed into sealed plastic
147 centrifuge tubes and moved to a room with a temperature of 15 °C to allow the samples
148 to melt, ensuring no pre-melting.

149 ***2.3 Isotopic Analysis***

150 The 84 samples from the four experiments were placed in vials and analysed in the
151 Keele University ICELAB with a Los Gatos Research (LGR) Triple Isotope Water
152 Analyser-DLT-EP, model 912-0032. The samples were measured at a precision of ± 0.4
153 for δD and ± 0.1 for $\delta^{18}O$. Samples were interleaved such that a manufacturer standard
154 was measured every ten samples. After being measured, sample data was exported to
155 LGR’s post-processing software to calibrate the measured samples against the included
156 LGR-supplied standards. We included standards that covered the isotopic range of the
157 measurements taken. The standards used, and their specifications are as follows:

- 158 • LGR2C: $\delta D = -123.7 \pm 0.5\text{‰}$ vs VSMOW: $\delta^{18}O = -16.24 \pm 0.15\text{‰}$ vs VSMOW
- 159 • LGR3C: $\delta D = -97.3 \pm 0.5\text{‰}$ vs VSMOW: $\delta^{18}O = -13.39 \pm 0.15\text{‰}$ vs VSMOW
- 160 • LGR4C: $\delta D = -51.6 \pm 0.5\text{‰}$ vs VSMOW: $\delta^{18}O = -7.94 \pm 0.15\text{‰}$ vs VSMOW

161 ***2.4 Freezing Slopes***

162 Regression slopes between $\delta^{18}O$ and δD (known as ‘freezing slopes’) can give insights
163 into refrozen water and water sources incorporated in the system and the associated

164 fractionation. For example, depending on the gradient of a freezing slope, it can be
165 determined whether the input of water into a system has a similar isotopic composition
166 as the initial reservoir. Consequently, freezing slopes can be used as a method of
167 determining basal ice formation. Hypothetically, if a basal ice facies formed from an
168 initial water which had a slope of 6.7, and a second facies formed from a different water
169 source with a slope of 7.5, it indicates that these two facies formed from distinctly
170 different water sources because of the different slopes. However, if both facies yielded
171 an identical freezing slope of 6.7, it would suggest that the facies formed from the same
172 initial water and process.

173 As we conducted stable isotope analysis in a closed-system, the freezing slope
174 model determined by Jouzel and Souchez (1982) was utilised (Equation 1). This was
175 achieved by using the isotopic composition of the initial reservoir to determine the
176 gradient of our freezing slopes.

$$177 \quad S = \frac{[(\alpha - 1)/(\beta - 1)]}{\times [(1000 + \delta D)/(1000 + \delta^{18}O)]} \quad (1)$$

179 Where S is the gradient of the freezing slope, α and β are the equilibrium fractionation
180 coefficients for deuterium and ^{18}O respectively (Jouzel and Souchez, 1982). We chose
181 values for our equilibrium coefficients from Lehmann and Siegenthaler (1991), who
182 conducted high precision measurements of the isotopic fractionation of ice grown on a
183 cooling plate from an agitated water mass. They calculated that ' α ' had a value of
184 1.0212 and ' β ' had a value of 1.00291. The closed-system models were applied to the
185 experiments to determine whether the models would predict the freezing slopes.
186 Freezing slopes will have a shallower gradient than the Global Meteoric Water Line
187 (GMWL) which has a gradient of 8 on a δD - $\delta^{18}\text{O}$ co-isotopic plot. The GMWL is used

188 as a comparison standard in this analysis rather than the Local Meteoric Water Line
189 (LMWL), because tap water was used as the source.

190 **3.0 Results**

191 *3.1 Experimental Observations*

192 Three facies froze in the four isolated experiments:

- 193 • Facies 1) Clear ice (frozen at 0 °C)
- 194 • Facies 2) Herringbone ice (artefact of supercooled water: frozen below 0 °C)
- 195 • Facies 3) Mixed ice (containing the herringbone and clear crystal structures)

196 The mixed ice facies contained both the herringbone and clear facies. It was treated as a
197 proxy for the bulk-scale sampling utilised in previous research, as it contained more
198 than one ice type. The herringbone ice has been suggested to be indicative of closed-
199 system supercooling freezing under laboratory conditions (Knight PG and Knight DA
200 2005, 2006; Cook et al. 2012). The herringbone facies formed at the lowermost section
201 of the container as this layer was nearest to the recirculating pump where the turbulence
202 was at its strongest, preventing freezing. The thickest layer was the mixed ice as it
203 contained two crystal structures (clear and herringbone) in the middle section of the
204 container. The clear facies froze as a relatively thin layer above the boundary of the
205 mixed facies because the turbulence had minimal impact at the uppermost layer of the
206 container.

207 *3.2 Isotopic Analysis*

208 Co-isotopic diagrams were constructed to highlight isotopic differences in the
209 documented facies (Figure 4). The facies mean isotopic values, freezing slopes and
210 adjusted R² coefficients can be seen in table 1. We report the adjusted R² values to show

211 goodness of fit for the freezing slopes. The lowest adjusted R^2 value is 0.93 for
212 experiment 3, indicating a strong agreement between the freezing slopes and the
213 measured isotopic values for all four experiments. The clear facies was the isotopically
214 lightest facies relative to the initial reservoir. The clear facies in experiment 1 was
215 lighter by -12.4‰ in δD and -1.8‰ in $\delta^{18}O$ relative to the parent water. The mixed
216 facies was isotopically heavier than the initial water, e.g. -12‰ in δD and -1.6‰ in $\delta^{18}O$
217 in experiment 1. The herringbone facies was the isotopically heaviest facies compared
218 to the initial water, e.g. heavier by -32‰ in δD and -4.5‰ in $\delta^{18}O$ in experiment 1. This
219 trend continued throughout the remaining three experiments, with the clear ice being the
220 isotopically lightest, the mixed facies being heavier, and the herringbone ice being the
221 heaviest. The clear facies isotopic compositions ranged by -14‰ for δD and -2.5‰ for
222 $\delta^{18}O$ across the four experiments. The mixed ice varied by -13.7‰ in δD and -2.3‰ in
223 $\delta^{18}O$ and the herringbone facies had an isotopic range of -22‰ for δD and -3.8‰ for
224 $\delta^{18}O$ across the four experiments. The parent water isotopically varied by -0.4‰ in δD
225 and -1.6‰ in $\delta^{18}O$.

226 [Figure 4 near here]

227 [Table 1 near here]

228 These variations in the $\delta^{18}O$ compositions resulted in experiments 3 and 4 parent
229 waters not plotting directly on the GMWL, suggesting the water had been modified
230 isotopically from its meteoric source. Variations in parent water are important as they
231 can result in an ice facies having a heavy or light isotopic composition, having
232 implications for the statistical difference between facies. For example, the parent water
233 in experiment 1 had a lighter $\delta^{18}O$ value (-7.7‰) compared to experiment 3 (-6.1‰).
234 Consequently, the facies which formed in these individual experiments had contrasting
235 compositions in their $\delta^{18}O$ values.

236 *3.2.1 Deuterium Excess*

237 Across the four experiments, the herringbone ice had the heaviest deuterium excess
238 values compared to the other facies and the clear ice had lightest values (Figure 5). The
239 mixed facies plotted between the clear and herringbone facies in each experiment when
240 placed on deuterium excess- δD diagrams.

241 [Figure 5 near here]

242 *3.3 Freezing Slopes*

243 The freezing slopes were not predicted by the Jouzel and Souchez (1982) closed-system
244 model. For example, experiment 3 had a freezing slope of 5.95, yet a slope of 7.74 was
245 predicted (Table 2). The freezing slopes had high adjusted R^2 values, ranging from 0.93
246 (experiment 3) to 0.99 (experiment 1 and 2), suggesting the slopes are a good fit for our
247 data across all the experiments.

248 [Table 2 near here]

249 *3.4 Analysis of Variance Testing*

250 Analysis of variance (ANOVA) testing determines the statistical difference between
251 individual parameters. A one-way ANOVA test was conducted for the four experiments
252 to determine whether the documented facies were significantly different isotopically.
253 After analysis and Tukey's post-hoc comparisons of the facies' mean value, the isotopic
254 compositions of the documented facies in in all four experiments were statistically
255 different from each other (p values < 0.005), and we can assert with 95% confidence
256 that the clear, herringbone and mixed facies are significantly different (Table 3).

257 [Table 3 near here]

258 **4.0 Discussion**

259 ***4.1 Implications for Glaciohydraulic Supercooling Studies***

260 Our results suggest that bulk-scale sampling of ice facies frozen from supercooled water
261 could be overlooking micro-scale isotopic differences. This is evident as the
262 herringbone facies is significantly isotopically distinct from the mixed facies (95%
263 confidence – p values < 0.005). Consequently, previous studies investigating
264 glaciohydraulic supercooling which bulk sampled basal ice facies may have lacked
265 methodological precision (e.g. Titus et al. 1999; Ensminger et al. 2001; Swift et al.
266 2006; Cook et al. 2010; Larson et al. 2010). It remains unclear whether bulk-scale
267 samples are isotopically distinct when compared to micro-scale samples in field-based
268 investigations. Had the mixed facies containing both the clear and herringbone crystal
269 structures been sampled to determine the isotopic signature of the herringbone facies,
270 the isotopic resolution would have been lost. This is shown through the mean isotopic
271 differences between the mixed and herringbone facies which were -12.2‰ to -14.6‰
272 for δD and -1.9 to -2.3‰ for $\delta^{18}O$ (Table 3). This indicates that a micro-scale sampling
273 approach has yielded a more accurate isotopic signature for the facies formed from
274 supercooled water, rather than a bulk-scale sampling approach containing numerous
275 facies.

276 Ice frozen from supercooled water at glaciers has been shown to be isotopically
277 lighter relative to the vent water (Lawson et al. 1998; Ensminger et al. 2001; Cook et al.
278 2010; Larson et al. 2010). However, in our experiments the herringbone facies frozen
279 from supercooled water was isotopically heavier relative to the initial reservoir and
280 surrounding facies (Figure 4). These results are not the norm with regards to isotopic
281 enrichment seen in stratified basal ice facies, anchor and frazil ice produced by
282 supercooling. In our experiments, the clear ice formed at the beginning of the system,

283 whereas the herringbone ice formed during the latter stages. Souchez and Jouzel (1984)
284 assert that ice which forms at the beginning of a system will be isotopically lighter,
285 whereas ice which forms last will be isotopically heavier, relative to the initial water.
286 Experiment 1 had a freezing slope of 7.23, yet the clear facies had a slope of 6.33, the
287 herringbone facies a slope of 6.15 and the mixed ice 3.96. Souchez and De Grootte
288 (1985) stated ice facies that form in a closed-system should have similar slopes to that
289 of the system because there is no mixing of external water sources. Despite the closed-
290 system experiments here, the facies have contrasting slopes. This could be because the
291 initial reservoir became isotopically heavier throughout the seven-day period and the
292 facies which froze at different periods of the experiments had different slopes. As the
293 clear facies formed at the start of the experiment when the initial reservoir was
294 relatively isotopically light. The herringbone facies formed in the latter stages of the
295 experiment when the water was isotopically heavier, compared to the water that formed
296 the clear ice at the start of the experiment. Thus, the isotopically heavy nature of the
297 herringbone ice can be explained by a Rayleigh fractionation process. Despite the facies
298 frozen from supercooled water not experiencing similar isotopic enrichment as seen in
299 field-based investigations, our results confirm the importance of sampling size in
300 correctly distinguishing the facies diagnostic of supercooling.

301 The statistical difference between the facies is because of the mixed facies
302 containing two separate crystal structures with contrasting isotopic compositions. We
303 suggest the mixed ice isotopic composition is being amalgamated because of the light
304 isotopic composition of the clear ice and the heavy isotopic composition from the
305 herringbone ice. This emphasises the need for a micro-scale sampling approach and
306 removal of alternate ice facies in a believed ‘supercooled’ sample. Consequently, the
307 assertions of Cook et al. (2010) that sample sizes of basal ice will be important for

308 isotopic analysis as bulk-scale sampling could be homogenising isotopic signatures are
309 correct in the case of this study.

310 Despite the aim of our study being to determine the potential difference between
311 the mixed and herringbone ice facies, it is also important to note that there is a
312 significant statistical difference between the clear and mixed facies. This suggests that
313 the mixed facies cannot distinguish a precise isotopic composition for both the clear and
314 herringbone facies, instead exhibiting a distinct isotopic signature. This supports the
315 concept that bulk-scale sampling techniques could be amalgamating isotopic
316 compositions from contrasting facies and a micro-scale approach is worth considering
317 to ensure more precise measurements.

318 ***4.2 Isotopic Analysis***

319 Our results indicate that the closed-system model by Jouzel and Souchez (1982) did not
320 align with the actual freezing slopes of our experiments (Table 3), suggesting a complex
321 freezing system. Had the model determined the correct freezing slope, it would have
322 suggested the water froze from simple freezing. Sharp et al. (1994) found basal ice
323 facies at Variegated Glacier, Alaska had formed from a different water source or the
324 stratified facies had been subject to modification post-formation. This was concluded
325 because the closed-system model calculated slopes of 6.37 and 6.64 for two initial
326 liquids, which did not correlate with the actual slope of 5.77 (Sharp et al. 1994).
327 Fitzsimons et al. (2008) determined an overriding apron at the Victoria Upper Glacier,
328 Antarctica did not form the basal ice because it was isotopically distinct, with a
329 predicted freezing slope of 5.6 which was not significantly similar to the actual slope of
330 6.6. Gordon et al. (1988) found the actual freezing slope at Flute's Glacier, Norway had
331 a gradient of 5.5 which was in close agreement with the closed-system model which
332 calculated a slope of 5.7, therefore basal ice formed from a melting-refreezing process.

333 *4.2.1 Initial Water Differences*

334 The Jouzel and Souchez (1982) model and the coefficients by Lehmann and
335 Siegenthaler (1991) were formulated based upon meteoric water, yet our study utilised
336 tap water. This mismatch in parent water could be the controlling parameter for the
337 failure of the models predicting the freezing slopes of the experiments. For example, the
338 isotopic composition of the tap water varied throughout the experimental period,
339 resulting in different experiments having different parent waters. Experiment 1's parent
340 water had an isotopic composition of -49.87‰ for δD and -7.674‰ for $\delta^{18}\text{O}$, whereas
341 experiment 4's composition was -50.12‰ for δD and -6.060‰ for $\delta^{18}\text{O}$. If the models
342 cannot be applied to a tap water source, other explanations of a complex freezing
343 system will be of secondary importance. This has presented a potential avenue for
344 further work to determine whether Jouzel and Souchez (1982) closed-system model can
345 be applicable for different water sources, other than meteoric.

346 *4.2.2 Potential Kinetic Isotope Effects*

347 The deuterium excess- δD diagram (Figure 5) demonstrates the facies isotopic values
348 tend to become heavier with progressive freezing through the closed-system. Souchez et
349 al. (2000) found δ -values decreased towards the base of the ice cover, suggesting the
350 downward movement of a freezing front. Our results indicate similar findings as our
351 system froze progressively downwards and consequently resulted in the heaviest
352 deuterium excess values contained in the herringbone facies as it was the last to freeze.
353 Yde et al. (2010) studied basal ice facies at Russell Glacier and found that apart from
354 the white ice, the other ice types had deuterium excess values between 2.0 and 4.2,
355 suggesting there was no evident correlation with δD . It was inferred that the basal ice
356 facies had been affected by; 1) kinetic parameters; 2) the local meteoric water had an
357 average deuterium excess value within the range; 3) partial freezing or 4) variations in

358 parent waters (Yde et al. 2010). Our results do see an inverse fractionation process. This
359 occurs when the isotopes which are substituted are stably bonded during the transitional
360 period and the molecules containing the heavy isotopes react quickly (Casciotti, 2009).
361 Our experimental method could have caused the water isotopes in the facies to be stably
362 bonded during transitional and progressive freezing of a downward front, resulting in an
363 inverse fractionation process.

364 ***4.3 Basal Ice Context***

365 We are aware that our experiments are laboratory based and do not perfectly replicate
366 real-world conditions. However, our results highlight the importance of the scale of
367 sample of basal ice collected for isotopic analysis. There have long been questions
368 regarding the importance of sample sizes of basal ice for isotopic analysis (Souchez et
369 al. 1998; Hubbard and Sharp. 1993; Cook et al. 2010). Hubbard and Sharp (1993)
370 demonstrated that a bulk-scale sampling approach could incorporate different laminae
371 of facies and may not allow a high enough resolution for a particular basal ice layer
372 which has formed from a singular freezing event. Consequently, the overall benefit of a
373 high-resolution sampling approach is more accurate isotopic signatures of basal ice
374 layers in question. If a sample amalgamates different facies formed from different initial
375 waters and formational processes, the isotopic resolution of the wanted basal ice layer
376 will be lost, as presented here. If the mixed facies in our experiments were used as the
377 only proxy for a supercooled formation, the diagnosis would have been misleading and
378 fundamentally inaccurate. This theory could be applied to basal ice studies in general
379 because of the complexities of stable water isotope analysis at glaciers. We have
380 provided a proof of concept experiment for all basal ice investigations to consider the
381 scale of samples for isotopic analysis. Further work is needed in basal investigations at

382 glaciers to determine whether our theory is correct and will hopefully develop our
383 understanding of sample size resolution in the real-world.

384 **5.0 Conclusions**

385 We have four overarching conclusions;

- 386 1) Our study concludes with confidence that previous bulk-scale sampling
387 approaches could have overlooked important isotopic differences in ice formed
388 from glaciohydraulic supercooling.
- 389 2) Studies should consider their sample sizes of stratified basal ice, as a micro-scale
390 approach could yield much more accurate and detailed isotopic compositions of
391 basal ice frozen from supercooled water.
- 392 3) Our results lend support to Cook et al. (2010), suggesting that bulk-scale
393 sampling techniques could be homogenising the isotopic signatures of
394 formational processes.
- 395 4) The results express the clear need for future research investigating
396 glaciohydraulic supercooling to determine whether similar results are found at a
397 micro-scale in basal ice investigations at glaciers.

398 If basal ice investigations revised their sampling strategy to a more micro-scale
399 approach, we could see more detailed isotopic signatures for ice formed from
400 supercooled water and would further advance our understanding of this important
401 subglacial process.

402 The freezing slopes identified in our four experiments were not predicted by the
403 model of Jouzel and Souchez (1982). We conclude that this was due to two factors; 1)
404 the system underwent a complex freezing process over the seven-day experiment and 2)
405 the use of tap water rather than meteoric water as the parent water source.

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411 **Declaration of interest statement**

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415 **Notes on contributors**

416 *Connor Shiggins* is a PhD student at the University of Liverpool, with a project directed
417 towards investigating and modelling calving events at marine-terminating glaciers in
418 Greenland. The research presented in this manuscript was conducted during his MSc
419 degree at Keele University.

420 *Matthew Harris* is a PhD student at Keele University using fluorescence spectroscopy
421 and stable water isotopes to reconstruct climate and ocean dynamics preserved in
422 Antarctic ice cores.

423 *Peter Knight* is a Reader in Geography at Keele University. His research focus is on
424 basal ice investigations.

425 *Chris Fogwill* is a Professor of Glaciology and Palaeoclimatology at Keele University.
426 His main research interests are past and future climate changes in Antarctica and the
427 Southern Ocean.

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514 **Appendices**

515 A1. Isotopic compositions of the ice facies presented in this study.

Sample	δD (‰)	$\delta^{18}O$ (‰)
Parent (experiment 1)	-49.87	-7.67
Parent (experiment 2)	-50.31	-7.44
Parent (experiment 3)	-50.12	-6.06
Parent (experiment 4)	-49.75	-6.06
Experiment 1		
Herringbone	-81.79	-12.21
Herringbone	-77.63	-11.51
Herringbone	-75.72	-11.31
Herringbone	-77.46	-11.21
Herringbone	-71.62	-10.67
Herringbone	-75.96	-11.22
Herringbone	-70.74	-10.34
Mixed	-60.50	-8.76
Mixed	-59.64	-8.66
Mixed	-63.97	-9.45
Mixed	-61.44	-9.53
Mixed	-63.23	-9.66
Mixed	-65.84	-10.24
Mixed	-59.01	-9.00
Clear	-44.15	-6.92
Clear	-44.01	-6.73
Clear	-39.64	-6.52
Clear	-37.51	-5.85
Clear	-43.50	-6.74
Clear	-48.27	-7.59
Clear	-44.67	-7.01

Experiment 2		
Herringbone	-73.34	-10.89
Herringbone	-67.81	-9.95
Herringbone	-80.95	-11.92
Herringbone	-84.15	-12.42
Herringbone	-87.71	-12.82
Herringbone	-73.79	-10.80
Herringbone	-76.76	-11.23
Mixed	-70.06	-10.17
Mixed	-56.31	-8.16
Mixed	-60.53	-8.75
Mixed	-63.90	-9.16
Mixed	-67.70	-9.74
Mixed	-73.37	-10.40
Mixed	-67.71	-9.63
Clear	-44.19	-6.32
Clear	-35.99	-5.27
Clear	-33.09	-4.83
Clear	-46.38	-7.34
Clear	-33.44	-5.46
Clear	-32.58	-5.39
Clear	-46.28	-7.28
Experiment 3		
Herringbone	-77.67	-10.96
Herringbone	-68.54	-10.27
Herringbone	-68.88	-9.63
Herringbone	-80.42	-11.67
Herringbone	-86.48	-12.67
Herringbone	-72.04	-11.00

Herringbone	-78.05	-11.54
Mixed	-65.10	-9.63
Mixed	-60.21	-7.77
Mixed	-58.48	-8.20
Mixed	-59.34	-8.93
Mixed	-67.11	-9.84
Mixed	-57.60	-7.81
Mixed	-62.37	-9.41
Clear	-54.31	-6.94
Clear	-55.40	-8.16
Clear	-55.74	-8.02
Clear	-46.20	-5.49
Clear	-41.86	-5.53
Clear	-40.04	-6.39
Clear	-43.17	-6.77
Experiment 4		
Herringbone	-71.70	-9.84
Herringbone	-83.91	-13.52
Herringbone	-71.93	-10.86
Herringbone	-62.32	-10.00
Herringbone	-84.37	-12.95
Herringbone	-73.40	-11.96
Herringbone	-84.64	-13.66
Mixed	-62.81	-10.43
Mixed	-63.37	-10.53
Mixed	-68.09	-10.13
Mixed	-61.89	-9.07
Mixed	-67.26	-9.70
Mixed	-60.48	-8.15

Mixed	-62.97	-8.59
Clear	-34.32	-4.04
Clear	-39.42	-4.44
Clear	-37.21	-3.78
Clear	-34.74	-3.41
Clear	-37.35	-3.46
Clear	-43.72	-6.04
Clear	-43.30	-6.01