

Temperature and Hydrologic Cycle Constraints on Snowball Earth Environments

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Abstract

Pre- and syn-glacial low-latitude carbonate sediments of the Elbobreen Formation, NE Svalbard, preserve evidence for dramatic climate changes associated with Cryogenian glaciations (720–635 Ma). We combine carbonate stable ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) and clumped isotope ($\Delta 47$) geochemistry with petrographic observations to assess the source of carbonate within glacial facies of the Petrobreen Member and their environmental significance. Calcite $\Delta 47$ temperatures reflect solid-state reordering under burial temperatures, whereas dolomites record lower temperatures that vary with depositional facies. Pre-glacial dolomites have $\Delta 47$ temperatures from 48–73°C, with a reconstructed fluid $\delta^{18}\text{O}$ value of +0.6‰. detrital carbonate clasts similar to pre-glacial strata in stable isotope composition, $\Delta 47$ temperature, and petrographic textures; and (2) autochthonous dolomicrite and re-worked dolomicrite clasts with heavier $\delta^{18}\text{O}$ values and colder $\Delta 47$ temperatures of 19–44 °C. Measured dolomite temperatures likely include a component of diagenetic alteration that elevated the sample temperature above that imparted at deposition. The statistically significant difference in temperatures between precipitated matrix and re-worked detrital clasts in diamictite indicates that matrix samples preserve some component of carbonate that records early temperature differences either reflecting the primary sediments or early dolomitization and shallow lithification. The higher source fluid $\delta^{18}\text{O}$ values in glacial carbonates is consistent with an active hydrological cycle, either through local evaporation or growth of continental ice sheets sourced from evaporation of seawater. Continued hydrological cycling and 20–30 °C offsets in temperature between glacial and non-glacial conditions constrain carbonate depositional environments in this first Cryogenian glaciation.

1

2 **Temperature and Hydrologic Cycle Constraints on Snowball Earth Environments**

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6

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8 **Key Points:**

- 9
- 10 • Neoproterozoic strata preserve differences in clumped isotope records of glacial and non-
glacial carbonates.
 - 11 • Dolomites are partially altered in burial, but the glacial dolomite mean temperature is 16–
12 36°C colder (95% CL) than pre-glacial dolomite.
 - 13 • Mineral and reconstructed fluid $\delta^{18}\text{O}$ values are higher in glacial facies, suggesting
14 continued hydrological cycling and evaporation.

15 Abstract

16 Pre- and syn-glacial low-latitude carbonate sediments of the Elbobreen Formation, NE Svalbard,
17 preserve evidence for dramatic climate changes associated with Cryogenian glaciations (720–635
18 Ma). We combine carbonate stable ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) and clumped isotope (Δ_{47}) geochemistry with
19 petrographic observations to assess the provenance of carbonate within glacial facies of the
20 Petrovreen Member and their environmental significance. Calcite Δ_{47} temperatures reflect solid-
21 state reordering under burial temperatures, whereas dolomites record lower temperatures that
22 vary with depositional facies. Pre-glacial dolomites have Δ_{47} temperatures from 48–73°C, with a
23 reconstructed fluid $\delta^{18}\text{O}$ value of +0.6‰ (VSMOW) in the coldest sample. Glacial dolomites
24 comprise: (1) detrital carbonate clasts similar to pre-glacial strata in stable isotope composition,
25 Δ_{47} temperature, and petrographic textures; and (2) autochthonous dolomicrite and re-worked
26 dolomicrite clasts with heavier $\delta^{18}\text{O}$ values and colder Δ_{47} temperatures of 19–44 °C. Measured
27 dolomite temperatures likely include a component of diagenetic alteration that elevated the
28 sample temperature above that imparted at deposition. The statistically significant difference in
29 Δ_{47} temperatures between *in situ* precipitated matrix and re-worked detrital clasts in diamictite
30 indicates that matrix samples preserve some component of carbonate that records early
31 temperature differences either reflecting the primary sediments or early dolomitization and
32 shallow lithification. The higher source fluid $\delta^{18}\text{O}$ values in glacial carbonates is consistent with
33 an active hydrological cycle, either through local evaporation or growth of continental ice sheets
34 sourced from evaporation of seawater. Continued hydrological cycling and 20–30 °C offsets in
35 temperature between glacial and non-glacial conditions constrain carbonate depositional
36 environments in this first Cryogenian glaciation.

37

38 Plain Language Summary

39 Glaciations known as Snowball Earth episodes took place in the late Precambrian (before 541
40 million years ago), and interpretations of their severity vary from more moderate conditions with
41 liquid seawater at the equator to “hard” Snowballs with complete freezing of the ocean surface. It
42 is important understand the severity of these glaciations as they are associated with many
43 changes moving from the Precambrian dominated by microscopic life to the Phanerozoic (541
44 million years ago to present) with expansion of larger complex life. In this study, we analyzed
45 carbonate sedimentary rocks from Svalbard that were originally deposited near the equator
46 before and during one of these Snowball Earth events, reconstructing the temperature when these
47 carbonates formed and the composition of their source waters. Carbonates maintain a record of
48 significantly (20–30°C) lower temperatures in glacial deposits than in non-glacial deposits, but
49 their composition also indicates that there was still evaporation taking place in the glacial
50 environment. This evidence is more consistent with an active hydrological cycle at intervals
51 during the Snowball Earth episode. Our results indicate that this approach to reconstructing
52 ancient conditions may lead to a better understanding of how the climate operated in these
53 pivotal periods of Earth history.

54 1 Introduction

55 Earth’s Phanerozoic climate was dominated by “greenhouse” conditions without polar
56 ice, with brief forays into “icehouse” states similar to today (Brenchley et al., 1994; Montañez &
57 Poulsen, 2013). Prior to the Phanerozoic Eon, peculiar, low-latitude, Neoproterozoic glacial

58 deposits provide evidence of a third, panglacial climate state colloquially referred to as a
59 “Snowball Earth” (Harland et al., 1966; Hoffman et al., 1998; Kirschvink, 1992). Snowball Earth
60 episodes are thought to represent a positive feedback between ice cover and albedo with
61 expansion of sea ice to low latitudes, locking the planet into a perennially frozen state until
62 volcanic outgassing and greenhouse warming overcomes albedo (Hoffman et al., 1998).
63 Accordingly, the Snowball Earth hypothesis predicts that the onset and termination of low
64 latitude glaciation should be globally synchronous (Kirschvink, 1992). Recent radiometric
65 constraints have confirmed the synchronous initiation and termination of Neoproterozoic
66 glaciations within the uncertainty of analyses (Macdonald et al., 2010; Rooney et al., 2015). This
67 revised chronology indicates the earlier of the two Neoproterozoic Snowball glaciations lasted at
68 least 57 Ma (Hoffman et al., 2017; Macdonald et al., 2010; Rooney et al., 2015), requiring
69 climate dynamics distinct from subsequent Phanerozoic glaciations.

70

71 Conceptual and climate models of a persistently ‘hard’ snowball state—one with km-
72 thick sea ice and initial mean annual equatorial temperatures $<-20^{\circ}\text{C}$ —predict a shutdown of the
73 hydrologic cycle for millions of years (Abbot et al., 2013). Alternative climate models assert that
74 such an extreme climate scenario is unnecessary to stabilize low latitude glaciations and that a
75 panglacial state could have maintained a narrow strip of open water at low latitudes. These so-
76 called “waterbelt” solutions avoid progression to a hard Snowball state due to negative feedbacks
77 on ice advance, including a lower albedo of ablating sea ice and reduced cloud cover at low
78 latitudes (Abbot et al., 2011). Differences in the hydrological cycling in these models make
79 unique predictions for the evolution of seawater oxygen isotope composition during glacial
80 intensification. Given the fractionation between liquid water and water vapor, evaporative export
81 of marine water to continental ice sheets increased marine water oxygen isotope composition
82 during Phanerozoic glacial-interglacial cycles (Shackleton, 1967), with marine $\delta^{18}\text{O}$ values
83 approximately 3‰ higher in peak Pleistocene glaciation over estimated ice-free marine values of
84 -1.2‰ (Cramer et al., 2011; Lea et al., 2000; Lear et al., 2000). This trend holds for the most
85 recent glacial-interglacial transitions (Raymo et al., 2018), as well as earlier glacial episodes of
86 the Late Paleozoic Ice Age (Grossman et al., 2008) and the end-Ordovician (Finnegan et al.,
87 2011). Predictions for Snowball Earth marine $\delta^{18}\text{O}$ differ depending on the severity of the
88 glaciation. A waterbelt solution would permit continued evaporation and precipitation from the
89 marine reservoir, whereas a hard Snowball Earth would be marked by freeze-concentration
90 during growth of the surrounding ice shell. Ice formation preferentially sequesters more ^{18}O -
91 enriched water (Horita, 2008), leaving a depleted marine reservoir. Such fluid isotopic evolution
92 commonly occurs via freeze-concentration in modern ice-covered environments in Antarctica,
93 where $\delta^{18}\text{O}$ values for seawater-sourced saline lakes can be 5‰ lower than source water (Bird et
94 al., 1991; Horita, 2008) and seawater-derived cryogenic brines reach $\delta^{18}\text{O}$ values of -8 to -11‰
95 after 1x freeze-concentration (Frank et al., 2010). Thus, reconstruction of marine fluid isotopic
96 composition may provide an important constraint on the severity of glacial conditions in
97 Snowball Earth episodes by assessing the relative contribution of evaporation and freeze
98 concentration to marine fluid evolution.

99

100 1.1 Carbonate records of temperature and seawater composition

101 Carbonates associated with Cryogenian glaciations may be informative for climate
102 models given predictions for seawater $\delta^{18}\text{O}$ values with different climate states. Marine fluid
103 $\delta^{18}\text{O}$ is recorded in carbonates, but this fractionation is temperature- and mineral-dependent
104 (Kim & O'Neil, 1997; Urey, 1948). For a specific mineralogy, temperature dependence
105 complicates predictions of precipitation fluid conditions. Furthermore, carbonate $\delta^{18}\text{O}$ values are
106 sensitive to alteration by diagenetic fluids, and primary $\delta^{18}\text{O}$ values can be diluted by
107 incorporation of cements or overprinted by dissolution and reprecipitation (Dickson & Coleman,
108 1980; Huntington et al., 2011; Lohmann, 1988; Winkelstern & Lohmann, 2016). Interpretation
109 of typical glacial climate from fluid $\delta^{18}\text{O}$ values is complicated, however, by significant
110 uncertainty in the completeness of the stratigraphic section. Average sedimentation rates of
111 Neoproterozoic glaciations are lower than for more recent glaciations, indicating that glacial
112 strata integrate significant surfaces of erosion or non-deposition (Hoffman et al., 2017; Partin &
113 Sadler, 2016). Interpretations of glacial severity from carbonate reconstructed fluid composition
114 is accordingly limited to the environments where carbonates were deposited, potentially missing
115 conditions typical of the Snowball Earth episodes. Nevertheless, any direct measurement of
116 environmental conditions would provide important anchors for interpretation of climate
117 dynamics within the Snowball Earth.

118

119 In order to constrain changes to seawater $\delta^{18}\text{O}$ values with glaciation, we have pursued
120 carbonate clumped isotope thermometry of both pre- and syn-glacial carbonates of the Elbobreen
121 Formation, NE Svalbard (Section 1.2). Carbonate clumped isotope thermometry is based on the
122 temperature-dependent clumping of ^{13}C and ^{18}O into multiply substituted carbonate
123 isotopologues (Eiler, 2007), which can be used to elucidate environments of carbonate
124 precipitation and alteration. This thermometer constrains the temperature-dependent equilibrium
125 water-carbonate ^{18}O fractionation for a given mineralogy (e.g. Kim & O'Neil, 1997), and can
126 accordingly be used to calculate the $\delta^{18}\text{O}$ value for the fluid source of carbonates.

127

128 At any point during burial, processes including dissolution and reprecipitation or changes
129 in mineralogy like dolomitization will move clumped isotope temperatures toward the local
130 geothermal gradient (Bergmann et al., 2018; Ryb & Eiler, 2018; Winkelstern & Lohmann, 2016).
131 Similarly, post-depositional cementation of primary grains also dilutes clumped isotope
132 signatures with carbonate material that is equilibrated to burial temperatures (Mangenot et al.,
133 2018). Thus, both the extent of alteration (itself a function of primary grain size, porosity and
134 mineralogy; e.g. Bergmann et al., 2018; Staudigel & Swart, 2019) and the burial depth at which
135 alteration takes place (Stolper et al., 2018) determine the magnitude of diagenetic change in
136 clumped isotope temperature. Such processes can be variably fluid- or rock-buffered and affect
137 carbonate $\delta^{18}\text{O}$ values differently. If carbonates experience fluid-buffered diagenesis, carbonates
138 will approach mineral $\delta^{18}\text{O}$ values in equilibrium with the diagenetic fluids for that burial
139 temperature (e.g. Bergmann et al., 2018; Huntington et al., 2011). In contrast, rock-buffered
140 carbonates can show increased clumped isotope temperatures without a concomitant changes in
141 mineral $\delta^{18}\text{O}$ values (e.g. Bergmann et al., 2018; Huntington et al., 2011; Staudigel & Swart,
142 2019).

143

144 Carbonate clumped isotope records can also be altered by solid state reordering. Solid
145 state reordering is the re-equilibration of individual multiply substituted isotopologues within a
146 carbonate mineral at elevated temperature (Henkes et al., 2014; Stolper & Eiler, 2015); this
147 process leads to resetting of clumped isotope temperatures associated with carbonate
148 precipitation to fully or partially reflect elevated burial temperatures. Models for this reordering
149 explain experimental observations of reordering kinetics by 1) including diffusive propagation of
150 defects (Henkes et al., 2014) or 2) a two-step reaction between adjacent carbonate molecules and
151 successive diffusion through the carbonate crystal lattice (Stolper and Eiler, 2015). The kinetics
152 of reordering over geologic timescales is temperature-dependent, and this relationship varies by
153 carbonate mineralogy. Reordering experiments and supporting field studies of carbonate strata
154 indicate that calcite reorders at temperatures above $\sim 100^{\circ}\text{C}$ over $10^6 - 10^8$ years (Henkes et al.,
155 2014), whereas dolomite begins to partially reorder above $\sim 150^{\circ}\text{C}$ over $>10^7$ years (Lloyd et al.,
156 2018). Carbonates with burial temperatures below the threshold for solid state reordering could
157 maintain primary and early diagenetic clumped isotope temperatures over 10^8 years (Bergmann
158 et al., 2018; Henkes et al., 2018).

159 160 1.2 Geologic Setting

161 The carbonate clumped isotope system is highly sensitive to post-depositional alteration,
162 which indicates that low maximum burial temperatures are necessary to preserve climatically
163 relevant information in deep time (e.g. Henkes et al., 2018). Thus, testing for Neoproterozoic
164 climate transitions with clumped isotopes requires the coincidence of a well-defined stratigraphic
165 record of carbonates across climate states and a shallow subsequent burial history. As presented
166 below, the stratigraphy of NE Svalbard likely records one instance of such conditions. Strata
167 consist of mixed siliciclastic and carbonate rocks originally deposited in a long-lived basin at low
168 paleolatitudes (Fairchild et al., 1989; Hoffman et al., 2012; Maloof et al., 2006). Strata are made
169 up of the Akademikerbreen, and Polarisbreen groups, and key sections are presently exposed
170 along a 180 km belt across northeast Olav V Land, Ny Friesland, and west Nordaustlandet
171 (Fairchild et al., 1989; Halverson et al., 2004; Harland et al., 1966) (Figure 1).

172
173 The onset of Cryogenian glaciation is preserved in the transition between the Russøya
174 and Petrovbreen members of the Elbobreen Formation in the Polarisbreen Group. These
175 members contain abundant carbonate and are the focus of this study. Regionally, the Russøya
176 Member begins with a transgression over peritidal facies of the Dartboard Dolomite Member in
177 the Backlundtoppen Formation of the Akademikerbreen Group. This transgression reflects the
178 start of two marine transgressive-regressive sequences in the Russøya Member (T-R7 and 8 of
179 Halverson et al., 2004; 2018). Lower transgressive Russøya Member strata are composed of
180 calcite, but transition to dolomite up section (Halverson et al., 2004; 2018). The overlying
181 Petrovbreen Member varies in thickness across NE Svalbard, with the thickest sections
182 exceeding 50 m in Ny Friesland. These strata include dolomitic rhythmite, wackestone
183 containing outsized clasts interpreted as glacial dropstones, and diamictite with siliciclastic or
184 dolomitic matrix (Fairchild et al., 1989; Halverson et al., 2004). Facies are interpreted as
185 marine or glaciolacustrine depositional environments and vary from subglacial and grounding
186 line facies to more distal facies with ice-rafting (Fairchild et al., 1989; Hambrey, 1982; Hoffman
187 et al., 2012).

188

189 Dolomicrites are only present intermittently in the Petrovbreen Member (Figure 1) and
190 are not a common facies in other correlated glacial sections (Spence et al., 2016; Spencer, 1971).
191 As such, it is possible that these carbonates do not capture the peak intensity of a ‘hard’
192 snowball, and may instead reflect conditions particular to this glaciated carbonate platform with
193 local increases in alkalinity from glacial processing of detrital carbonate (c.f. Fairchild et al.,
194 2004). Stratigraphic relationships suggest that Petrovbreen Member dolomicrites do not
195 represent deposition within the final deglaciation, as the diamictite successions in Svalbard are
196 cross-cut by sediment-filled wedges interpreted as periglacial exposure surfaces (Fairchild et al.,
197 1989). Such exposure surfaces require progressive fall in base level, possibly indicative of
198 glacial intensification subsequent to emplacement of strata hosting glacial carbonates.

199

200 The Petrovbreen Member lacks direct geochronological constraints but has been
201 correlated to the first glacial episode of the Cryogenian (Halverson et al., 2018; Hoffman et al.,
202 2012), colloquially termed the Sturtian glaciation. Chemical evidence to support the Sturtian age
203 assignment comes from the similarity of the upper Russøya Member $^{87}\text{Sr}/^{86}\text{Sr}$ values to Tonian
204 values (Hoffman et al., 2012) and corresponding stratigraphic association with a negative carbon
205 isotope excursion identified as the Islay anomaly (Halverson et al., 2018; Hoffman et al., 2012).
206 If the Sturtian correlation is valid, the upper Russøya Member was deposited between ~740–735
207 Ma (Halverson et al., 2018; MacLennan et al., 2018; but see Fairchild et al., 2017 for discussion
208 of ambiguity in pre-Sturtian carbon isotope stratigraphy). Biostratigraphy further supports a pre-
209 Sturtian correlation for the Russøya Member. Vase-shaped microfossils (VSM) are present in the
210 Russøya Member in NE Svalbard (Knoll & Calder, 1983), similar to other pre-Sturtian strata
211 where geochronology is well-constrained (Cohen & Riedman, 2018). Together, chemo- and
212 biostratigraphy highlight the potential for these carbonates to record meaningful information
213 about the onset of glacial conditions in the Cryogenian.

214

215 The burial history of Ny Friesland is poorly constrained, but regionally Ordovician strata
216 of the Oslobreen Group disconformably overlying Neoproterozoic strata have organic
217 preservation inconsistent with deep burial. In NE Ny Friesland, conodont color alteration indices
218 are 1 (Bergström, 1980), which indicates burial temperatures $<80^\circ\text{C}$ (Epstein et al., 1977). These
219 strata also contain intact biomarkers consistent with mid-oil window thermal maturity (Lee et al.,
220 2019). Despite such evidence for low thermal alteration, Ny Friesland was affected by the
221 Caledonian Orogeny (Gasser, 2014 and references therein); Neoproterozoic and overlying
222 Cambro-Ordovician strata are steeply dipping and faulted (Fairchild & Hambrey, 1984; Hoffman
223 et al., 2012). Across Ny Friesland, thermal modeling from apatite fission track analysis indicates
224 that there is a strong local fault control on exhumation history, with total exhumation of
225 Caledonian granites estimated at 4–6 km on some fault blocks since 180–80 Ma (N. Dörr et al.,
226 2012; Nina Dörr et al., 2019). Such maximum burial exceeds the constraints from local organic
227 preservation (Bergström, 1980; Lee et al., 2019), highlighting the potential for significant
228 heterogeneity in maximum burial among fault blocks.

229

230 1.3 Neoproterozoic clumped isotope thermometry in Svalbard

231 Here we present carbonate clumped isotope data for carbonate-rich pre- and syn-glacial
 232 strata associated with the first Cryogenian glaciation cropping out in the Elbobreen Formation,
 233 NE Svalbard (Fairchild et al., 1989; Halverson et al., 2004; Harland et al., 1966; Figure 1). Given
 234 the sensitivity of the carbonate clumped isotope system to reordering with burial and the local
 235 diagenetic environment and solid state reordering during burial (Section 1.1), any attempt to
 236 assess changes in climate using this thermometer must first characterize evidence for solid state
 237 reordering as well as both diagenetic alteration and timing of crystallization events. In order to
 238 avoid confounding lateral heterogeneity in maximum burial throughout Ny Friesland, we have
 239 restricted this study to the Ny Friesland Dracoisen nunatak. Carbonates include both calcites and
 240 early fabric-retentive dolomites, and because of the different susceptibility of these minerals to
 241 solid state reordering (Henkes et al., 2014; Stolper & Eiler, 2015), the divergence of clumped
 242 isotope temperatures can be used to estimate of maximum burial temperatures and to constrain
 243 the extent of solid state reordering in strata at the Dracoisen nunatak. With the understood
 244 complications of burial diagenesis and solid state reordering, the juxtaposition of carbonates
 245 across contrasting climate states available at the Dracoisen nunatak provides an ideal test for the
 246 preservation of differences in carbonate clumped isotope temperatures and reconstructed fluid
 247 $\delta^{18}\text{O}$ values set by climate extremes of the Cryogenian.

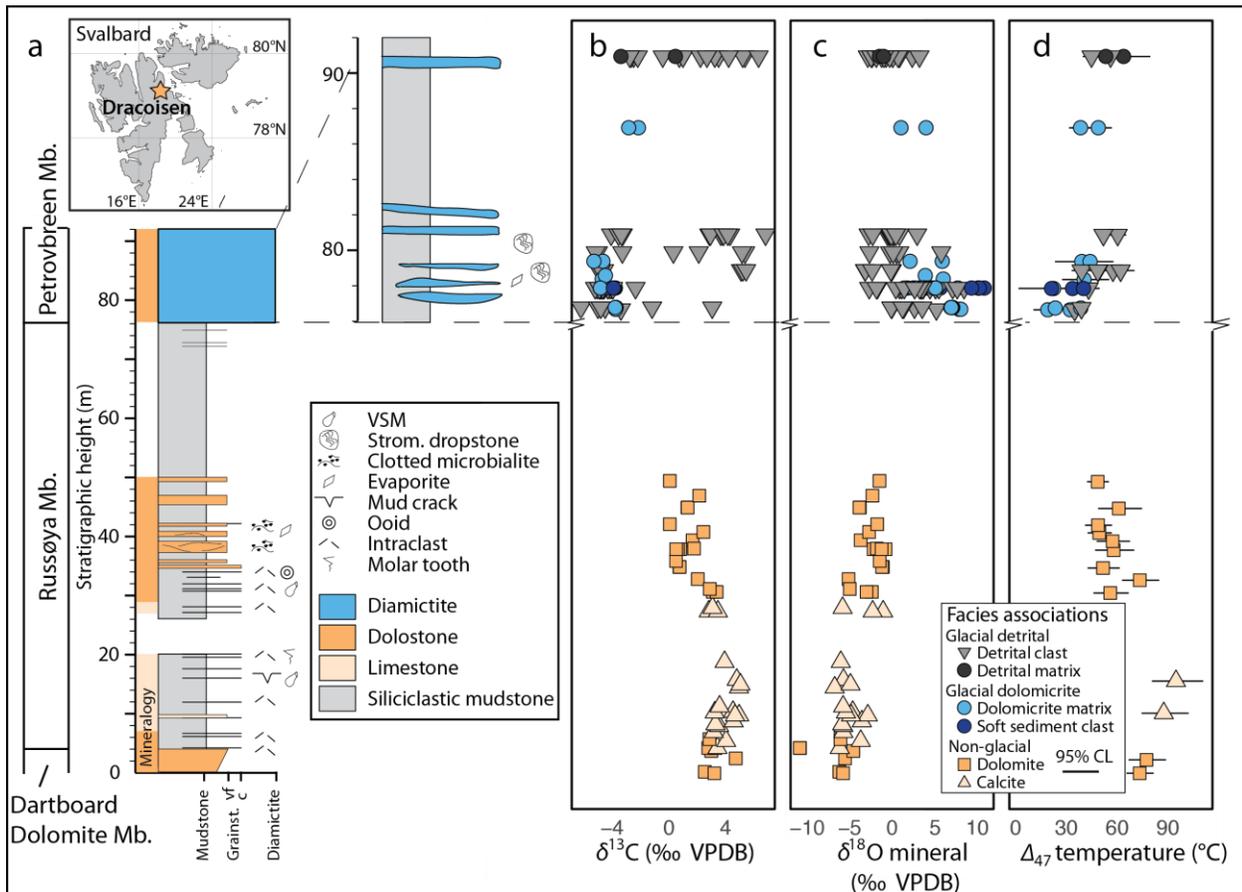


Figure 1: Stratigraphy of the latest Tonian (Dartboard Dolomite and Russøya members) and earliest Cryogenian (Petrovbreem Member) at the Dracoisen Nunatak, NE Svalbard. a) Stratigraphic column highlighting transitions among the dominant carbonate mineralogies. The scale of the Petrovbreem Member is extended to display diamicite distribution. b) Composite of $\delta^{13}\text{C}$ values and c) Mineral $\delta^{18}\text{O}$ value through stratigraphic section. d) Clumped-isotope temperatures and 95% CL error.

249 **2 Materials and Methods**

250 2.1 Field localities and sampling

251 Carbonates from the Dartboard Dolomite Member of the Backlundtoppen Formation,
252 Akademikerbreen Group and overlying Russøya and Petrovbreen members of the Elbobreen
253 Formation, Polarisbreen Group were collected in stratigraphic context on the Dracoisen nunatak,
254 NE Ny Friesland, Svalbard on a field campaign in 2014 (GPS 79.204931, 18.345240). Carbonate
255 samples were collected at approximately 1 m intervals where present (Table S1). This suite was
256 supplemented with four samples of the Petrovbreen Member previously collected by Ian
257 Fairchild (University of Birmingham) from the Dracoisen nunatak. Due to lateral heterogeneity
258 in Petrovbreen Member stratigraphy these samples are integrated into the section detailed in this
259 study using their stratigraphic height relative to marker beds. The section targeted for this study
260 was previously mapped (e.g. Fairchild et al., 1989; Halverson et al., 2004). Our additional
261 observations of stratigraphic relationships and facies in these strata are placed within this
262 framework for correlation.

263

264 2.2 Petrography and mineral identification

265 Carbonate samples were cut to remove weathered surfaces prior to petrographic and
266 geochemical analysis. All samples collected for clumped isotope analysis (n=24) were slabbed,
267 polished and scanned (Figure S1) to aid in the identification of target carbonate textures to drill
268 for subsequent subsampling and analysis (n=41). Of the 24 slabbed samples, 20 were thin
269 sectioned for petrographic characterization of target textures. We further analyzed 17 drill sites
270 for mean crystal size using 25 representative crystals from each sampled carbonate texture.
271 Measurements were made using ImageJ software from thin section photomicrographs following
272 the method of Bergmann et al., 2018a (Table S1).

273

274 Sample mineralogy was determined based on X-ray diffraction (XRD) or dilute acid
275 reaction (Table S1). For XRD, splits of powdered samples were analyzed on a PANalytical
276 X'Pert PRO x-ray powder diffractometer (XRPD) housed in the MIT Center for Materials
277 Science and Engineering (MIT-CMSE) to quantify the abundance of calcite, dolomite, and other
278 minerals. For each sample, approximately 500 µg of powder was analyzed for two hours from 5°
279 to 90° on a spinning stage at a fixed irradiated length. We describe carbonate microfacies after
280 Fairchild et al. (1989) and adopt the term (dolo)micrite in reference to carbonate crystals less
281 than 10 µm in diameter, (dolo)microspar for crystals between 10 and 50 µm in diameter, and
282 spar for mean crystal diameter > 50 µm.

283

284 2.3 Isotopic analysis

285 Carbonate $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and clumped isotopic (Δ_{47}) analyses were performed at MIT on a
286 Nu Perspective isotope ratio mass spectrometer coupled to a Nu Carb automated carbonate
287 sampler. Samples of specific carbonate textures were drilled using carbide bits at low speed to
288 produce homogeneous powders for isotopic analyses. Clumped isotope analysis had different
289 methods from samples solely analyzed for bulk $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$; these methods are presented
290 separately below.

291

292 2.3.1 Carbonate clumped isotope (Δ_{47}) analysis

293 For Δ_{47} measurements, we analyzed ~450 μg of carbonate powder drilled from polished
294 sample slabs; weights for samples with lower weight percent carbonate as determined by CO_2
295 yield were increased to match the carbonate mass of the pure standards and ranged from ~450 to
296 900 μg . Carbonates were digested in sample vials with 150 μL H_3PO_4 (1.94–1.95 g/cm^3); see
297 supporting information for detailed description of clumped isotope analytical methods (Text S1).
298 Clumped isotope data were processed using Easotope software (John and Bowen, 2016), ^{17}O
299 corrections after Schauer et al. (2016) and Daëron et al. (2016). Raw $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and clumped
300 isotopic (Δ_{47}) measurements were transferred to VPDB and Carbon Dioxide Equilibrium Scale
301 (CDES) (Dennis et al., 2011), respectively, using four ETH carbonate standards (after
302 Bernasconi, et al., 2018). Calcite and dolomite Δ_{47} values were further corrected with a 70°C
303 acid fractionation factor of 0.062 (Defliese et al., 2015; Müller et al., 2017). All samples passed
304 screening for contamination using Δ_{48} values; all samples had Δ_{48} values with a lower absolute
305 value than the cutoff of <0.5‰. Samples were only incorporated into this study where ≥ 3
306 replicates passed all screening tests (Text S2).

307

308 Analyses were carried out over the course of 1.5 years (6/2017–11/2018), during which
309 time instrument upgrades and repairs led to changes in precision of analyses. In the course of this
310 study, long term standard deviation of reference materials (1 SD) varied from 0.02 to 0.04‰,
311 0.02 to 0.07‰, and 0.06 to 0.20‰ for Δ_{47} , $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values respectively. Raw data for all
312 standards and sample replicates are available in supporting information and are posted at
313 EarthChem (Table S2 to be submitted to EarthChem on manuscript acceptance).

314

315 We calculated precipitation temperature following the Δ_{47} –temperature relationship of
316 Bernasconi et al. (2018). Additional discussion of dolomite temperature calibrations are
317 presented in the supporting information (Text S3). Precipitating fluid $\delta^{18}\text{O}$ values were
318 calculated from mineral $\delta^{18}\text{O}$ values and Δ_{47} temperatures, assuming equilibrium fractionation
319 between fluid and mineral $\delta^{18}\text{O}$ following the temperature–fractionation relationship of Kim and
320 O’Neil (1997) for calcite and Horita (2014) for dolomite. Error for clumped isotope temperatures
321 are presented as 95% confidence levels from sample replicates (Fernandez et al., 2017) for
322 conservative estimates of error in reconstruction, whereas populations of data points from
323 different samples are discussed with reference to one standard deviation to highlight the
324 distribution of temperatures in the population.

325

326 2.3.1 Carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ microvolume analysis

327 Samples of ~100 μg carbonate were analyzed for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. Samples spanned the
328 Dracoisen stratigraphy at the m-scale resolution of sampling, and select carbonate textures
329 analyzed for Δ_{47} were drilled at the mm-scale to assess compositional heterogeneity (Figure S2).
330 Microvolume analysis of drilled samples consisted of digestion in H_3PO_4 (1.91–1.92 g/cm^3) at
331 70°C, followed by cryogenic purification. Sample beam analysis consisted of 6 cycles of 20s
332 integration. Results were processed using Easotope software (John & Bowen, 2016) translated to

333 the VPDB reference frame using ETH and in-house standard materials. Long term standard
334 deviation of reference materials (1 SD) throughout the course of analysis (01/2018–09/2018)
335 varied from 0.04–0.09‰ and 0.07–0.17‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively, in individual
336 correction intervals.

337

338 **3 Results**

339 3.1 Carbonate petrography

340 The stratigraphic distribution of facies documented in our study is broadly consistent with
341 those of previous authors (Fairchild et al., 1989; Halverson et al., 2004, 2018); we build on these
342 facies associations and our petrographic observations to group the isotope analyses in Dracoisen
343 section pre- and syn-glacial carbonates (Figure 2).

344

345 The lowest stratigraphic section examined in this study is the upper Dartboard Dolomite
346 Member. These strata are composed of stylotized dolomicrospar (mean crystal sizes 14–23 μm),
347 with local sheet crack-filling dolospar. The Dartboard Dolomite Member transitions upwards to
348 limestones of the lower Russøya Member, which are composed of microspar and intraclastic
349 grainstone. Rare mud cracks and molar tooth textures are also present. Up section, Russøya
350 Member carbonates change to dolomite composed of stromatolites with a clotted microtexture,
351 intraclastic and rare oolitic grainstones, and contain rare evaporite pseudomorphs. The crystal
352 size of Russøya Member dolomites varies with texture. The finest dolomicrites (<5 μm) are
353 present in stromatolite clots, whereas laminated dolomites are typically micritic to microsparitic
354 (mean crystal sizes 17 ± 8 μm , 1 sd), including laminae intercalated on the mm-scale with the
355 finest dolomitic clots.

356

357 The overlying Petrovbreen Member carbonates analyzed here are dolomitic, with varying
358 contribution of chert clasts, silicate minerals, and subsidiary siliciclastic grains. Siliciclastic
359 grains include rare grain aggregates, and we have interpreted these aggregates as till pellets
360 (Figure S3), consistent with the prevailing interpretation of a glaciomarine or glaciolacustrine
361 depositional environment (Fairchild et al., 1989; Halverson et al., 2018; Hambrey, 1982).
362 Dolomites consist of three components defined by their crystal/grain size, texture, and
363 relationship to surrounding sediments. (1) Dolomicrite (mean crystal size <5 μm) is present in
364 the Petrovbreen Member as homogeneous beds, interlaminated with coarser carbonate grains in
365 varves, within ductily deformed soft sediment clasts, or as a matrix between larger clasts.
366 Dolomicrite matrix is present in both stratified diamictites and matrix-supported diamictite
367 samples without lamination or clast sorting. Dolomicrite purity varies in samples analyzed by
368 XRD, with compositions ranging from >70% dolomite to a subsidiary component mixed with
369 more abundant quartz as well as other silicate minerals (Table S3). (2) >1 mm angular to well-
370 rounded clasts with constituent carbonate fabrics that are stromatolitic, clotted, fenestral,
371 laminated, intraclastic, and dolomicritic. These larger angular to well-rounded clasts are hereafter
372 referred to as detrital clasts. Detrital clasts have a range of mean crystal sizes, with stromatolitic,
373 clotted, fenestral, laminated, and intraclastic carbonate fabrics having mean crystal sizes ≥ 10 μm
374 in contrast to the finer dolomicrites. Rare detrital clasts from the stratified diamictite have
375 circumgranular sparry crusts up to 100 μm thick (Figure S3) (3) Carbonate clasts <1 mm form

376 the matrix between the larger detrital clasts. Petrovreen Member dolomite components vary
 377 stratigraphically. Dolomicrite is most abundant in the lowermost 2 m of the Petrovreen Member
 378 below a brecciated surface (Fairchild, pers. comm.) containing abundant pseudomorphs
 379 consistent with sulfate minerals. Additional dolomicrite is present above this surface as
 380 homogeneous dolomicrite, diamictite matrix and fine rhythmite laminae, but the majority of
 381 carbonates consist of detrital clasts in diamictite beds or dropstones in siliciclastic mudstone
 382 (Figure 1A).

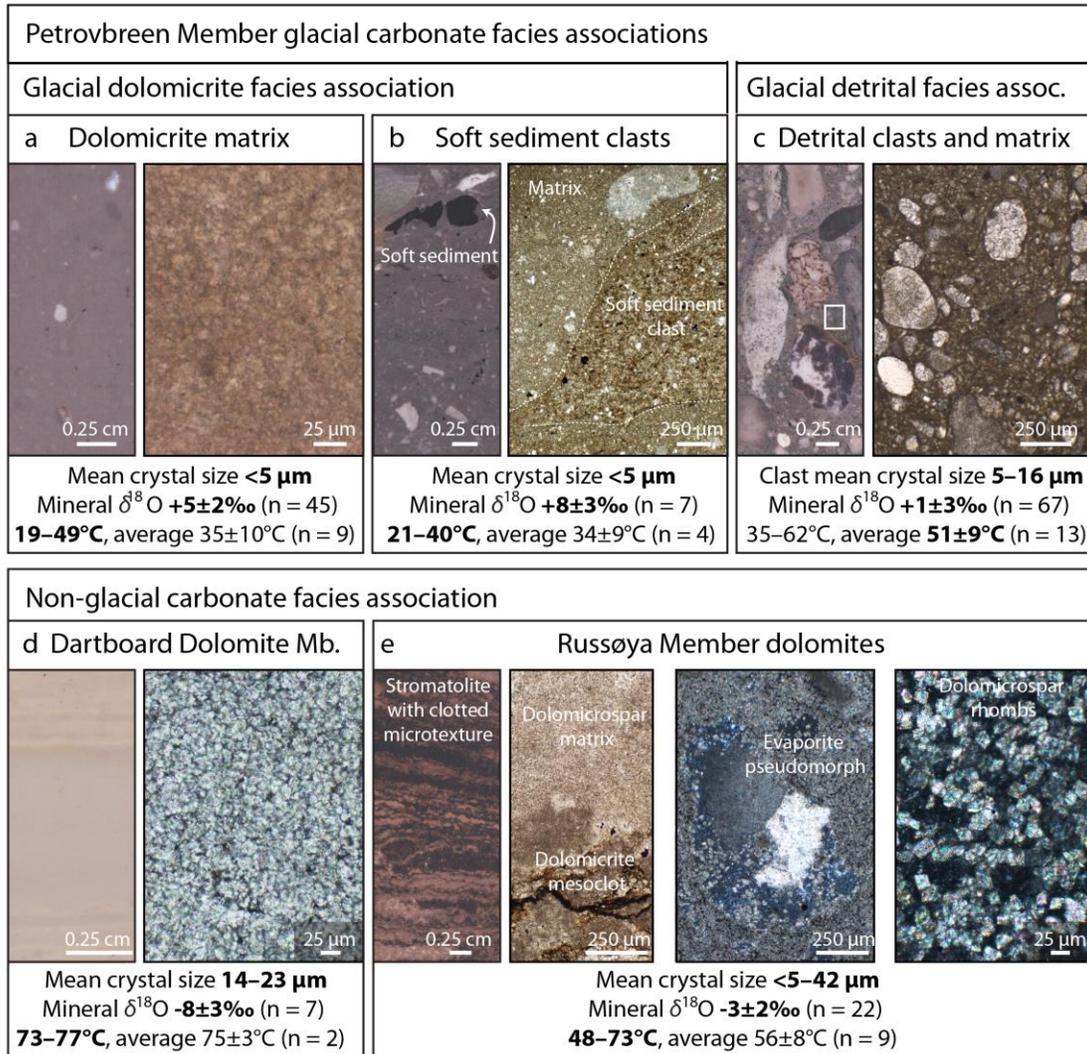


Figure 2: Petrographic textures of the Dracöisen section dolomites; where images are paired, left is a scanned polished sample and right is thin section photomicrograph. a–c) Glacial carbonates of the Petrovreen Member consisting of a) homogeneous dolomicrite matrix, b) discrete soft sediment clasts in diamictite, c) detrital clasts and matrix consisting of <1 mm detrital clasts. d and e) non-glacial carbonates of the d) peritidal Dartboard Dolomite Member of the Akademikerbreen Formation and e) overlying Elbobreen Formation Russøya Member. Russøya Member dolomite facies pictured here include stromatolites with a clotted microtexture, evaporite pseudomorphs partially replaced by dolomite and silica (here cross-polarized to highlight twinning after gypsum), and homogeneous dolomicrospar rhombs in wedged thin section. Mean crystal sizes indicate range in mean sizes for analyzed samples, and isotope data present the mean mineral $\delta^{18}\text{O}$ values and clumped-isotope temperatures ± 1 standard deviation to describe the population analyzed, and the range of mean clumped isotope temperatures.

384 Together, the Dracoisen stratigraphy comprises three broad facies associations. The
385 Dartboard Dolomite and Russøya members make up (1) the non-glacial facies association, which
386 are possible source strata for subsequent glacial erosion and redeposition. The Petrovbreen
387 Member carbonates make up two facies associations based on petrographic texture: (2) the
388 glacial dolomicrite facies association includes homogeneous dolomicrite, dolomicrite matrix,
389 soft sediment clasts, and fine varve laminae; (3) the glacial detrital facies association includes
390 both the larger detrital dolomite clasts and matrix material composed of recognizable finer <1
391 mm dolomite clasts. The geochemistry of these three facies associations are detailed in the
392 following sections.

393

394 3.2 Non-glacial facies association isotope analyses

395 Carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopic composition vary stratigraphically (Figure 1B and C).
396 $\delta^{13}\text{C}$ values greater than +2‰ characterize the Dartboard Dolomite and lowermost Russøya
397 members. $\delta^{13}\text{C}$ values peak at +5.1‰ in the calcite strata of the lower Russøya Member and
398 decrease to +0.5‰ over 20 m up section through the transition to dolomite. $\delta^{13}\text{C}$ values in the
399 subsequent dolomite beds remain between +0.1‰ and +2.4‰ through the transition to shale in
400 the upper Russøya Member. Mean mineral $\delta^{18}\text{O}$ values increase through the Dartboard Dolomite
401 and Russøya members, from $-7\pm 2\%$ (1 sd) in the Dartboard Dolomite Member, to $-5\pm 2\%$ (1 sd)
402 in the lower Russøya Member calcites and $-2\pm 1\%$ (1 sd) in the overlying Russøya Member
403 dolomites (Figures 1 and 3, Table S1).

404

405 Reconstructed clumped isotope temperatures through the non-glacial facies also show
406 distinct trends across lithology and depositional environment (Figure 1D). Where calcite beds
407 and veins co-occur in the Russøya Member, these facies record warmer temperatures than
408 dolomite. Calcite samples from bedded strata and cross-cutting veins record mean temperatures
409 of $92\pm 5^\circ\text{C}$ (n=2, 1 sd) and $122\pm 4^\circ\text{C}$ (95% CL), respectively (Figure 3A). Dolomites in non-
410 glacial strata preserve a range of clumped isotope temperatures from 48 to 77°C (Figure 1D,
411 Table S1). Peritidal facies of the Dartboard Dolomite member record higher temperatures
412 ($75\pm 3^\circ\text{C}$, n=2, 1 sd) compared to the immediately overlying Russøya Member dolomites
413 ($56\pm 8^\circ\text{C}$, n=9, 1 sd) (Figure 1D, Table S1).

414

415 Reconstructed fluid compositions calculated from mineral $\delta^{18}\text{O}$ and clumped isotope
416 temperatures also vary by facies and mineralogy across the non-glacial stratigraphy (Figure 3A).
417 Samples of the Dartboard Dolomite member have reconstructed fluid compositions of
418 $+1.9\pm 0.9\%$ (1 sd, n=2, Table S1). Reconstructed fluid composition of the Russøya Member
419 varies with mineralogy (Figure 4A): calcite reconstructed fluid $\delta^{18}\text{O}$ values are $+8.3\pm 0.1\%$ (1 sd,
420 n=2), whereas Russøya Member dolomites have reconstructed fluid $\delta^{18}\text{O}$ values from +0.7 to
421 $+3.0\%$ ($+1.9\pm 0.8\%$, 1 sd n=9, Table S1).

422

423 3.3 Glacial dolomicrite facies isotope analyses

424 Relative to the underlying non-glacial stratigraphy, dolomicrite of the Petrovbeen
425 Member has negative $\delta^{13}\text{C}$ ($-4.4\pm 0.6\%$, 1 sd n=45) and positive $\delta^{18}\text{O}$ values ($+5\pm 2\%$ 1 sd n=45).
426 The fine-scale isotopic variability of this dolomicrite differs between matrix-supported and
427 stratified diamictite samples, however. The dolomicrite of matrix supported diamictite is
428 isotopically homogeneous where subsampled for microvolume analyses, with $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
429 values within analytical uncertainty ($-3.75\pm 0.02\%$ and $+6.98\pm 0.08\%$, respectively, 1 sd n=8).
430 Where dolomicrite forms the matrix of stratified diamictites 1 m above the matrix supported
431 diamictite, $\delta^{18}\text{O}$ values vary at the mm-scale through stratified layers, from +1.4 to +7.7‰ (mean
432 $+4.1\pm 1.2\%$, 1 sd n=29). $\delta^{13}\text{C}$ values are more consistent, with a mean of $-4.7\pm 0.1\%$ (1 sd n=29).
433 Within the same sample, soft sediment clasts have similar $\delta^{13}\text{C}$ values as the mean matrix
434 dolomicrite ($-3.9\pm 0.2\%$ 1 sd n=6), but with higher $\delta^{18}\text{O}$ values ($+9.4\pm 1.8\%$ 1 sd n=6; Figure
435 S2).
436

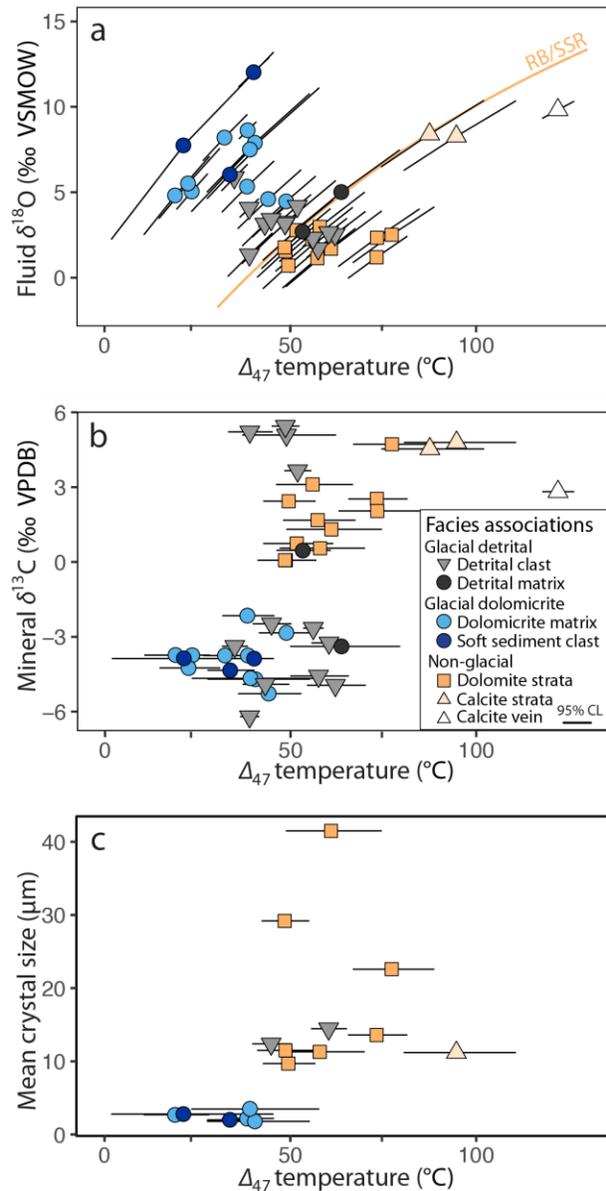


Figure 3: Summary of standard and clumped isotope values with petrographic observation. a) Measured clumped-isotope temperature for carbonate samples versus the reconstructed fluid $\delta^{18}\text{O}$ values. 95% CL error bars are diagonal due dependence of reconstructed fluid $\delta^{18}\text{O}$ values on measurement temperature. RB/SSR line denotes reconstructed fluid composition for dolomites (Horita, 2014) under purely rock-buffered alteration or solid state reordering, given a starting fluid composition of -1.2‰ . b) Measured clumped isotope temperature versus mineral $\delta^{13}\text{C}$. c) Mean crystal size varies with clumped isotope temperatures. Mean crystal size of diamictite clasts is consistent with the source stratigraphy inferred from reconstructed $\delta^{18}\text{O}$ fluid values and clumped-isotope temperatures. Calcite versus dolomite mineralogy does not appear to correspond to a significant difference in mean crystal size, despite elevated calcite temperatures interpreted as evidence of solid-state reordering. Crystal sizes $<5\ \mu\text{m}$ are approximate due to thickness of petrographic thin sections.

437

438 Matrix dolomiticrite clumped isotope temperatures range from 19 to 49°C, with mean
 439 temperatures $35\pm 10^\circ\text{C}$ ($n=10$, 1 sd; Figures 1D; 3A). Within a hand sample, dolomiticrite with
 440 coarser crystal sizes associated with local alteration (Fairchild, 1983) has warmer clumped
 441 isotope temperatures than in adjacent finer dolomiticrite ($49\ +8/-7^\circ\text{C}$ versus $38\pm 7^\circ\text{C}$, 95% CL;
 442 Table S1). Clasts featuring soft sediment deformation also have clumped isotope temperatures
 443 similar to the dolomiticrite matrix, ranging from 21 to 40°C ($31\pm 10^\circ\text{C}$, $n=3$, 1 sd, Figure 1D;
 444 Table S1). The reconstructed fluid $\delta^{18}\text{O}$ values for the lowest temperature ($<25^\circ\text{C}$, $n=4$)
 445 dolomiticrite samples and soft sediment clasts range from $+4.8$ to $+7.7\text{‰}$ (Figure 3A).

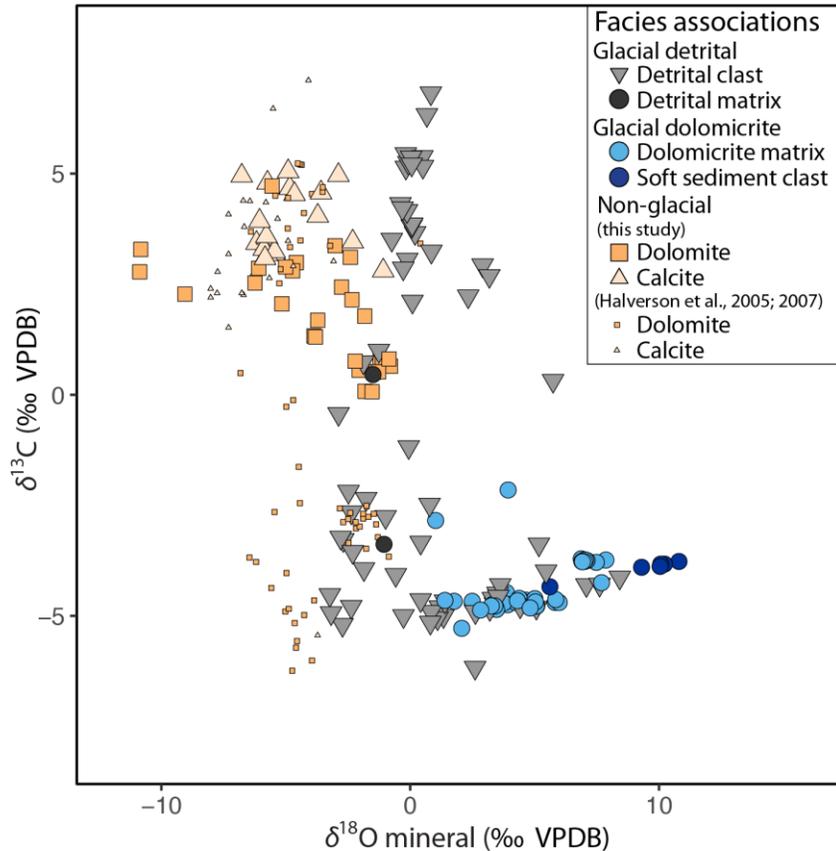


Figure 4: Cross plot of carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from the Tonian–Cryogenian in NE Svalbard. Pre-glacial carbonates from Halverson et al. (2005; 2007) sample the Russøya Member regionally. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for the underlying Akademikerbreen Formation are presented in Figure S4. Glacial Petrovbreen Member carbonates sampled here are exclusively dolomitic. Diamictite clasts span the full range of $\delta^{13}\text{C}$ values in the underlying stratigraphy, but are generally more enriched in ^{18}O . Heterogeneous Petrovbreen Member carbonate isotopic values are consistent with multiple carbonate sources, here interpreted as a detrital carbonate source with comparable $\delta^{18}\text{O}$ values to underlying non-glacial stratigraphy and a glacial source with higher $\delta^{18}\text{O}$ values.

446

447

448

3.4 Glacial detrital facies association isotope analyses

449

Clumped isotope temperatures and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of detrital clasts span much of

450 the range of both the non-glacial and glacial dolomitic facies associations (Δ_{47} 35–62°C, n=12;

451 $\delta^{13}\text{C}$ -5.2 to +6.8‰, and $\delta^{18}\text{O}$ -3.2 to +8.4‰, n=68; Figures 1, 3 and 4). Comparable clumped

452 isotope temperatures and $\delta^{18}\text{O}$ values between detrital clasts and surrounding stratigraphy

453 correspond to a similar range of reconstructed fluid $\delta^{18}\text{O}$ values (+1.3 to +5.9‰; Figure 3A).

454 Where the diamictite matrix is composed of fine detrital clasts, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are

455 comparable to the surrounding detrital clasts (Figure 4). These samples also have clumped

456 isotope temperatures similar to the warmest clasts ($59 \pm 7^\circ\text{C}$, n=2, 1 sd; Figure 3A, B).

457

458 Clumped isotope temperatures and mineral $\delta^{18}\text{O}$ values also correlate with carbonate
459 texture. Detrital clasts that resemble non-glacial strata with stromatolitic, clotted, or fenestral
460 textures share similar isotopic compositions with them: $\delta^{18}\text{O}$ values span -3.2 to +0.8‰ for seven
461 such clasts, and their clumped isotope temperatures range from 39 to 62°C (Table S1).

462 463 **4 Discussion**

464 Tonian and Cryogenian carbonates from the Dracoisen section preserve aspects of the
465 timing and style of their diagenesis through petrographic textures and isotopic compositions. In
466 the following discussion, we explore the source and preservation of Petrovbreen Member glacial
467 carbonates to interpret clumped isotope record at the onset of the Cryogenian.

468 469 **4.1 Records of calcite reordering with deep burial**

470 Isotopic composition varies systematically with carbonate lithofacies, petrographic
471 relationships and, where co-occurring in the non-glacial facies association, mineralogy. Within
472 the Russøya Member, clumped isotope temperatures and reconstructed fluid compositions are
473 higher in calcite than dolomite (Figure 3). The preferential solid state reordering of calcite at
474 lower temperatures than dolomite explains this mineral-dependent relationship (Lloyd et al.,
475 2018; Passey & Henkes, 2012; Stolper & Eiler, 2015). Clumped isotope temperatures from
476 carbonate strata and reconstructed fluid $\delta^{18}\text{O}$ values follow trajectories consistent with low
477 water-rock alteration or solid state reordering from an original marine source (Figure 3). In
478 addition to these alteration trajectories, comparison of calcite strata temperatures ($92\pm 5^\circ\text{C}$; $n=2$,
479 1 sd) and cross-cutting calcite vein cement ($122\pm 4^\circ\text{C}$; 95% CL) provides a minimum burial
480 temperature estimate. Based on laboratory reordering experiments and field observations, over
481 100 Ma calcite begins to be impacted at $\sim 100^\circ\text{C}$, and calcites are 99% reordered at 144°C
482 (values for brachiopod calcite, Passey and Henkes, 2012; Henkes et al., 2014). Thus, although
483 calcites have likely been impacted by solid state reordering, preservation of temperature
484 differences between calcite strata and cross-cutting vein calcite indicates only partial solid state
485 reordering of the calcites. Taken together, these results indicate that calcite clumped isotope
486 temperatures represent a signature of deep burial rather than depositional or early diagenetic
487 conditions. Burial temperatures are not likely to have significantly exceeded that recorded in
488 calcite veins, however, as the kinetics of reordering would lead to rapid equilibration of calcite to
489 higher temperatures.

490
491 Burial temperatures reflected by calcite reordering is within the upper bounds predicted
492 for preservation of dolomite clumped isotope temperatures (Lloyd et al., 2018), consistent with
493 their lower clumped isotope temperatures in the Dracoisen strata. Non-glacial dolomite
494 temperatures do exceed expectations for reasonable surface conditions ($48\text{--}77^\circ\text{C}$), indicating that
495 they contain a signature of burial diagenesis. In the following discussion, we assess the
496 relationships among petrographic textures, bulk isotope compositions, and clumped isotope
497 temperatures to characterize the effect of diagenetic alteration on original climate signatures.

498 499 **4.2 Dolomite sources across facies and timing of precipitation**

500 The dolomite facies associations defined in this study have distinct petrographic textures,
501 standard carbonate isotope compositions and clumped isotope temperatures. Carbonates from the
502 non-glacial and glacial dolomicrite facies associations cluster separately by these metrics, but the
503 detrital facies association contains clasts that display similar petrographic texture, crystal size
504 distribution, and isotopic composition with both of the other facies associations (Figures 3 and
505 4). Taken together the wide range of $\delta^{13}\text{C}$ values found in Russøya Member carbonates
506 regionally ($>+7$ to $<-4.5\%$; Hoffman et al., 2012; Halverson et al., 2018) is consistent with the
507 composition of carbonate clasts found in the Petrovbreen Member. Indeed, petrographically
508 distinctive clasts, such as stromatolite morphologies like those found in the nadir of the
509 purported Islay negative carbon isotope excursion (Hoffman et al., 2012; Table S1), have $\delta^{13}\text{C}$
510 values ($<-4.5\%$), low mineral $\delta^{18}\text{O}$ values, and clumped isotope temperatures consistent with the
511 underlying interpreted source stratigraphy. Temperatures of $\leq 25^\circ\text{C}$ ($n=4$) are restricted to
512 Petrovbreen Member samples of matrix dolomicrite and clasts featuring soft sediment
513 deformation (Figures 1D and 4).

514

515 Temperature, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ heterogeneity is maintained on the scale of clasts and matrix
516 material (Figure S1), indicating that dolomites represent distinct populations with different
517 depositional or early diagenetic histories. Temperature differences between the clasts and matrix
518 of Petrovbreen Member diamictite require that dolomitization of clasts predated redeposition in
519 the diamictite; dolomitization would affect clumped isotope composition of carbonates, even
520 under low water-rock conditions that could have preserved primary carbonate $\delta^{18}\text{O}$ values (e.g.
521 Ferry et al., 2011). Petrographic textures support this early dolomite source, including both
522 dolomite crystal size distributions and accessory mineral assemblages. For example,
523 heterogeneous petrographic textures, mineral $\delta^{18}\text{O}$ values, and clumped isotope temperatures are
524 most consistent with a depositional or early diagenetic source of dolomite within pre-glacial
525 stratigraphy, prior to erosion and re-deposition as clasts in the overlying diamictite. In addition to
526 these distinct pre-glacial clasts in the diamictite, some stratified diamictite samples also contain
527 clasts compositionally and texturally similar to the matrix dolomicrite. This relationship is
528 consistent with local reworking of dolomicrite material in the depositional environment prior to
529 sedimentation of the stratified diamictite.

530

531 The high $\delta^{18}\text{O}$ values of the Petrovbreen Member dolomicrite are also distinct from other
532 dolomites in this stratigraphic section. The fine size of dolomicrite crystals has previously been
533 interpreted as evidence for deposition as carbonate rock flour (Fairchild, 1983), however the
534 coincidence of high $\delta^{18}\text{O}$ and low $\delta^{13}\text{C}$ mineral values in the diamictite matrix differ from the
535 regional composition of dolomitic strata that could serve as the rock flour protolith (Halverson et
536 al., 2018; Figure 4S). The isotopic composition of fine-grained glacial strata and soft sediment
537 clasts instead fall on a mixing line away from underlying strata and recognizable exogenous
538 carbonate clasts (Figure 4). The glacial dolomicrite of the Petrovbreen Member is also
539 geochemically distinct from overlying cap dolostone and dolomitic silt-shale of the
540 MacDonaldryggen Member, which have lower $\delta^{18}\text{O}$ values than the glacial dolomicrite ($-8.6 -$
541 $+0.6\%$ with a mean of -3.7% ; Fairchild et al., 2016; Figure S4). Interglacial dolomite
542 petrography indicates that MacDonaldryggen Member dolomite precipitation predated

543 compaction; pore-filling calcite interpreted as later burial cements are also associated with more
544 negative $\delta^{18}\text{O}$ values around -9‰ (Fairchild et al., 2016).

545

546 Clumped isotope temperatures of Petrovreen Member dolomicrite further constrain the
547 source and timing of dolomite formation. Temperatures as low as $19 \pm 9/-8^\circ\text{C}$ (95% CL) are
548 inconsistent with precipitation in deep burial conditions during nonglacial periods, particularly
549 given low reconstructed paleolatitudes (Maloof et al., 2006). Thus, the composition of the glacial
550 dolomicrite facies association is consistent with a distinct carbonate precipitating at low
551 temperatures from a fluid with a higher $^{18}\text{O}/^{16}\text{O}$ ratio than associated detrital dolomites. The wide
552 range of high $\delta^{18}\text{O}$ values of the reconstructed fluid composition (+4–12‰) will be discussed in
553 section 4.4).

554

555 Evidence for early dolomitization in both the Russøya and Petrovreen members is
556 consistent with studies of Tonian carbonates in Svalbard (Knoll & Swett, 1990) and other
557 Neoproterozoic strata (Hood et al., 2011; Shuster et al., 2018; Tucker, 1982). Deep water
558 dolomicrite firm or hardgrounds in non-glacial Cryogenian strata are interpreted as deep water
559 authigenic deposits formed during sediment starvation (Wallace et al., 2019). The stratified
560 diamictite above contains localized sulfate pseudomorphs and is laterally associated with sand
561 wedges and brecciation (Fairchild and Hambrey, 1984; Fairchild, pers. comm.), interpreted as a
562 syn-glacial depositional hiatus. If these Petrovreen Member dolomicrites have a similar origin
563 to other Cryogenian authigenic dolomicrites, then they originated under significantly different
564 glacial environments than the ultimate subaerial exposure inferred by cross-cutting sand wedges
565 (Fairchild & Hambrey, 1984).

566

567 4.3 Preservation of isotopic records in non-glacial facies

568 Despite evidence for early dolomite precipitation and coherence between clumped isotope
569 temperatures and sedimentary indicators of climate, within the non-glacial dolomites clumped
570 isotope temperatures vary from $48\text{--}77^\circ\text{C}$. The highest temperature samples are associated with
571 consistent reconstructed fluid $\delta^{18}\text{O}$ values (Figure 3A), and this correspondence is consistent
572 with fluid-buffered diagenetic alteration, wherein carbonates partially equilibrate to fluid $\delta^{18}\text{O}$
573 under elevated burial temperatures (Bergmann et al., 2018; Ryb & Eiler, 2018; Winkelstern &
574 Lohmann, 2016). On account of this distinct fluid-buffered alteration signal, we have excluded
575 the highest temperature non-glacial samples ($\geq 73^\circ\text{C}$, $n=3$) from any paleoenvironmental
576 analysis. Also excluded is two samples (one glacial, one preglacial; Table S1) with coarse
577 dissolution and reprecipitation textures inconsistent with the textural preservation of surrounding
578 strata. These samples are together referred to as the “altered dolomites” in subsequent discussion.

579

580 The remaining best-preserved samples from the Russøya Member have consistent
581 clumped isotope temperatures ($53 \pm 4^\circ\text{C}$, 1 sd $n=7$; Figure 5B). The traditional carbonate $\delta^{18}\text{O}$
582 thermometer (Horita, 2014) for these same samples also gives consistent, though lower,
583 temperatures ($37 \pm 4^\circ\text{C}$, 1 sd $n=7$) assuming modern seawater $\delta^{18}\text{O}$ values and no polar ice (-1.2‰
584 VSMOW, Lear et al., 2000; Cramer et al., 2011; see Bergmann et al., 2018a, 2018b and Henkes

585 et al., 2018 for discussion of paleomarine $\delta^{18}\text{O}$ values). The higher clumped isotope temperatures
586 measured for all non-glacial facies correspond to higher reconstructed fluid $\delta^{18}\text{O}$ values than the
587 assumed ice-free value of -1.2‰ VSMOW; non-glacial samples $<50^\circ\text{C}$ have fluid $\delta^{18}\text{O}$ values of
588 $+0.7$ to $+1.8\text{‰}$ VSMOW (Figure 4). Higher fluid $\delta^{18}\text{O}$ values at elevated clumped isotope
589 temperatures are consistent with rock-buffered dissolution and reprecipitation, cementation, or
590 partial solid-state reordering increasing temperature with burial (Staudigel & Swart, 2019;
591 Stolper et al., 2018). Given the association of evaporite pseudomorphs and stromatolites in the
592 non-glacial facies association, it is also possible that fluid $\delta^{18}\text{O}$ values were higher from primary
593 restriction and evaporative concentration in the depositional environment.

594

595 Uncertainty in the starting fluid composition complicates back-calculation of temperature
596 from mineral $\delta^{18}\text{O}$, but assumption source fluid composition provides an estimate for diagenetic
597 increase in clumped isotope temperature with rock-buffered alteration. If we take cross-cutting
598 vein temperature of 122°C as a maximum burial temperature (see Discussion section 4.1),
599 dolomites did not likely exceed the threshold for solid state reordering based on Arrhenius
600 parameters of Lloyd et al. (2018). In this case, measured sample clumped isotope temperatures
601 would instead represent a mixture between one component of carbonate equilibrated to
602 depositional or early diagenetic conditions and another component equilibrated to deeper burial
603 temperatures; under rock-buffered alteration, both components would have the same mineral
604 $\delta^{18}\text{O}$ value. It would require at least a 16% contribution of burial-equilibrated dolomites to
605 account for observed reconstructed $\delta^{18}\text{O}$ values if early dolomites precipitated from a -1.2‰
606 $\delta^{18}\text{O}$ VSMOW fluid as described above. Source waters with lower $\delta^{18}\text{O}$ values (e.g. Galili et al.,
607 2019) would require proportionately greater burial alteration to explain the composition of the
608 pre-glacial dolomites (Table 1).

Data treatment	Strata	$\delta^{18}\text{O}$ mineral (‰ VPDB)	Temp (°C)	Initial fluid $\delta^{18}\text{O}$ (‰ VSMOW)	% equilibrated to burial estimate (122°)
Raw data	Pre-glacial	-1.5/-2.2	48/53	+1.8/+1.9	0%
Raw data	Glacial	+7.9/+6.8	19/33	+4.8/+6.9	0%
Pre-glacial fluid $\delta^{18}\text{O}$ -1.2‰	Pre-glacial	-1.5/-2.2	34/37	-1.2	22%/23%
Pre-glacial fluid $\delta^{18}\text{O}$ -1.2‰	Glacial	+7.9/+6.8	2/16	-0.1/+2.8	22%/23%
Pre-glacial fluid $\delta^{18}\text{O}$ -5‰	Pre-glacial	-1.5/-2.2	18/21	-5	39%/41%
Pre-glacial fluid $\delta^{18}\text{O}$ -5‰	Glacial	+7.9/+6.8	-16/-2	-6.3/-2.8	39%/41%
<i>15% equilibrated</i>	<i>Pre-glacial</i>	<i>-1.5/-2.2</i>	39/44	-0.1/0.2	<i>15%</i>
<i>15% equilibrated</i>	<i>Glacial</i>	<i>+7.9/+6.8</i>	8/23	+1.8/+4.5	<i>15%</i>
30% equilibrated	Pre-glacial	-1.5/-2.2	27/33	-2.7/-2.3	30%
30% equilibrated	Glacial	+7.9/+6.8	-6/10	-2.6/+0.9	30%

Table 1: Summary of mineral $\delta^{18}\text{O}$, temperature, and initial source fluid $\delta^{18}\text{O}$ for pre- and syn-glacial dolomites. Data are presented for the lowest/mean sample temperatures associated with each climate state. Raw data are transformed via possible rock-buffered alteration trajectories based on hypothetical initial source fluid $\delta^{18}\text{O}$ values or the percent of dolomite equilibrated to peak burial estimate. For each data treatment, the pre-glacial percent equilibrated is used to estimate the initial fluid $\delta^{18}\text{O}$ values for glacial conditions. In each row of the transformed data, $\delta^{18}\text{O}$ mineral is held constant, and the treatment is used to calculate either the percent equilibrated (with initial fluid assumed) or initial fluid composition (with percent equilibrated assumed). Calculated values are in bold, and the preferred interpretation is italicized. In all treatments, the difference in minimum temperatures between pre-glacial and glacial states are similar to that of the raw data.

609

610

611 4.4 Stratigraphic changes in isotope geochemistry

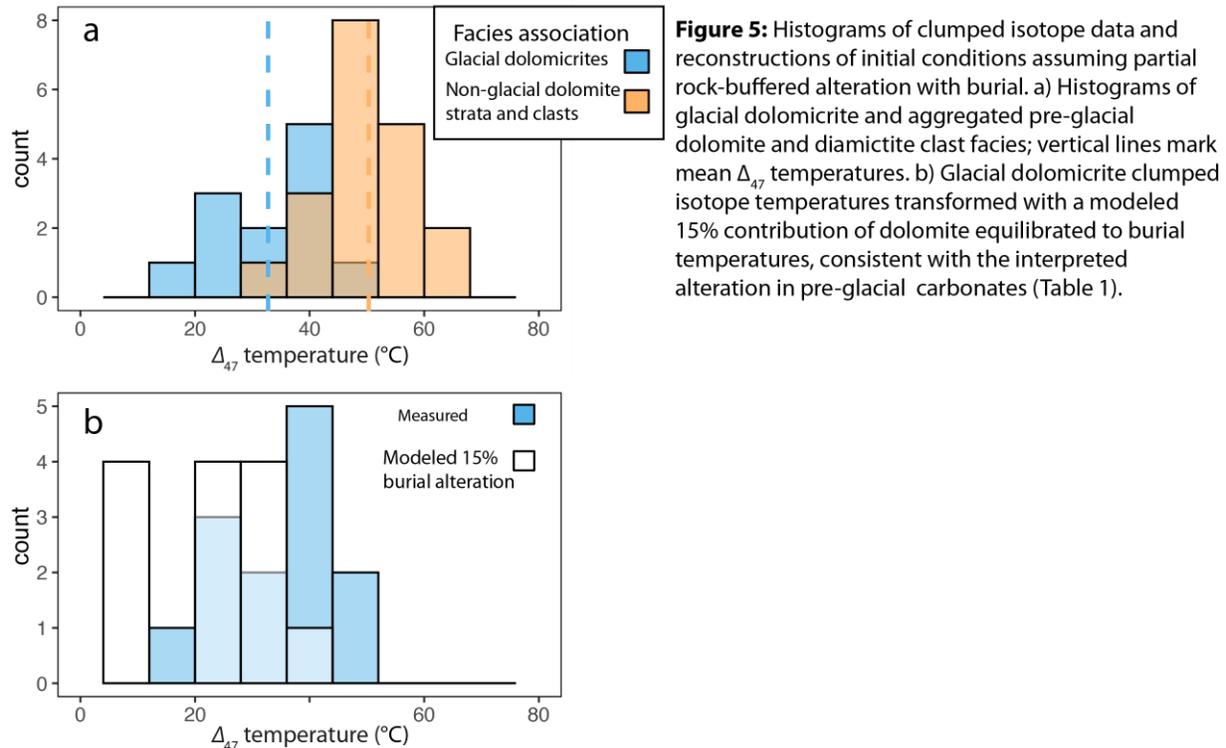
612 If early dolomites have maintained a signal of their early clumped isotope composition
613 through burial at Dracoisen, we predict that clumped isotope temperatures should covary with
614 independent sedimentary records of climate. Indeed, the coldest reconstructed clumped isotope
615 temperatures of Russøya Member non-glacial dolomite are 29°C warmer than the coldest
616 temperatures recorded in the diamictite dolomicrite matrix. Taking the Russøya and Petrovbre
617 Member temperatures together, mean non-glacial temperatures are significantly warmer than
618 glacial dolomicrites. The mean temperature of the non-glacial facies is between 16 and 36°C
619 warmer than glacial dolomicrite by the Welch Two Sample t-test ($n = 19$, 95% confidence
620 interval), excluding the altered dolomites (Section 4.3). This relationship is similar when all
621 detrital clasts are binned with the non-glacial facies, giving a mean temperature between 12 and
622 29°C warmer than glacial dolomicrite ($n = 31$, 95% confidence interval; Figure 5A).

623

624 Changes to the local diagenetic environment and/or extent of dissolution and
625 reprecipitation are not sufficient to explain the difference between the chemistry of the non-
626 glacial facies and the overlying glacial dolomicrite facies. The lower temperatures, more positive
627 fluid $\delta^{18}\text{O}$ values, and negative mineral $\delta^{13}\text{C}$ values of glacial diamictite matrix and soft
628 sediment clasts are inconsistent with alteration trajectories of non-glacial facies. Rock-buffered
629 alteration with burial or dolomitization by basinal brines would have the opposite trend with

630 higher reconstructed fluid $\delta^{18}\text{O}$ values at greater temperatures (e.g. Mangenot et al., 2018).
 631 Instead, the clumped isotope results of the Petrovreen Member dolomicrite are consistent with
 632 early dolomite formation under different depositional or early diagenetic environments prior to
 633 deep burial. If both glacial and non-glacial facies experienced similar rock-buffered dissolution
 634 and reprecipitation (see Discussion section 4.3), then the early temperature and source fluid $\delta^{18}\text{O}$
 635 values for glacial dolomicrite may have also been lower than measured in this clumped isotope
 636 analysis ($33\pm 9^\circ\text{C}$ and $+7\pm 2\text{‰}$, respectively; $n = 12$, 1 SD). For the lowest temperature
 637 dolomicrite and soft sediment samples (19°C and 21°C , respectively) and the hypothetical 15%
 638 contribution of dolomite equilibrated to burial temperatures (see Discussion section 4.3, Table
 639 1), initial temperatures would have been $+8^\circ\text{C}$ and $+10^\circ\text{C}$ with a reconstructed fluid $\delta^{18}\text{O}$ values
 640 of $+1.8\text{‰}$ and $+4.5\text{‰}$, respectively (Figure 5B). The reconstructed fluid $\delta^{18}\text{O}$ values are more
 641 positive than modern seawater, albeit with less extreme values than initially calculated from the
 642 clumped isotope thermometer ($+4.8\text{‰}$ and $+7.7\text{‰}$). Higher levels of rock-buffered alteration
 643 would correspond to lower initial temperatures and lower source fluid $\delta^{18}\text{O}$ values (Table 1).

644



645

646 High $\delta^{18}\text{O}$ values for primary or early diagenetic glacial fluids are consistent with
 647 evaporative concentration, though the value cannot discern whether this evaporation relates to
 648 sequestration of precipitation in continental ice sheets (e.g. Raymo et al., 2018; Shackleton,
 649 1967) or more local restriction (e.g. Gat, 1995; Horita, 2008). The association of these dolomites
 650 with diamictite does suggest at least some contribution from the former, however. Regardless of
 651 the mechanism for increase in fluid $\delta^{18}\text{O}$ values, results from the Petrovreen Member
 652 dolomicrites suggest either net marine evaporation feeding ice sheet growth or local atmospheric
 653 exposure in this depositional environment to allow for continued evaporation. Other mechanisms
 654 for concentrating solutes in glacial environments like freeze-concentration (Staudigel et al.,

655 2018) cannot explain the observed trends here, as freeze concentration is associated with lower
656 fluid $\delta^{18}\text{O}$ values (Horita, 2008).

657

658 4.5 Implications for Neoproterozoic glacial episodes

659 Evidence for evaporation coincident with the deposition of Petrovreen Member cold
660 water carbonate beds constrains depositional and early diagenetic conditions at points within this
661 glacial episode. Relatively high fluid $\delta^{18}\text{O}$ values in glacial carbonates compared to underlying
662 non-glacial strata, is most consistent with intervals of moderate glaciation with an active
663 hydrologic cycle, rather than the permanent ice shell predicted by more severe hypotheses for
664 Snowball Earth. Relative changes in temperature between non-glacial and glacial facies also
665 inform reconstructions of the magnitude of climate perturbation represented by these strata. The
666 offset in minimum temperatures (29°C) between non-glacial and glacial low latitude carbonates
667 is more severe than reconstructed for Phanerozoic glaciations (Finnegan et al., 2011; Grossman
668 et al., 2008; Raymo et al., 2018), but more moderate than predicted for the most severe
669 hypotheses of Snowball glaciation (Abbot et al., 2013; Hoffman et al., 2017 and references
670 therein).

671

672

673 5 Conclusions

674 The Neoproterozoic Elbobreen Formation of NE Svalbard contains carbonate-rich facies
675 preceding and coincident with the first Cryogenian Snowball Earth episode. These carbonates
676 preserve shifts in $\delta^{18}\text{O}$ composition and Δ_{47} temperature records alongside sedimentological
677 evidence of environmental change. When combined in stratigraphic and petrographic context,
678 these geochemical records indicate that primary to early diagenetic conditions have been
679 partially preserved in these Neoproterozoic carbonates. Whereas calcite clumped isotope
680 temperatures have been partially altered ($92\pm 5^\circ\text{C}$, 1 sd) through solid state reordering during
681 deep burial, the more recalcitrant dolomites retain informative clumped isotope temperature
682 relationships. Dolomite clumped isotope temperatures are warmer than expected for surface
683 depositional environments, but relative temperatures and reconstructed source water $\delta^{18}\text{O}$ values
684 co-vary with independent sedimentological evidence for climate change. Minimum temperatures
685 for glacial facies are 29°C colder than non-glacial facies, and detrital dolomitic clasts from the
686 glacial diamictites retain temperatures and mineral $\delta^{18}\text{O}$ values consistent with diverse glacial
687 and non-glacial sources. Source waters for glacial facies also have higher $\delta^{18}\text{O}$ values than non-
688 glacial facies, with minimum reconstructed $\delta^{18}\text{O}$ fluid values $>3\%$ higher between these facies.
689 Together, results indicate that there were both detrital and autochthonous sources of dolomite in
690 these glacial environments. Temperature changes and higher fluid $\delta^{18}\text{O}$ values are consistent
691 with moderate glacial environments with an active hydrological cycle, indicating some
692 combination of evaporative concentration of surface waters or growth of ice sheets with
693 evaporation from of a marine reservoir. Results are not consistent with interpretations of ice
694 sheets formed by freeze concentration and persistent shutdown of the hydrological cycle
695 expected in the most severe models for Snowball Earth episodes. Further constraints on
696 conditions surrounding panglacial climate episodes may be feasible through judicious application
697 of carbonate clumped isotope thermometry in other well-preserved Neoproterozoic strata.

698 **Data**

699 All data used in this study are available in this article and its online supplemental
 700 materials. Raw data from carbonate clumped isotope analysis are submitted for review as
 701 supplemental materials and will be submitted to the EARTHCHEM Database by acceptance.

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969 **Figure 1:** Stratigraphy of the latest Tonian (Dartboard Dolomite and Russøya members) and
 970 earliest Cryogenian (Petrovbreen Member) at the Dracoisen Nunatak, NE Svalbard. **a)**
 971 Stratigraphic column highlighting transitions among the dominant carbonate mineralogies. The
 972 scale of the Petrovbreen Member is extended to display diamictite distribution. **b)** Composite of
 973 $\delta^{13}\text{C}$ values and **c)** Mineral $\delta^{18}\text{O}$ value through stratigraphic section. **d)** Clumped isotope
 974 temperatures and 95% CL error for a subset of these samples.

975 **Figure 2:** Petrographic textures of the Dracoisen section dolomites; where images are paired, left
 976 is a scanned polished sample and right is thin section photomicrograph. **a–c)** Glacial carbonates
 977 of the Petrovbreen Member consisting of **a)** homogeneous dolomicrite matrix, **b)** discrete soft
 978 sediment clasts in diamictite, **c)** detrital clasts and matrix consisting of <1 mm detrital clasts. **d)**
 979 and **e)** non-glacial carbonates of the peritidal Dartboard Dolomite Member of the
 980 Akademikerbreen Formation and overlying Elbobreen Formation Russøya Member. Russøya
 981 Member dolomite facies pictured here include stromatolites with a clotted microtexture,
 982 evaporite pseudomorphs partially replaced by dolomite and silica (here cross-polarized to
 983 highlight twinning after gypsum), and homogeneous dolomicrospar rhombs in wedged thin
 984 section. Mean crystal sizes indicate range in mean sizes for analyzed samples, and isotope data

985 present the mean mineral $\delta^{18}\text{O}$ values and clumped-isotope temperatures ± 1 standard deviation to
 986 describe the population analyzed, and the range of mean clumped-isotope temperatures.

987 **Figure 3:** Summary of standard and clumped isotope values with petrographic observation. **a)**
 988 Measured clumped-isotope temperature for carbonate samples versus the reconstructed fluid
 989 $\delta^{18}\text{O}$ values. 95% CL error bars are diagonal due dependence of reconstructed fluid $\delta^{18}\text{O}$ values
 990 on measurement temperature. RB/SSR line denotes reconstructed fluid composition for
 991 dolomites (Horita, 2014) under purely rock-buffered alteration or solid state reordering, given a
 992 starting fluid composition of -1.2‰. **b)** Measured clumped isotope temperature versus mineral
 993 $\delta^{13}\text{C}$. **c)** Mean crystal size varies with clumped isotope temperatures. Mean crystal size of
 994 diamictite clasts is consistent with the source stratigraphy inferred from reconstructed $\delta^{18}\text{O}$ fluid
 995 values and clumped-isotope temperatures. Calcite versus dolomite mineralogy does not appear to
 996 correspond to a significant difference in mean crystal size, despite elevated calcite temperatures
 997 interpreted as evidence of solid-state reordering. Crystal sizes $< 5 \mu\text{m}$ are approximate due to
 998 thickness of petrographic thin sections.

999 **Figure 4:** Cross plot of carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from the Tonian–Cryogenian in NE
 1000 Svalbard. Pre-glacial carbonates from Halverson et al. (2005; 2007) sample the Russøya Member
 1001 regionally as well as the underlying Akademikerbreen Formation. Glacial Petrovbreen Member
 1002 carbonates sampled here are exclusively dolomitic. Diamictite clasts span the full range of $\delta^{13}\text{C}$
 1003 values in the underlying stratigraphy, but are generally more enriched in ^{18}O . Petrovbreen
 1004 Member carbonate isotopic values are consistent with both a detrital carbonate source and a
 1005 glacial source with higher $\delta^{18}\text{O}$ values, with soft sediment clasts making up the end member with
 1006 the highest $\delta^{18}\text{O}$ values.

1007 **Figure 5:** Histograms of clumped isotope data and reconstructions of initial conditions assuming
 1008 partial rock-buffered alteration with burial. **a)** Histograms of glacial dolomicrite and aggregated
 1009 pre-glacial dolomite and diamictite clast facies; vertical lines mark mean Δ_{47} temperatures. **b)**
 1010 Glacial dolomicrite clumped isotope temperatures transformed with a modeled 15% contribution
 1011 of dolomite equilibrated to burial temperatures, consistent with the interpreted alteration in pre-
 1012 glacial carbonates (**Table 1**).

1013 **Table 1:** Summary of mineral $\delta^{18}\text{O}$, temperature, and initial source fluid $\delta^{18}\text{O}$ for pre- and syn-
 1014 glacial dolomites. Data are presented for the lowest/mean sample temperatures associated with
 1015 each climate state. Raw data are transformed via possible rock-buffered alteration trajectories
 1016 based on hypothetical initial source fluid $\delta^{18}\text{O}$ values or the percent of dolomite equilibrated to
 1017 peak burial estimate. For each data treatment, the pre-glacial percent equilibrated is used to
 1018 estimate the initial fluid $\delta^{18}\text{O}$ values for glacial conditions. In each row of the transformed data,
 1019 $\delta^{18}\text{O}$ mineral is held constant, and the treatment is used to calculate either the percent
 1020 equilibrated (with initial fluid assumed) or initial fluid composition (with percent equilibrated
 1021 assumed). Calculated values are in bold, and the preferred interpretation is italicized. In all
 1022 treatments, the difference in minimum temperatures between pre-glacial and glacial states are
 1023 similar to that of the raw data.

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Temperature and Hydrologic Cycle Constraints on Snowball Earth Environments

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Additional Supporting Information (Files uploaded separately)

Figure S1
Tables S1 and S2

Introduction

This supporting information includes supplemental text (S1–S3) on the analytical methods followed for the study. Methods are paired with Tables S1 and S2, which provide the raw and processed isotopic data underpinning the study; raw isotopic data (Table S2) is also submitted to EarthChem database and includes the analytical information for all standards and unknowns used in generating clumped isotope reconstructions. Figure S1 and Table S2 are uploaded separately as a PDF and an Excel workbook (.xlsx), respectively. The full results of XRD analysis are listed in Table S3, following the methods in the main manuscript text. Supplemental Figures S1–S5 provide additional context on sampling sites analyzed in this study (Figures S1 and S2), petrographic textures referenced in the text (Figure S3), and visualization of geochemical data sets that complement the figures in the main manuscript text (Figure S4 and S5).

Text S1. Clumped isotope analytical methods

Clumped isotope analyses were carried out on the Bergmann Lab Nu Perspective IRMS with an interfaced NuCarb autosampler held at 70°C. All carbonates were converted to CO₂ with injection of 150 µl of concentrated H₃PO₄ (1.94–1.95 g/cm³) into the evacuated sample vial. Acidification progressed for 600 sec in the closed vial, followed by continuing reaction for

an additional 600 sec while freezing onto a -160 °C cold finger for a total reaction time of 1200 sec. This two-step digestion prevented aspiration of bubbles and associated acid residue into the autosampler valves (Nu Instruments, pers. comm.). Recent work has indicated that prolonged interactions between water vapor originating from H₃PO₄ and evolved CO₂ can affect Δ_{47} values (Swart et al., 2019). The small volume of concentrated H₃PO₄ injected and short length of exposure of CO₂ to acid-sourced water vapor are insufficient to impact the primary CO₂ Δ_{47} values. Following carbonate acidification, evolved CO₂ was purified with a cold finger water trap (-60 °C) and passive passage through a -30°C passive porapak trap (1/4" inner diameter tube filled with 0.4 g 50-80 mesh PorapakQ bracketed by silver wool) to freeze onto a second cold finger. Evolved CO₂ was subsequently transferred to a third cold finger in a microvolume and warmed to room temperature before having the pressure balanced by beam size on the reference side. Both sample and reference side microvolumes depleted together in the course of analysis. The resulting beam intensities were collected in three blocks with 20 cycles each of 20s integration. Initial voltage was 8–20 V on the m/z 44 beam for standard and unknown analyses, and this depleted by approximately 50% through analysis.

The NuCarb is equipped with a 50-vial carousel, which is analyzed over approximately 72 hours. Laboratory protocols for organization of standards to unknowns within a run changed in the course of this study (6/2017–11/2018). Throughout all analyses, four ETH standards were used to transfer values to VPDB and Carbon Dioxide Equilibrium Scale (CDES) (Dennis et al., 2011); $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47} values for ETH standards were taken from Bernasconi et al. (2018). Queues were planned for >18 ETH standards run alongside in house standards and <23 unknowns prior to 2/2018, and after this point the format was standardized to 22 ETH standards alongside in house standards and <25 unknowns. Shorter runs exceeded these standard:unknown ratio. In all cases, replicates for unknowns were dispersed throughout a run queue. Analytical failures due to autosampler malfunction or failure of standards and unknowns for data quality screening (Text S2) led to some differences between planned standard:unknown distributions and actual analyses. The full list of standards and unknowns run in the study is available in Table S2.

Text S2.

All samples were screening for CO₂ volume and yield using the measured carbonate mass and pressure transducer readings of CO₂ after passage through the porapak trap and cryogenic purification. Analyses with CO₂ pressures less than the equivalent of 250–300 µg of carbonate were excluded from this study.

Both standard and unknown replicates were screened for consistency within the cycles of a single analysis. In 103/1241 analyses (standards and unknowns), anomalous voltage spikes were present in cycles of specific analyses. Spikes were interpreted as instrumental errors related to reductions in the backing pressure of the dual inlet changeover block and possible arcing in the source. Spikes were clear outliers in the cycles of a given analysis, and were screened by disabling individual cycle Δ_{47} values outliers >3 standard deviations from the mean of the three analytical blocks if the analysis standard deviation for Δ_{47} values exceeded 0.05‰. Analyses were disabled if ≥ 10 cycles out of 60 were >3 standard deviations from the analysis mean (n = 5) or if removal of outliers did not reduce the standard deviation to less than 0.05‰ (n = 14). In the 84 analyses corrected by screening in this study, an average of

4/60 cycles were disabled, taking the average standard deviation across analysis blocks from 0.09 to 0.03‰.

Text S3.

An acid fractionation factor of 0.062‰ (Defliese et al., 2015; Müller et al., 2017) was used to convert our raw Δ_{47} data analyzed at 70°C to the 25°C Carbon Dioxide Equilibrium Scale (CDES) (Dennis et al., 2011). All measurements were translated to the VPDB and CDES reference frames using ETH standard values from Bernasconi et al. (2018). The temperature calibrations of Bernasconi et al. (2018) were also used for calculation of all Δ_{47} temperatures: $\Delta_{47} = 0.0449 \cdot \frac{10^6}{T^2} + 0.167$. We used this temperature calibration for both calcites and dolomites, given the findings of Petersen et al. (2019) that temperature reconstructions for consistent clumped isotope behavior for these mineralogies in their reprocessed interlaboratory comparison. These results are consistent with other interlab comparison studies (Bonifacie et al., 2017). The recent protodolomite thermometer of Müller et al. (2019) yields temperatures 6–14°C warmer than our preferred temperature calibration from Bernasconi et al. (2018). Non-glacial samples in our data set are more sensitive to the recalculations of this thermometer than glacial dolomites, increasing the 95% CL difference between the glacial and non-glacial dolomites from 16–36°C to 19–41°C. Our interpretations of partial preservation of changing climatic conditions are not impacted by the specific dolomite temperature calibration used.

Figure S1. Compilation of drill sites for clumped isotope analysis and microvolume sites from stratified diamictite slab; scale bar demarcations are millimeters. Data for each drill site are listed in Table S1. (File uploaded separately)

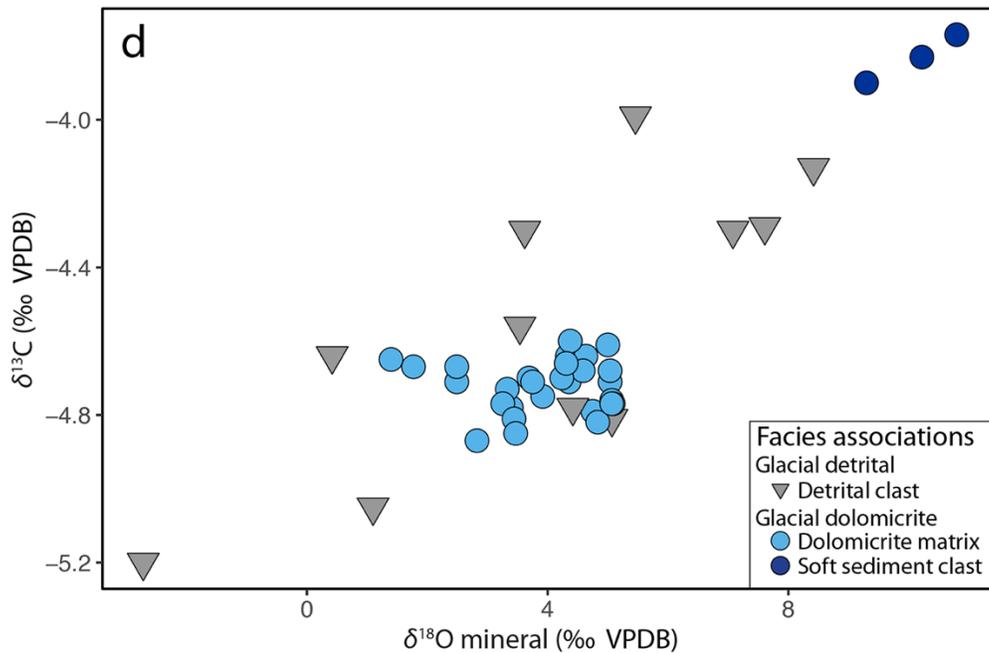
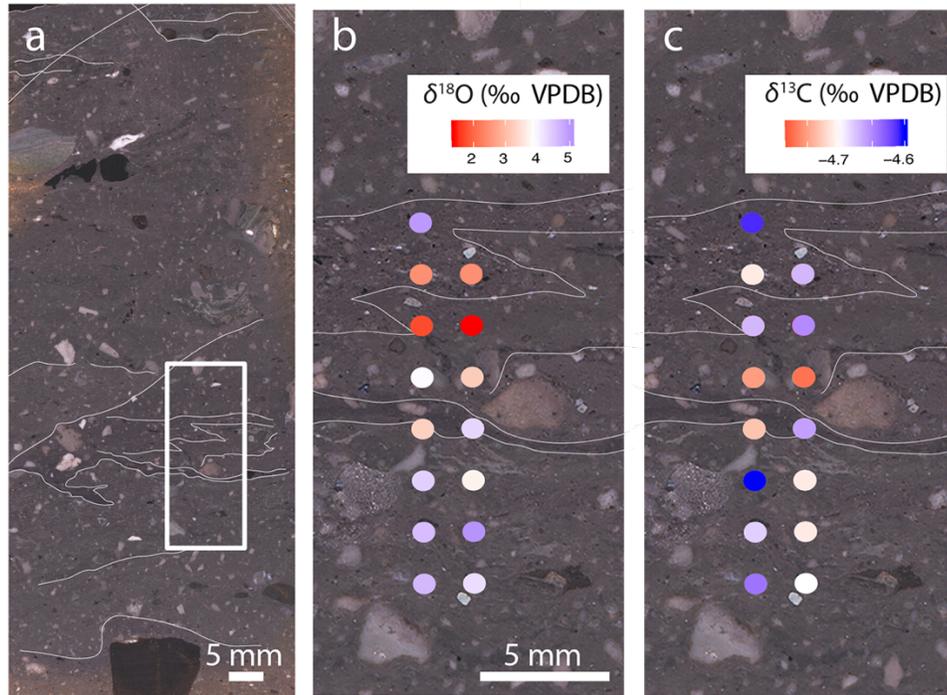


Figure S2. Microvolume analyses of stratified diamictite sample (PD5-78) $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. a) Polished slab with stratification outlined. Irregular layering is interpreted as localized glaciotectionism. b and c) Inset area from (a) with $\delta^{18}\text{O}$ (b) and $\delta^{13}\text{C}$ (c) sampling spots targeting

dolomicrite matrix across stratified layers. d) Cross plot of microvolume analyses from the PD5-78 slab. All drilled locations for this slab are presented in Figure S1.

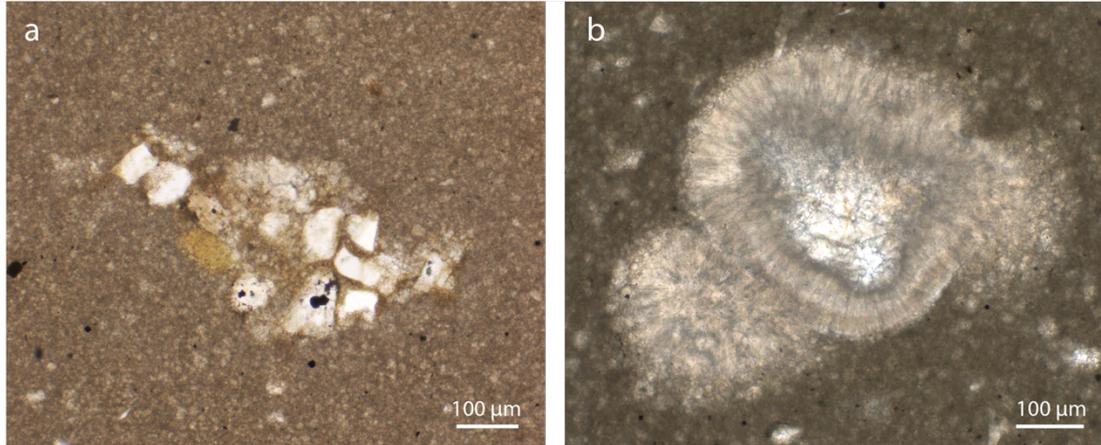


Figure S3. Supplemental petrographic attributes of Petrovbeen Member stratified diamictite referenced in the main text. a) Aggregate of siliciclastic grains in dolomicrite matrix interpreted as a till pellet. b) Carbonate grain with circumgranular sparry rims consistent with in situ precipitation (c.f. Fairchild et al., 2004).

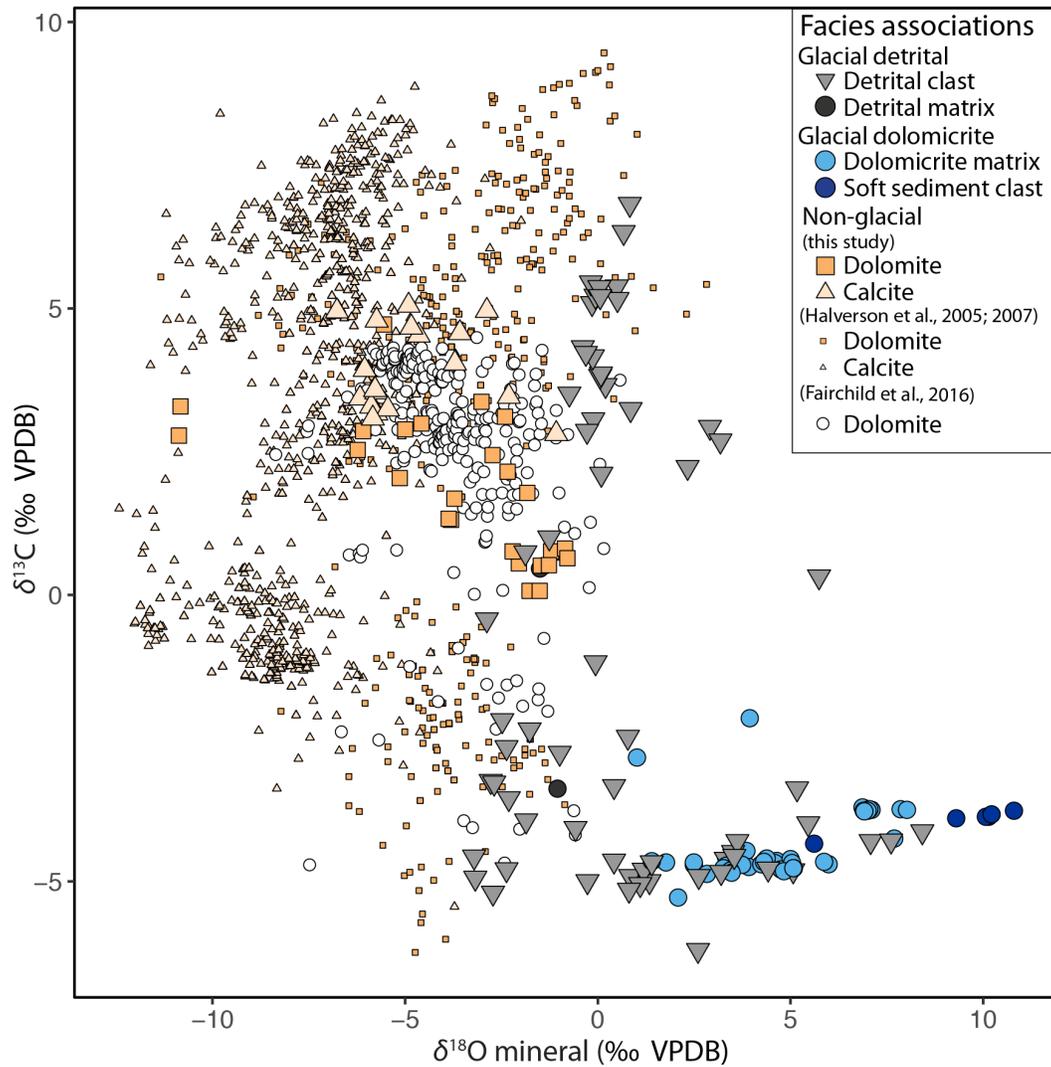


Figure S4. Cross plot of carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from the Tonian–Cryogenian in NE Svalbard, as in Figure 3 of the main text, but with the addition of pre-glacial Akademikerbreen Formation carbonates from Halverson et al. (2005; 2007) and interglacial dolomite from the MacDonaldryggen Formation (Fairchild et al., 2016).

Table S1. Summary of data collected in this study including stratigraphic context, mean crystal size, isotope results, and notes. (File uploaded separately)

Table S2. Full report of unknown and standard clumped isotope replicate results used in compilation of summary data. Table to be formatted for EarthChem and submitted upon manuscript acceptance. (File uploaded separately)

Table S3. Summary of XRD results. Approximate mineral percent quantities are provided where available; if no percentages provided, the mineral order signifies order of abundance.

Sample	mineral 1	mineral 2	mineral 3	mineral 4	mineral 5
PD5 0.5 A	dolomite				
	100%				
PD5 2.75 A	dolomite				
	100%				
PD5 16.0 A	calcite	quartz			
	88%	22%			
PD5 30.8 A	dolomite	quartz	clinochlore	albite	
	n/a	n/a	n/a	n/a	
PD5 35.0 A-A	dolomite	quartz	albite		
	47%	37%	16%		
PD5 36.0	dolomite	albite	quartz		
	50%	29%	21%		
PD5 38.0 B	albite	dolomite	quartz		
	44%	34%	22%		
PD5 40.9 A	quartz	pyrite	dolomite	goethite	albite
	n/a	n/a	n/a	n/a	n/a
PD5 42.2 A	dolomite	quartz	pyrite	clinochlore	
	n/a	n/a	n/a	n/a	
PD5 31.3 A	quartz	dolomite	albite	clinochlore	
	n/a	n/a	n/a	n/a	

PD5 45.0 A	dolomite	albite	quartz		
	62%	19%	19%		
PD5 49.5 A	quartz	dolomite	clinochlore		
	n/a	n/a	n/a		
PD5 76.9 a A	dolomite	quartz	clinochlore		
	n/a	n/a	n/a		
PD5 78 A	dolomite	quartz	clinochlore	cristobolite?	albite
	n/a	n/a	n/a	n/a	n/a
PD5 78 B	quartz	dolomite	clinochlore	kaolinite	
	n/a	n/a	n/a	n/a	
PD5 79 C DS1	dolomite	quartz	clinochlore		
	n/a	n/a	n/a		
PD5 79 B DS2	dolomite				
	100%				
F6975 A	dolomite	quartz			
	73%	27%			
PD5 45 B	dolomite	pyrolusite			
	95%	5%			
PD5 78 C	quartz	dolomite	albite	clinochlore	
	n/a	n/a	n/a	n/a	
PD5 78 D	quartz	dolomite	albite	clinochlore	
	n/a	n/a	n/a	n/a	
PD5 27.7 A	quartz	dolomite	calcite	albite	pyrite
	n/a	n/a	n/a	n/a	n/a

PD5 38.0 C	dolomite	quartz	albite		
	46%	44%	11%		

Sample Name	Mineralogy	Method	Stratigraphy	Section height (m)	Mean crystal size (µm)	d13C (‰ VPDB)	d18O (‰ VPDB)	Δ47 (‰ CDES25)	Δ47 SD	n	Temp (°C)	Fluid d18O (‰ VSMOW)	Notes
PD5-0_5	dolomite	XRD	Dartboard Dolomite Member	0.5	13.6	2.53	-6.23	0.541	0.018	5	73	1.2	
PD5-2_75-A	dolomite	XRD	Dartboard Dolomite Member	2.75	22.6	4.72	-5.55	0.533	0.024	5	77	2.5	
PD5-10_6A	calcite	Acid	Russøya Member	10.6	NA	4.53	-4.65	0.512	0.028	5	88	8.4	
PD5-16_0-A	calcite	XRD	Russøya Member	16	11.2	4.79	-5.74	0.499	0.028	5	95	8.3	Contains VSM
PD5-27_7-B	calcite	Acid	Russøya Member (vein)	27.7	NA	2.82	-7.57	0.454	0.005	4	122	9.8	
PD5-30_8-A	dolomite	XRD	Russøya Member	30.8	NA	3.11	-2.41	0.582	0.027	5	56	2.2	
PD5-32_95-A	dolomite	Acid	Russøya Member	32.95	NA	2.04	-5.14	0.541	0.02	4	73	2.3	Contains VSM
PD5-35A-A	dolomite	XRD	Russøya Member	35	NA	0.74	-1.12	0.593	0.026	5	52	2.8	
PD5-38_0B	dolomite	XRD	Russøya Member	38	11.3	0.55	-2.05	0.577	0.03	5	58	3	
PD5-39_5-A	dolomite	Acid	Russøya Member	39.5	NA	1.68	-3.72	0.578	0.026	5	57	1.1	
PD5-40_9-A	dolomite	XRD	Russøya Member	40.9	9.7	2.44	-2.73	0.598	0.02	5	49	0.7	Contains sulfate pseudomorphs
PD5-42_2-A	dolomite	XRD	Russøya Member	42.2	11.5	0.07	-1.77	0.6	0.022	5	49	1.6	
PD5-45-A	dolomite	XRD	Russøya Member	45	41.5	1.31	-3.81	0.569	0.032	5	61	1.7	Coarse dissolution and reprecipitation
PD5-49_5-A	dolomite	XRD	Russøya Member	49.5	29.2	0.07	-1.51	0.601	0.018	5	48	1.8	
PD5-76_8-B	dolomite	Acid	Petrovreen Member (dolomicrite)	76.8	2.7	-3.74	7.86	0.693	0.033	5	19	4.8	
PD5-76_8-C	dolomite	Acid	Petrovreen Member (dolomicrite)	76.8	NA	-3.75	8.02	0.648	0.016	4	32	8.2	
PD5-76_8-D	dolomite	Acid	Petrovreen Member (clast)	76.8	NA	-3.38	5.17	0.64	0.009	4	35	5.9	Laminated
PD5-76_9a-B	dolomite	Subsample of XRD	Petrovreen Member (dolomicrite)	76.9	NA	-3.74	6.99	0.677	0.012	4	23	5	
PD5-76_9a-C	dolomite	Subsample of XRD	Petrovreen Member (dolomicrite)	76.9	NA	-3.75	7.1	0.629	0.006	4	39	8.6	
PD5-76_9a-D	dolomite	Acid	Petrovreen Member (clast)	76.9	NA	-6.2	2.6	0.628	0.006	4	39	4.1	
PD5-78-A	dolomite	XRD	Petrovreen Member (dolomicrite)	78	NA	-4.25	7.69	0.681	0.017	3	23	5.5	
PD5-78-B	dolomite	Subsample of XRD	Petrovreen Member (soft sediment)	78	2	-4.34	5.61	0.644	0.017	4	34	6	
PD5-78-C	dolomite	XRD	Petrovreen Member (soft sediment)	78	2.8	-3.87	10.14	0.685	0.045	3	21	7.7	
PD5-78-F	dolomite	Acid	Petrovreen Member (clast)	78	NA	-4.91	0.84	0.616	0.015	4	43	3.1	Clotted
PD5-78E	dolomite	Subsample of XRD	Petrovreen Member (soft sediment)	78	NA	-3.87	10.07	0.624	0.01	4	40	12	
F7304-B	dolomite	Acid	Petrovreen Member (dolomicrite)	78.5	1.8	-4.7	5.99	0.623	0.042	5	41	7.9	Section height approximate; rhythmite
PD5-79_0-DS1-C	dolomite	XRD	Petrovreen Member (clast)	79	NA	-4.57	-3.21	0.578	0.012	3	58	1.7	Stromatolitic drop stone 1
PD5-79_0-DS2-B	dolomite	XRD	Petrovreen Member (clast)	79	NA	5.09	-0.15	0.6	0.02	3	49	3.3	Stromatolitic drop stone 2
PD5-79-DS1-B	dolomite	Subsample of XRD	Petrovreen Member (clast)	79	NA	-4.94	-3.18	0.567	0.02	5	62	2.5	Stromatolitic drop stone 1
PD5-79-DS2-A	dolomite	Subsample of XRD	Petrovreen Member (clast)	79	NA	5.22	-0.06	0.628	0.019	5	39	1.3	Stromatolitic drop stone 2
PD5-79-DS2-C	dolomite	Subsample of XRD	Petrovreen Member (clast)	79	NA	5.45	-0.18	0.601	0.009	4	49	3.2	Stromatolitic drop stone 2
F7318-A	dolomite	Acid	Petrovreen Member (dolomicrite)	79.5	3.5	-4.66	5.87	0.627	0.03	3	39	7.5	Section height approximate
F7318-B	dolomite	Acid	Petrovreen Member (dolomicrite)	79.5	NA	-5.28	2.08	0.613	0.02	4	44	4.6	Section height approximate
PD5-81-A	dolomite	Acid	Petrovreen Member (clast)	81	14.5	-3.25	-2.78	0.571	0.01	4	60	2.6	Fenestral; Fig. S3 C, clast 1
PD5-81-B	dolomite	Acid	Petrovreen Member (clast)	81	NA	3.66	0.2	0.592	0.008	4	52	4.2	Stromatolitic; Fig. S3 C, clast 2
F6975-A	dolomite	XRD	Petrovreen Member (dolomicrite)	87	2.2	-2.15	3.94	0.63	0.025	6	38	5.3	Section height approx.; analyzed in Fairchild (1983), homogeneous dolomicrite
F6975-B	dolomite	Subsample of XRD	Petrovreen Member (dolomicrite)	87	NA	-2.84	1.02	0.6	0.018	4	49	4.5	Section height approx.; analyzed in Fairchild (1983), altered dolomicrite
PD5-91	dolomite	Subsample of XRD	Petrovreen Member (detrital matrix)	91	NA	-3.38	-1.05	0.563	0.021	3	64	5	
PD5-91-B	dolomite	Acid	Petrovreen Member (clast)	91	12.4	-2.48	0.78	0.611	0.012	4	45	3.4	
PD5-91-C	dolomite	Acid	Petrovreen Member (clast)	91	NA	-2.66	-2.37	0.581	0.007	5	56	2.3	Clotted; Fig. S3 D, clast
PD5-91-D	dolomite	Acid	Petrovreen Member (detrital matrix)	91	NA	0.46	-1.5	0.588	0.02	5	53	2.7	
F7308-A	dolomite	Acid	Petrovreen Member (dolomicrite)	78.7	NA	-4.47	3.86	NA	NA	1	NA	NA	Section height approx.
PD5-00_25-A	dolomite	Acid	Dartboard Dolomite Member	0.25	NA	3.21	-5.78	NA	NA	2	NA	NA	
PD5-04_0-A	dolomite	Acid	Dartboard Dolomite Member	4	NA	2.99	-4.58	NA	NA	2	NA	NA	

PD5-04_5-A	dolomite	Acid	Dartboard Dolomite Member	4.5	NA	3.29	-10.83	NA	NA	2	NA	NA
PD5-04_5-B	dolomite	Acid	Dartboard Dolomite Member	4.5	NA	2.78	-10.87	NA	NA	1	NA	NA
PD5-04_5-C	dolomite	Acid	Dartboard Dolomite Member	4.5	NA	2.27	-9.05	NA	NA	2	NA	NA
PD5-04_5-float-A	calcite	Acid	Dartboard Dolomite Member	4.5	NA	3.43	-6.17	NA	NA	2	NA	NA
PD5-05_7-A	calcite	Acid	Russøya Member	5.7	NA	4.04	-3.71	NA	NA	2	NA	NA
PD5-06-A	dolomite	Acid	Russøya Member	6	NA	2.86	-6.09	NA	NA	1	NA	NA
PD5-07_2-A	calcite	Acid	Russøya Member	7.2	NA	3.17	-5.75	NA	NA	2	NA	NA
PD5-08_2-A	calcite	Acid	Russøya Member	8.2	NA	3.54	-5.75	NA	NA	2	NA	NA
PD5-08_5-A	calcite	Acid	Russøya Member	8.5	NA	3.29	-5.88	NA	NA	2	NA	NA
PD5-09-A	calcite	Acid	Russøya Member	9	NA	4.57	-3.58	NA	NA	2	NA	NA
PD5-10_0a-A	calcite	Acid	Russøya Member	10	NA	4.96	-2.88	NA	NA	2	NA	NA
PD5-10_0b-A	calcite	Acid	Russøya Member	10	NA	4.67	-4.84	NA	NA	1	NA	NA
PD5-10_5-A	calcite	Acid	Russøya Member	10.5	NA	3.24	-5.45	NA	NA	1	NA	NA
PD5-11_5-A	calcite	Acid	Russøya Member	11.5	NA	3.58	-5.78	NA	NA	2	NA	NA
PD5-14_7-A	calcite	Acid	Russøya Member	14.7	NA	4.95	-6.77	NA	NA	1	NA	NA
PD5-15_2-A	calcite	Acid	Russøya Member	15.2	NA	5.05	-4.91	NA	NA	2	NA	NA
PD5-19_0-A	calcite	Acid	Russøya Member	19	NA	3.93	-6.05	NA	NA	2	NA	NA
PD5-27_5-A	calcite	Acid	Russøya Member	27.5	NA	2.81	-1.08	NA	NA	2	NA	NA
PD5-27_5-B	calcite	Acid	Russøya Member	27.5	NA	3.46	-2.31	NA	NA	2	NA	NA
PD5-28_1-A	calcite	Acid	Russøya Member	28.1	NA	3.08	-5.84	NA	NA	2	NA	NA
PD5-30_8-B	dolomite	Acid	Russøya Member	30.8	NA	3.37	-3.02	NA	NA	1	NA	NA
PD5-31_3-A	dolomite	Acid	Russøya Member	31.3	NA	2.89	-5	NA	NA	1	NA	NA
PD5-35_0-A	dolomite	Acid	Russøya Member	35	NA	0.76	-1.21	NA	NA	1	NA	NA
PD5-36_0-A	dolomite	Acid	Russøya Member	36	NA	0.51	-1.48	NA	NA	1	NA	NA
PD5-38_0-B	dolomite	Acid	Russøya Member	38	NA	0.76	-2.21	NA	NA	1	NA	NA
PD5-38_0-C	dolomite	Acid	Russøya Member	38	NA	0.81	-0.85	NA	NA	1	NA	NA
PD5-38_0C	dolomite	Acid	Russøya Member	38	NA	0.64	-0.79	NA	NA	2	NA	NA
PD5-38_1-A	dolomite	Acid	Russøya Member	38.1	NA	1.78	-1.83	NA	NA	1	NA	NA
PD5-38-A	dolomite	Acid	Russøya Member	38	NA	0.52	-1.27	NA	NA	2	NA	NA
PD5-45_0-A	dolomite	Acid	Russøya Member	45	NA	1.33	-3.87	NA	NA	1	NA	NA
PD5-47_0-A	dolomite	Acid	Russøya Member	47	NA	2.15	-2.34	NA	NA	1	NA	NA
PD5-76_9a-A	dolomite	Acid	Petrovreen Member (dolomicrite)	76.9	NA	-3.71	6.87	NA	NA	2	NA	NA
PD5-76_9a-E01	dolomite	Acid	Petrovreen Member (dolomicrite)	76.9	NA	-3.75	7	NA	NA	1	NA	NA
PD5-76_9a-E02	dolomite	Acid	Petrovreen Member (dolomicrite)	76.9	NA	-3.74	7.05	NA	NA	1	NA	NA
PD5-76_9a-E03	dolomite	Acid	Petrovreen Member (dolomicrite)	76.9	NA	-3.77	6.9	NA	NA	1	NA	NA
PD5-76_9a-E04	dolomite	Acid	Petrovreen Member (dolomicrite)	76.9	NA	-3.77	7	NA	NA	1	NA	NA
PD5-76_9a-E05	dolomite	Acid	Petrovreen Member (dolomicrite)	76.9	NA	-3.78	6.92	NA	NA	1	NA	NA
PD5-76_9a-F	dolomite	Acid	Petrovreen Member (clast)	76.9	NA	-1.18	-0.06	NA	NA	1	NA	NA
PD5-76_9a-G	dolomite	Acid	Petrovreen Member (clast)	76.9	NA	-5	1.34	NA	NA	1	NA	NA
PD5-76_9a-H	dolomite	Acid	Petrovreen Member (clast)	76.9	NA	3.06	-0.12	NA	NA	1	NA	NA
PD5-76_9a-I	dolomite	Acid	Petrovreen Member (clast)	76.9	NA	-4.49	3.51	NA	NA	1	NA	NA
PD5-76_9b	dolomite	Acid	Petrovreen Member (clast)	76.9	NA	-4.8	1.19	NA	NA	1	NA	NA
PD5-78_0-D	dolomite	Acid	Petrovreen Member (clast)	78	NA	-4.72	3.4	NA	NA	2	NA	NA
PD5-78-A01	dolomite	Acid	Petrovreen Member (clast)	78	NA	-4.81	5.07	NA	NA	1	NA	NA
PD5-78-A05	dolomite	Acid	Petrovreen Member (clast)	78	NA	-5.05	1.1	NA	NA	1	NA	NA
PD5-78-A14	dolomite	Acid	Petrovreen Member (dolomicrite)	78	NA	-4.64	4.33	NA	NA	1	NA	NA
PD5-78-A16	dolomite	Acid	Petrovreen Member (dolomicrite)	78	NA	-4.7	3.69	NA	NA	1	NA	NA
PD5-78-A38	dolomite	Acid	Petrovreen Member (soft sediment)	78	NA	-3.77	10.8	NA	NA	1	NA	NA
PD5-78-A39	dolomite	Acid	Petrovreen Member (soft sediment)	78	NA	-3.83	10.22	NA	NA	1	NA	NA
PD5-78-B14	dolomite	Acid	Petrovreen Member (dolomicrite)	78	NA	-4.71	4.36	NA	NA	1	NA	NA
PD5-78-B16	dolomite	Acid	Petrovreen Member (dolomicrite)	78	NA	-4.78	3.4	NA	NA	1	NA	NA
PD5-78-B34	dolomite	Acid	Petrovreen Member (clast)	78	NA	-4.3	3.62	NA	NA	1	NA	NA

PD5-78-C23	dolomite	Acid	Petrobreen Member (clast)	78	NA	-3.99	5.46	NA	NA	1	NA	NA	
PD5-78-D	dolomite	Acid	Petrobreen Member (clast)	78	NA	-4.61	3.32	NA	NA	1	NA	NA	
PD5-78-E13	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.64	4.64	NA	NA	1	NA	NA	
PD5-78-E14	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.68	4.59	NA	NA	1	NA	NA	
PD5-78-E15	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.6	4.38	NA	NA	1	NA	NA	
PD5-78-E16	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.73	3.33	NA	NA	1	NA	NA	
PD5-78-E17	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.75	3.92	NA	NA	1	NA	NA	
PD5-78-E18	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.67	1.77	NA	NA	1	NA	NA	
PD5-78-E19	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.71	2.49	NA	NA	1	NA	NA	
PD5-78-E20	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.61	5	NA	NA	1	NA	NA	
PD5-78-F13	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.7	4.24	NA	NA	1	NA	NA	
PD5-78-F14	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.71	5.04	NA	NA	1	NA	NA	
PD5-78-F15	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.71	3.75	NA	NA	1	NA	NA	
PD5-78-F16	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.66	4.31	NA	NA	1	NA	NA	
PD5-78-F17	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.77	3.26	NA	NA	1	NA	NA	
PD5-78-F18	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.65	1.4	NA	NA	1	NA	NA	
PD5-78-F19	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.67	2.49	NA	NA	1	NA	NA	
PD5-78-G02	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.87	2.83	NA	NA	1	NA	NA	
PD5-78-G03	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.79	4.75	NA	NA	1	NA	NA	
PD5-78-G04	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.76	5.07	NA	NA	1	NA	NA	
PD5-78-G15	dolomite	Acid	Petrobreen Member (clast)	78	NA	-5.2	-2.72	NA	NA	1	NA	NA	
PD5-78-G30	dolomite	Acid	Petrobreen Member (clast)	78	NA	-4.78	4.42	NA	NA	1	NA	NA	
PD5-78-H02	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.81	3.44	NA	NA	1	NA	NA	
PD5-78-H03	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.68	5.04	NA	NA	1	NA	NA	
PD5-78-H04	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.77	5.09	NA	NA	1	NA	NA	
PD5-78-H28	dolomite	Acid	Petrobreen Member (clast)	78	NA	-4.3	7.08	NA	NA	1	NA	NA	
PD5-78-H29	dolomite	Acid	Petrobreen Member (clast)	78	NA	-4.13	8.42	NA	NA	1	NA	NA	
PD5-78-I02	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.85	3.47	NA	NA	1	NA	NA	
PD5-78-I03	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.82	4.83	NA	NA	1	NA	NA	
PD5-78-I04	dolomite	Acid	Petrobreen Member (dolomicrite)	78	NA	-4.77	5.07	NA	NA	1	NA	NA	
PD5-78-J15	dolomite	Acid	Petrobreen Member (clast)	78	NA	-4.56	3.54	NA	NA	1	NA	NA	
PD5-78-K34	dolomite	Acid	Petrobreen Member (clast)	78	NA	-4.29	7.61	NA	NA	1	NA	NA	
PD5-78-L33	dolomite	Acid	Petrobreen Member (clast)	78	NA	-4.64	0.42	NA	NA	1	NA	NA	
PD5-78-Z38	dolomite	Acid	Petrobreen Member (soft sediment)	78	NA	-3.9	9.3	NA	NA	1	NA	NA	
PD5-78b-A	dolomite	Acid	Petrobreen Member (clast)	78	NA	-2.35	-1.77	NA	NA	1	NA	NA	
PD5-78b-B	dolomite	Acid	Petrobreen Member (clast)	78	NA	-4.67	1.4	NA	NA	1	NA	NA	
PD5-78b-C	dolomite	Acid	Petrobreen Member (clast)	78	NA	-3.94	-1.86	NA	NA	1	NA	NA	
PD5-78b-E	dolomite	Acid	Petrobreen Member (clast)	78	NA	-4.84	3.2	NA	NA	1	NA	NA	
PD5-78b-F	dolomite	Acid	Petrobreen Member (clast)	78	NA	-4.91	2.62	NA	NA	1	NA	NA	
PD5-79-DS1-A	dolomite	Acid	Petrobreen Member (clast)	79	NA	-4.79	-2.37	NA	NA	2	NA	NA	
PD5-80b-A	dolomite	Acid	Petrobreen Member (clast)	80	NA	5.38	0.49	NA	NA	1	NA	NA	
PD5-80b-B	dolomite	Acid	Petrobreen Member (clast)	80	NA	5.16	0.51	NA	NA	1	NA	NA	

PD5-80b-C	dolomite	Acid	Petrovbreem Member (clast)	80	NA	-5	-0.27	NA	NA	1	NA	NA
PD5-80b-D	dolomite	Acid	Petrovbreem Member (clast)	80	NA	-5.15	0.81	NA	NA	1	NA	NA
PD5-80b-E	dolomite	Acid	Petrovbreem Member (clast)	80	NA	-3.28	-2.69	NA	NA	1	NA	NA
PD5-80b-F	dolomite	Acid	Petrovbreem Member (clast)	80	NA	2.11	0.09	NA	NA	1	NA	NA
PD5-80b-G	dolomite	Acid	Petrovbreem Member (clast)	80	NA	0.32	5.74	NA	NA	1	NA	NA
PD5-81b-A	dolomite	Acid	Petrovbreem Member (clast)	81	NA	3.82	0.06	NA	NA	1	NA	NA
PD5-81b-B	dolomite	Acid	Petrovbreem Member (clast)	81	NA	-4.07	-0.58	NA	NA	1	NA	NA
PD5-81b-C	dolomite	Acid	Petrovbreem Member (clast)	81	NA	4.32	-0.39	NA	NA	1	NA	NA
PD5-81b-D	dolomite	Acid	Petrovbreem Member (clast)	81	NA	2.86	-0.28	NA	NA	1	NA	NA
PD5-81b-E	dolomite	Acid	Petrovbreem Member (clast)	81	NA	2.93	2.91	NA	NA	1	NA	NA
PD5-81b-F	dolomite	Acid	Petrovbreem Member (clast)	81	NA	6.82	0.83	NA	NA	1	NA	NA
PD5-81b-G	dolomite	Acid	Petrovbreem Member (clast)	81	NA	-3.55	-2.31	NA	NA	1	NA	NA
PD5-81b-H	dolomite	Acid	Petrovbreem Member (clast)	81	NA	3.86	0.08	NA	NA	1	NA	NA
PD5-81b-I	dolomite	Acid	Petrovbreem Member (clast)	81	NA	4.16	-0.13	NA	NA	1	NA	NA
PD5-81b-J	dolomite	Acid	Petrovbreem Member (clast)	81	NA	-3.34	0.42	NA	NA	1	NA	NA
PD5-91-E	dolomite	Acid	Petrovbreem Member (clast)	91	NA	-0.43	-2.88	NA	NA	1	NA	NA
PD5-91-F	dolomite	Acid	Petrovbreem Member (clast)	91	NA	-2.19	-2.48	NA	NA	1	NA	NA
PD5-91-G	dolomite	Acid	Petrovbreem Member (clast)	91	NA	5.37	0.04	NA	NA	1	NA	NA
PD5-91-H	dolomite	Acid	Petrovbreem Member (clast)	91	NA	5.21	0.06	NA	NA	1	NA	NA
PD5-91-I	dolomite	Acid	Petrovbreem Member (clast)	91	NA	3.51	-0.74	NA	NA	1	NA	NA
PD5-91-J	dolomite	Acid	Petrovbreem Member (clast)	91	NA	0.74	-1.88	NA	NA	1	NA	NA
PD5-91-K	dolomite	Acid	Petrovbreem Member (clast)	91	NA	1	-1.26	NA	NA	1	NA	NA
PD5-91b-L	dolomite	Acid	Petrovbreem Member (clast)	91	NA	2.23	2.33	NA	NA	1	NA	NA
PD5-91b-M	dolomite	Acid	Petrovbreem Member (clast)	91	NA	3.24	0.85	NA	NA	1	NA	NA
PD5-91b-N	dolomite	Acid	Petrovbreem Member (clast)	91	NA	6.33	0.67	NA	NA	1	NA	NA
PD5-91b-O	dolomite	Acid	Petrovbreem Member (clast)	91	NA	4.22	-0.31	NA	NA	1	NA	NA
PD5-91b-P	dolomite	Acid	Petrovbreem Member (clast)	91	NA	2.69	3.18	NA	NA	1	NA	NA
PD5-91b-Q	dolomite	Acid	Petrovbreem Member (clast)	91	NA	-2.76	-0.99	NA	NA	1	NA	NA