

1 **Dolomitization in the Lower Ordovician Watts Bight Formation of the St Georges**
2 **Group, Western Newfoundland**

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17

18 **Abstract**

19 The Watts Bight Formation in western Newfoundland consists of a succession of shallow
20 water carbonates and has been extensively dolomitized. These dolomites occur as both
21 replacements and cements and are associated with complex changes in the rock porosity
22 and permeability. Early and pervasive replacement micritic dolomites (D1) are fine
23 grained and indicate that dolomitisation began during early stages of diagenesis. The $\delta^{18}\text{O}$
24 of the earliest (D1) dolomitizing fluids (-6.4 to -8.4‰ VSMOW) fall between the
25 estimated $\delta^{18}\text{O}$ values of the Tremadoc seawater and meteoric waters and suggest mixing-
26 zone dolomitization. Later-stage replacement dolomites (D2) are associated with
27 enhancement in porosity and permeability through the development of intercrystalline
28 pores, while latest stage saddle dolomite (D3) and late burial calcite cements significantly
29 occluded the pores in some horizons. Petrography, fluid inclusions and geochemistry
30 show that D2 and D3 dolomites formed from warm (65 to 125°C) saline (10 to 25 eq.
31 wt% NaCl + CaCl₂) hydrothermal fluids. The $\delta^{18}\text{O}_{\text{fluid}}$ of D2 ranges from -4.5 to 3.6 ‰
32 VSMOW and for D3 dolomites $\delta^{18}\text{O}_{\text{fluid}}$ ranges from 1.4 to 8.4 ‰ VSMOW, suggesting
33 an influx of basinal brines. D2 dolomite crystals are often coated by a bituminous
34 material which suggests either possible hydrocarbon charge after D2 dolomitisation or
35 some local forced thermal maturation of organic matter.

36 The occurrence of high porosity associated with D2, combined with the laterally sealing
37 tight limestone beds, presence of favourable source rocks and thermal maturation, may
38 suggest that the Watts Bight carbonates are possible potential hydrocarbon reservoirs and
39 suitable targets for future hydrocarbon exploration in Western Newfoundland.

40 **1. Introduction**

41 Hydrothermal dolomite (HTD) hydrocarbon reservoirs have been recognised as an
42 important exploration target and are major hydrocarbon producers in North America (e.g.,
43 Davies and Smith 2006). This is because HTD reservoirs typically retain porosity and
44 permeability much better than precursor limestones. Recently, dolostones including
45 hydrothermal dolomites in the lower Paleozoic rocks of eastern Canada and the United
46 States have been the focus of a number of studies (e.g., Cooper et al. 2001; Lavoie et al.
47 2005; Lavoie and Chi 2006; Smith 2006; Azmy et al. 2008). A number of factors point
48 towards the hydrocarbon prospectivity of the Lower Ordovician St. George Group,
49 Western Newfoundland, including the proximity of mature sources rocks (organic rich
50 shales in the Green Point Formation) and impermeable cap rocks (Table Point Formation)
51 and the successful drilling of the Port au Port #1 well in 1995 (Fowler et al. 1995; Cooper
52 et al. 2001). In early 2007 extended testing from the reservoir in the upper part of the St.
53 George Group, by Canadian Imperial Venture Corporation, resulted in the production of
54 high API (50-56°) oil (315 barrels per day) and significant volume of natural gas (10^6 ft³/
55 day).

56 The current study is focused on the Watts Bight Formation in the St. George Group,
57 which is of particular interest for hydrocarbon exploration as it is extensively dolomitized
58 and associated with significant porosity development (up to 30%; Cooper et al. 2001).
59 The main objectives of this study are: (1) to identify and characterize (petrographically
60 and geochemically) the dolomitization phases in the Watts Bight Formation; and (2) to
61 investigate the origin and nature of the dolomitizing fluids of each phase to understand
62 the diagenetic controls on porosity development and distribution. The results build upon

63 previously published data from the overlying Aguathuna and Boats Harbour Formations
64 (Azmy et al. 2008, in press) and will contribute to predictive models of the porosity
65 distribution in offshore and deeply buried onland counterparts

66 **2. Geological setting**

67 The Lower Paleozoic shelf rocks form part of the outer domain of the Humber zone in
68 Western Newfoundland, the westernmost of five tectono-stratigraphic zones in the
69 Canadian Appalachians (Fig. 1; Williams 1979). The evolution of these rocks during the
70 Lower Paleozoic has been discussed by several authors and summarized by Cooper et al.
71 (2001). Significant rifting, associated with the opening of the Iapetus Ocean, began
72 during the Late Proterozoic and Early Cambrian (Waldron and van Staal 2001; van Staal
73 2005) and is first recorded in Western Newfoundland by late Proterozoic, fault-bounded,
74 terrestrial clastics and volcanics of the lower Labrador Group. These deposits were
75 separated by a 90 million year hiatus from unconformably overlying clastic rocks of the
76 late Early Cambrian, upper Labrador Group (James et al. 1989). These mixed clastic-
77 carbonate sediments were overlain by a thick (1.5 km) Middle Cambrian to Lower
78 Ordovician carbonate platform succession, deposited on a passive margin to the south of
79 Laurentia. The Middle to Late Cambrian Port au Port Group is a narrow, high-energy
80 carbonate platform which evolved into a wide, low-energy carbonate platform
81 represented by the Early to Middle Ordovician St. George Group (James et al. 1989). A
82 regional unconformity, the St. George Unconformity, marks the top of the St. George
83 Group and a shift from a passive margin to a foreland basin (Knight et al. 1991). The St.
84 George Group is overlain by shelf carbonates of the Middle Ordovician Table Head
85 Formation (Stenzel et al. 1990), which were deposited in the foreland basin where they

86 are sporadically overlain by deep water carbonates and shales of the Table Cove
87 Formation (Stenzel et al. 1990).

88 The Ordovician St. George Group forms a sequence of subtidal and peritidal limestones
89 and dolostones and is widely exposed in western Newfoundland. The succession is
90 subdivided, in ascending order, into the Watts Bight, Boat Harbour, Catoche and
91 Aguathauna Formations (Fig. 2; Knight and James 1987) and represents at least two
92 sequences of Tremadoc and Arenigian age, termed megacycles by Knight and James
93 (1987). Each of these megacycles consists of a thin lower peritidal layer, a thick middle
94 subtidal layer and a thick upper peritidal layer (Knight and James 1987).

95 The Watts Bight Formation overlies the largely dolomitized peritidal carbonates of the
96 Upper Cambrian to Lower Ordovician Berry Head Formation of the Port au Port Group
97 (Knight et al. 2008) . It has been mapped throughout western Newfoundland (Knight and
98 James 1987) and is extensively dolomitized in many areas (Knight et al. 2008). On the
99 western shore of Isthmus Bay (Fig. 1), Port au Port Peninsula, a continuous ~69m section
100 of the formation (Fig. 2), described in detail by Knight et al. (2008), consists of two
101 sequences of low-energy bioturbated and mound carbonates overlain by higher energy
102 facies associations of mounds and grainstones. Knight et al. (2008) considered that these
103 sequences represented transgression and drowning of a shallow shelf, followed by
104 gradual accretion into the tidal zone.

105 At Isthmus Bay, dolomitization of the Watts Bight Formation is extensive particularly in
106 the lower and middle members where sucrosic dolostones replace both bioturbated and
107 thrombolitic limestone (Knight et al. 2008). These dolostones are dark-grey, fine to
108 medium grained and commonly have a strong condensate smell. Porosity is locally

109 developed in these dolostones, particularly is a section of dolomitized grainstones from
110 the top of the middle member and in a thrombolitic dolostone ~12m above the base of the
111 formation.

112 **3. Methodology**

113 The Isthmus Bay section was sampled approximately at intervals of ~ 2m (\pm 0.5m) and a
114 total of forty three (43) samples were collected from the Watts Bight Formation. In
115 addition, five samples were collected from the underlying Berry Head Formation of the
116 Port au Port Group. Samples were analysed following the procedure outlined in detail by
117 Azmy et al. (2008). In total 48 stained (Alizarin Red S-potassium ferricyanide; Dickson
118 1966) conventional thin sections were examined using transmitted light microscopy and
119 cathodoluminescence (CL). Permeability was measured in selected dolomite samples
120 using a computer controlled steady state permeameter (Temco Model MP-401).

121 Microthermometric fluid-inclusion analyses were performed using a Linkam THMSG600
122 heating-freezing stage. Calibration with precision of \pm 0.2°C at -56.6°C and \pm 1°C at
123 300°C was conducted using synthetic H_2O and CO_2 fluid inclusion standards. Salinities
124 were calculated using a program by Chi and Ni (2006) for the system of H_2O - NaCl - CaCl_2 .
125 A polished mirror-image slab of each thin section was also prepared for microsampling.

126 For C and O isotope analyses approximately 220 μg of powder sample was reacted in an
127 inert atmosphere with ultrapure concentrated (100%) orthophosphoric acid at 70°C in a
128 Thermo Finnigan Gasbench II and the produced CO_2 was automatically delivered to the
129 source of a Thermo Finnegan DELTA V plus isotope ratio mass spectrometer in a stream
130 of helium, where the gas was ionized and measured for isotope ratios. Precision of the
131 data is better than $\pm 0.1\%$ for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ ratios. For major and trace element

132 analyses ~ 4mg of sample powder was digested in 2.5% (v/v) pure H₃PO₄ acid for 70-80
133 minutes and analysed for Ca, Mg, Sr, Fe and Mn (Coleman et al. 1989) using a
134 HP4500plus inductively coupled plasma – mass spectrometer (ICP-MS). The relative
135 uncertainties of these measurements are less than 5%.

136 Based on petrographic examination representative samples of dolomite were selected for
137 Sr-isotope analysis at the at the Institut für Geologie, Mineralogie und Geophysik, Ruhr
138 Universität, Bochum, Germany, following the procedures outlines in Azmy et al. (2008).
139 The ⁸⁷Sr/⁸⁶Sr measurements were normalized to NBS 987 values bracketing the samples
140 (0.710247) and corrected for deviation from value stated by McArthur (1994).

141 **4. Results**

142 **4.1. Petrography**

143 Based on petrography and CL, three distinct dolomitization events have been recognized.
144 In addition, late-stage calcite diagenetic cementation phases and other diagenetic features
145 (i.e. stylolites, sulphides and silicification) were described.

146 *Micritic algae, limemud and early calcite cements*

147 Micritic limemud (C1) was generally observed in limestone and dolomitic limestone
148 samples. Limestones consist of peloidal and intraclastic micrite aggregates, with a
149 micritic matrix or very fine-grained limemuds. Rarely skeletal grains (brachiopods and
150 crinoids) are preserved, these are invariably replaced by coarser grained (100 to 300µm)
151 anhedral Fe-poor calcite. In addition early calcite cement has been recorded in some of
152 the interparticular pores (C2).

153 *First dolomite*

154 The first dolomite (D1) recognized in the samples is characterized by a fine-grained (< 25
155 to 50µm) crystals replacing C1 in dolomitic limestones (Fig. 3a). D1 commonly replaced
156 sedimentary laminations and peloidal and intraclastic micrite aggregates and consists of
157 tightly packed anhedral to subhedral rhombs with no visible intercrystalline porosity.

158 *Second dolomite*

159 A later phase of dolomites (D2) postdates D1, and comprises two sub-populations of
160 dolomite replacement, designated D2a and D2b (Fig. 3b). D2a dolomite rhombs range in
161 size from 40 to 150µm, are anhedral to subhedral and exhibit a dull luminescence under
162 cathodoluminescence. Intercrystalline porosity in D2a is commonly low (<1%).

163 D2b dolomite is coarser grained than D2a (50 to 300µm) and rhombs are euhedral to
164 subhedral with planar boundaries and an idiomorphic texture. D2b dolomite rhombs often
165 show conspicuous zoning, with inclusion rich cores and inclusion poor rimes. D2b
166 dolomite is associated with a significant increase in porosity (up to 7% intercrystalline
167 porosity) and permeability (up to 16 md) although some of these pores are often filled by
168 later diagenetic dolomite and calcite. Under CL, D2b dolomite displays a dull red
169 luminescence, and commonly shows compositional zoning (Fig. 3e-f). When viewed
170 under ultraviolet (UV) light, D2b rhombs showed yellow/dull luminescence zoning. D2a
171 and D2b dolomite rhombs are also commonly coated by bituminous organic material.

172 *Third dolomite*

173 The latest void-filling dolomite (D3) occurs in previously uncemented pores and/or
174 fractures. The D3 dolomite is relatively rare and consists of dolomite rhombs, which are
175 euhedral to subhedral and range in size from 100 to 400µm. It usually displays undulose

176 extinction and commonly has non-planar boundaries, features typical of saddle dolomite
177 (Warren, 2001). D3 dolomite displays a uniform red fluorescence under CL.

178 *Other diagenetic features*

179 D2 dolomite is both crosscut and bounded by high amplitude microstylolites, which
180 postdate the early burial diagenesis. A translucent, coarse blocky calcite cement (C3) is
181 common and fills pores and fractures still open after D3 precipitation (Fig. 3c). C3 calcite
182 ranges in size from 50 to 400 μ m and both Fe-poor and Fe-rich calcite has been recorded.
183 Under CL, it shows a uniform bright yellow luminescence. In addition rare pore-filling
184 sphalerite and micro-quartz have been recorded.

185 **4.2. Fluid inclusion analysis**

186 Fluid inclusions were examined in D2 and D3 dolomite and C3 calcite and
187 microthermometric data is summarized in Table 1. The fluid inclusions in dolomite (D2
188 and D3) were hosted in clusters in the core of dolomite crystals or in discrete zones
189 within dolomite rhombs, and inclusions were commonly elongate in the direction of
190 growth (Fig. 4a). Inclusions in C3 calcite were found in clusters in the core of crystals
191 and can be very large with respect to their host crystals (up to 50 μ m; Fig. 4b). Therefore
192 inclusions in dolomite and calcite are considered primary in origin and represent samples
193 of fluid trapped during growth (Goldstein 2003).

194 *D2 dolomite*

195 Fluid inclusions in D2a and D2b dolomite are biphasic and range in size from 2 to 20 μ m.
196 Homogenization temperatures (T_h), representing the minimum estimates of entrapment
197 temperatures, ranged from 44.6 to 108.6 $^{\circ}$ C (average of 81.8 $^{\circ}$ C \pm 14.2 $^{\circ}$ C; Figs. 5 and 6),
198 with no significant variations recorded between inclusions hosted in the cores and rims of

199 D2b crystals. The initial melting temperatures (T_i) ranged from -55.2 to -51.3°C (Table
200 1), corresponding to the eutectic temperature for the $H_2O-NaCl-CaCl_2\pm MgCl_2$ system
201 (Shepherd et al. 1985). Hydrohalite melting ($T_m(\text{hydrohalite})$) occurred between -39.1°C
202 and -31.9°C yielding X_{NaCl} values of between 0.14-0.28. Ice melting temperatures
203 ($T_m(\text{ice})$) ranged from -25 to -6.2°C, giving a wide range of fluid salinities (10.1 to 23.3
204 eq. wt% NaCl + CaCl₂; Fig. 6).

205 *D3 dolomite*

206 The fluid inclusions in D3 dolomite are biphasic and range in size from 2 to 10µm.
207 Inclusions homogenize (T_h) to the liquid phase between 91.4 and 130.1°C (114°C ±
208 13.3°C; Figs. 5 and 6). Initial ice melting temperatures (T_i) of -52 to -50.2°C indicate the
209 presence of $CaCl_2 \pm MgCl_2$. $T_m(\text{hydrohalite})$ of -31.5 to -30.2 was used to calculate X_{NaCl}
210 of 0.29 to 0.34. $T_m(\text{ice})$ ranged from -14.7 to -21.3°C, with calculated salinities from 17.8
211 to 21.7 eq. wt% NaCl + CaCl₂.

212 *C3 calcite*

213 Fluid inclusions in C3 calcite display a wide range of size (2 to 50µm) and degree of fill
214 (0.6 to 0.95) and a large number of inclusions show evidence of post-entrapment leaking
215 and/or stretching (e.g. microfractures at edge of inclusions: Fig. 4b). Care was taken only
216 to record microthermometric data from inclusions which displayed small T_h variations
217 within an individual inclusion group (e.g. a cluster), usually less than 10°C, suggesting
218 that post-entrapment effects are not important (Goldstein and Reynolds 1994). T_h values
219 range from 68 to 126.7°C (average of 94.1 ± 17.3°C; Fig. 5). T_i ranged from -55.2 to -
220 51°C (close to the eutectic temperature of the $H_2O-NaCl-CaCl_2\pm MgCl_2$). Hydrohalite
221 melting occurred between -26.1°C and -34.6°C yielding X_{NaCl} values of between 0.22-

222 0.54. $T_m(\text{ice})$ occurred between -14.7 and -20.1°C corresponding to salinities ranging
223 between 17.9 to 21 eq. wt% $\text{NaCl} + \text{CaCl}_2$.

224 **4.3. Carbon and oxygen isotopes**

225 The carbon and oxygen isotopic compositions of calcite and dolomite analysed are
226 summarized in Figure 7 and Table 2. Because C1 and C2 were inseparable by
227 conventional microdrilling, they are reported indistinctively and great care has to be taken
228 in interpreting the data.

229 *Calcites*

230 Twelve analyses of C1/C2 calcite from the Watts Bight Formation yielded $\delta^{13}\text{C}$ values
231 from -1.3 to -2.2‰ and $\delta^{18}\text{O}$ values of -7.4 to -8.4‰ . The C3 cement was analysed from
232 four samples and gave $\delta^{13}\text{C}$ values of -1.5 to -5.1‰ and $\delta^{18}\text{O}$ values of -7 to -8.5‰ .

233 *Dolomites*

234 Two samples of D1 were collected from dolomitic limestones and gave $\delta^{13}\text{C}$ values of $-$
235 1‰ and $\delta^{18}\text{O}$ values of -5.5 to -6.3‰ . Fourteen D2a and twelve D2b dolomite samples
236 yield very similar carbon and oxygen isotope values (Fig. 7, Table 2) with $\delta^{13}\text{C}$ values of
237 -0.6 to -1.9‰ and $\delta^{18}\text{O}$ values of -5.5 to -11.4‰ . Three analyses of D3 dolomite gave
238 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values ranging from -1 to -2.1‰ , and -5.6 to -9.6‰ , respectively.

239 **4.4. Strontium isotopes**

240 A single sample of D1 dolomite yielded an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.709283 ± 0.000007 (Fig 8;
241 Appendix A). The range of $^{87}\text{Sr}/^{86}\text{Sr}$ for D2 dolomite is between 0.709106 ± 0.000007
242 and 0.708953 ± 0.000007 and the D3 dolomite yielded values (0.709075 ± 0.000007 to
243 0.7091 ± 0.000007) (Fig. 8; Appendix A).

244 **4.5. Major and trace element geochemistry**

245 The distribution of major and trace elements in calcite (C1/C2, C3) and dolomite (D1,
246 D2, D3) from the Watts Bight Formation is summarized in Table 2. C1/C2 calcite is
247 characterized by Sr concentrations of 319 ± 50 ppm and low Mn and Fe values ($168 \pm$
248 82 ppm and 64 ± 23 ppm, respectively). Dolomites from the Watts Bight Formation had
249 Ca concentrations ranging from 64.1 to 54.2%. D1 dolomites had similar Sr contents to
250 C1 (257ppm) but were relatively enriched in Fe (1323ppm) and Mn (96ppm). Compared
251 to early diagenetic phases (C1/C2 and D1), Sr concentrations were significantly depleted
252 (< 200 ppm) in later dolomite and carbonate phases (D2a, D2b, D3, C3). Mn
253 concentrations were relatively constant between D2a, D2b and D3 (63 ± 14 ppm, $69 \pm$
254 20 ppm and 59 ppm respectively). .

255 **5. Discussion**

256 In the following section, petrographic and geochemical observations and data are
257 presented in order to support our contention that hydrothermal fluids (e.g., fluids having
258 temperature at least 5°C higher than ambient formation temperature; White 1957; Smith
259 and Davies 2006) circulated in the Watts Bight Formation and are responsible for most of
260 the dolomite observed in the unit.

261 **5.1 Dolomite petrography**

262 Dolomite 1 (D1) is fabric retentive dolomicrite, which commonly replaces early micrite
263 and micritic peloids and intraclasts (C1) and it appears dull to non luminescent under
264 luminescope. It predates all other dolomite generations and stylolites and was most likely
265 formed during the early diagenetic history prior to significant burial and compaction.
266 Dolomite 2 (D2) includes 2 subphases, D2a and D2b, and is crosscut by and associated
267 with microstylolites, which is consistent with dolomitization likely during shallow to

268 intermediate burial (e.g., Azmy et al., 2008). D2 dolomites are also often coated by a
269 bituminous material which suggests that hydrocarbons migrated in pore space after D2
270 dolomitization.

271 Petrographic studies of the Watts Bight dolomites have shown that early diagenetic
272 dolomitization (D1) led to a low porosity end-product (< 1%), whereas significant
273 intercrystalline porosity (up to 7%) resulted from D2b dolomitization (Appendix A), as
274 has been recorded from other successions in the St. George Group (Azmy et al. 2008, in
275 press). This may indicate that early shallow dolomitization was extensive and occurred
276 under open-system conditions with the circulation of a large volume of dolomite-
277 saturated diagenetic fluids, so that no open pores were preserved. On the contrary, the
278 higher intercrystalline porosity and non-stoichiometric nature of D2b dolomites is
279 consistent with dolomitization of limestones under relatively closed-system conditions
280 with a much lower fluid/rock ratio and a limited local supply of Mg^{2+} and CO_3^{2-} ions, as
281 dolomite has a lower molar volume than calcite or aragonite (Warren 2000). The lower
282 porosity associated with D2a dolomite may reflect the replacement of D1 dolomite,
283 where no volume reduction would be expected.

284 A large number of intercrystalline pores in D2 dolomite have been occluded by D3
285 dolomite and C3 calcite (Fig. 4c, e, f), reducing the effective porosities of these early
286 hydrothermal dolomites. However Knight et al. (2008) recognized two intervals at
287 Isthmus Bay with increased intercrystalline and vuggy porosity. The upper porous
288 interval is a dolomitized, crossbedded grainstone at the top of the middle member
289 (porosity of 4 to 5%; Appendix A) and the lower porous interval is a thrombotic
290 boundstone dolomite ~12m above the base of the formation (porosity of ~7%; Appendix

291 A). Permeability measurements from selected dolomites (Appendix A) show that
292 permeability in the upper porous interval is low (<2 mD) and is similar to permeability in
293 other non-porous dolomites. However the lower porous interval is characterized by much
294 higher permeability (10 to 16 mD), indicating a higher degree of interconnectivity
295 between intercrystalline pores in D2b dolomite from this horizon. Cooper et al. (2001)
296 reported similar high porosity and high permeability horizons associated with
297 hydrothermal dolomites in the Watts Bight Formation from a series of exploration wells
298 around Port au Port peninsula. Although there is no evidence that these porous horizons
299 are laterally continuous this demonstrates that significant and preserved porosity can be
300 associated with dolomites throughout the Watts Bight Formation.

301 **5.2 Fluid inclusion data**

302 There is an increase in the average homogenization temperature (T_h) of primary fluid
303 inclusions from D2 dolomite ($81.8 \pm 14.2^\circ\text{C}$) to D3 dolomite ($114 \pm 13.3^\circ\text{C}$). This is
304 consistent with an increase in burial depth during dolomitization and/or hydrothermal
305 fluid influxes resulting in high temperature dolomitization. Maximum burial temperatures
306 of 75°C have been estimated from conodont alteration indices (CAI), acritarch alteration
307 indices (AAI) and graptolite reflectance data from the Lower Ordovician rocks of the Port
308 au Port peninsula (Nowlan and Barnes 1987; Williams et al. 1998). Although the
309 interpretation of this data is not straightforward (Williams et al. 1998) it suggests that
310 most of the dolomitization in the Watts Bight Formation likely proceeded from fluids at
311 temperature significantly higher than formation temperature at the time of alteration and,
312 by commonly accepted definition, can be designated as hydrothermal. In the absence of
313 local igneous intrusions, the most likely source of these hydrothermal fluids is from the

314 upwelling of basinal fluids from depth along extensional to transtensional faults and
315 fractures (Davies and Smith 2006). Basin modelling of Cambrian and Ordovician
316 successions in western Newfoundland have predicted that fault footwalls became the foci
317 for dolomitizing fluids (Cooper et al. 2001) and this is similar to Ordovician
318 hydrothermal dolomites elsewhere in eastern Canada (Lavoie et al. 2005; Lavoie and Chi
319 in press) and the northeastern United States (Smith 2006). Fluid inclusions in C3 calcite
320 are characterized by homogenization temperatures that are higher than maximum burial
321 temperatures (94.1 ± 17.3) but lower than T_h from D3 dolomite, the late carbonate
322 cementation is likely associated with slighter cooler hydrothermal fluid influxes after
323 dolomitization of the Watts Bight Formation, possibly after a relative tectonic uplift.

324 Primary inclusions in D2 dolomite have a wide range of salinities (9.5 to 25.6 eq. wt%
325 NaCl + CaCl₂; Fig. 6) over a narrow temperature range, indicative isothermal mixing
326 between two end member fluids of contrasting salinities (Shepherd et al. 1985). The low
327 salinity fluid may represent residual meteoric fluids, seawater or low salinity groundwater
328 in interstitial pore space. The high salinity fluid most likely represents basinal brines
329 which circulated through the basin along faults and fractures. In the absence of significant
330 volume of evaporite deposits in the Cambrian and Ordovician rocks of western
331 Newfoundland, the origin of these high salinity brines is largely unknown as is common
332 in structurally-controlled hydrothermal dolomite (Davies and Smith 2006). No discernible
333 relationship between T_h values and calculated salinities was recorded in D3 or C3 hosted
334 inclusions.

335 **5.3 Carbon and oxygen isotope data**

336 The $\delta^{13}\text{C}$ data from C1/C2 calcite (Fig.7) show a narrow range of values (-0.3 to -2.2‰).
337 These values are within the range of $\delta^{13}\text{C}$ values for the best preserved carbonates
338 precipitated from Tremadoc seawater (0.0 to -2.5‰; Shields et al. 2003) and indicate that
339 C1/C2 calcite preserves its Carbon isotope signature. Carbon isotope signatures from D1,
340 D2 and D3 dolomite overlap those of C1 calcite (-0.6 to -2.1‰), reflecting the low CO_2
341 content of the dolomitizing waters in sedimentary basins (Land 1992), as such, the early
342 to late dolomitization of the Watts Bight Formation occurred in a largely rock-buffered,
343 closed diagenetic system.

344 The $\delta^{18}\text{O}$ of D1, D2 and D3 dolomites likely reflect the Oxygen isotopic composition of
345 the dolomitizing fluids since dolomitization involves large volumes of waters to provide
346 the Mg needed for the process. Therefore, the $\delta^{18}\text{O}$ of dolomites can be used to calculate
347 the isotopic signature of the dolomitizing fluid ($\delta^{18}\text{O}_{\text{fluid}}$) and constrain the origin of these
348 fluids. The $\delta^{18}\text{O}_{\text{fluid}}$ can be estimated using the equation of Land (1983), providing that
349 the temperature of dolomitization can be obtained from the fluid inclusion
350 homogenization temperatures. The dolomicritic grain size and fabric retention of D1
351 suggest formation at near surface temperature (<50°C) likely around 25°C (e.g., Budd,
352 1997; Warren, 2000; Azmy et al., 2001; 2008). Therefore, $\delta^{18}\text{O}_{\text{D1}}$ of -5.5 to -6.3‰ may
353 suggest a parent fluid having $\delta^{18}\text{O}_{\text{fluid}}$ of -6.4 to -8.4‰ VSMOW (Vienna Standard Mean
354 Ocean Water) (Fig. 9). The micritic lime mudstones and other depositional facies in the
355 Watts Bight sediments indicate tropical shallow shelf water conditions. In similar
356 present-day environments the $\delta^{18}\text{O}$ of seawater is $\sim 0\text{‰}$ and that of meteoric water is
357 depleted by $\sim 4\text{‰}$ (Clark and Fritz 1997). The documented $\delta^{18}\text{O}$ of the best preserved
358 primary calcite precipitated from the Tremadoc seawater during the deposition of the

359 Watts Bight carbonates is estimated at $\sim -9.8\text{‰}$ (Veizer et al. 1999; Shields et al. 2003),
360 which translate to $\delta^{18}\text{O}_{\text{seawater}}$ of a warm (20 to 25°C) tropical zone of $\sim -6.3\text{‰}$ VSMOW
361 (Shields et al. 2003). Assuming that the relationship between the $\delta^{18}\text{O}$ of Tremadoc
362 meteoric and seawaters were similar to those of our present day environment, the $\delta^{18}\text{O}$ of
363 meteoric fluids were likely about -10.3‰ VSMOW. The calculated $\delta^{18}\text{O}$ values (-5.5 to $-$
364 6.3‰ VSMOW) of the dolomitizing fluids of D1 (Fig. 9) seems to plot between the
365 estimated $\delta^{18}\text{O}$ of the Tremadoc sea and meteoric waters (-6.3 and -10.3‰ VSMOW,
366 respectively) and likely indicate a mixing zone model for early dolomitization as has been
367 suggested for early dolomitization elsewhere in the St. George Group (e.g., Azmy et al.,
368 2008, in press). This is also consistent with the low Sr contents in D1 (257 ppm) and the
369 lack of evaporites deposits that do not support an evaporated brine origin as was believed
370 by earlier studies (e.g., Lane, 1990).

371 Using the homogenization temperatures (estimates of minimum entrapment temperatures)
372 recorded from primary fluid inclusions in D2 and D3 dolomites as proxies for
373 temperature of dolomitization, the $\delta^{18}\text{O}_{\text{fluid}}$ has been calculated (Fig. 9). For D2 dolomite
374 $\delta^{18}\text{O}_{\text{fluid}}$ ranges from -4.5 to 4.7‰ VSMOW and for D3 dolomites $\delta^{18}\text{O}_{\text{fluid}}$ range from
375 1.4 to 8.4‰ VSMOW. These values are much higher than would be expected from
376 seawater or meteoric fluids and are consistent with dolomitization associated with an
377 influx of basinal brines, which are commonly enriched in $\delta^{18}\text{O}$ (Goldstein and Reynolds
378 1994). The slightly lower $\delta^{18}\text{O}$ calculated for D2 dolomites may represent mixing of these
379 brines with $\delta^{18}\text{O}$ depleted residual meteoric fluids as was suggested by the wide scatter of
380 fluid inclusion salinity data.

381 **5.4 Strontium isotope data**

382 The $^{87}\text{Sr}/^{86}\text{Sr}$ value of the earliest D1 dolomite is close to that of early Ordovician
383 (Tremadocian) seawater (Fig. 8; Shields et al. 2003). The Sr isotopic signature of
384 replacive dolomite usually reflects the Sr isotopic signature of the precursor carbonate
385 phase (Banner 1995) and this suggests that fabric retentive D1 dolomites preserve the
386 primary signature of their precursor carbonates. The $^{87}\text{Sr}/^{86}\text{Sr}$ values are also supportive
387 of a largely rock-buffered early dolomitization as suggested from $\delta^{13}\text{C}$ ratios. Our limited
388 dataset of $^{87}\text{Sr}/^{86}\text{Sr}$ signatures for D2 and D3 dolomite indicate significant overlap with
389 both D1 and the accepted value for Tremadocian seawater (Fig. 8). This indicates the lack
390 of significant interaction between the dolomitizing fluid with any feldspar (Rubidium)-
391 rich unit (crystalline basement or sandstone). This observation is again supportive of our
392 contention of a largely rock-dominated diagenetic system with the ultimate source of the
393 radiogenic strontium being Tremadocian limestones altered through circulation of the
394 hydrothermal fluid. This scenario is consistent with previous studies of dolomitization in
395 stratigraphically younger units of the St. George Group (Azmy et al. 2008, in press) but
396 strongly differs from the more open diagenetic conditions recorded from the largely
397 coeval Romaine Formation from nearby Anticosti Island (Lavoie et al. 2005; Lavoie and
398 Chi, in press).

399 **5.5 Major and trace element geochemistry**

400 The major element geochemistry of Watts Bight Formation dolomites (Appendix 1, Table
401 2) show that all dolomites (D1 to D3) are non-stoichiometric and Ca-rich (Ca
402 concentrations range from 64.1 to 54.2%). No trends of increasing stoichiometry in
403 hydrothermal dolomites from D2a (early) to D3 (late) has been observed, as would be
404 expected for dolomites formed in open diagenetic systems and continuing dissolution and

405 re-precipitation (Sperber 1984; Montanez and Read 1992). Non-stoichiometric
406 dolomitization indicate formation in a relatively close and rock-buffered diagenetic
407 systems characterized by low volumes of fluid throughout (Sperber 1984; Kirmaci and
408 Akdag 2005).

409 With the exception of early D1 dolomite (Sr concentration = 257ppm), the Sr
410 concentration of later dolomites are low (101 ± 59 ppm). These values are lower than
411 would be expected from dolomites associated with hypersaline waters (<550ppm; Tucker
412 and Wright 1990) and likely suggests that dolomitizing fluids were modified seawater
413 that circulated in the sedimentary basin. The relative higher Sr concentrations in D1
414 might be related to some contamination from precursor calcite that was very difficult to
415 avoid during microsampling since the Sr content is still within the low zone (257ppm),
416 suggesting that D1 originated from also modified seawater possibly in a mixing zone
417 environment (e.g., Azmy et al., 2008).

418 The iron and manganese content of dolomites may reflect, at times, the redox state of the
419 dolomitizing fluids since Fe and Mn are commonly enriched in the later diagenetic phases
420 (Tucker and Wright 1990). Hydrothermal dolomites (D2 to D3) in the Watts Bight
421 Formation have low Fe contents (< 1250ppm) when compared to hydrothermal dolomites
422 from elsewhere in the St. George Group (Azmy et al. 2008). In addition the general, but
423 statistically not significant, trend of decreasing Fe from D2a (early hydrothermal)
424 dolomite to D3 (late-stage) dolomite in the Watts Bight Formation (Table 2) is contrary
425 to what is normally seen during burial diagenesis (Tucker and Wright 1990) and may
426 reflect lower Fe and Mn concentrations due to lack of sources of these elements in the

427 surrounding rocks, particularly under closed system conditions of circulation, rather than
428 variations in the redox state of the hydrothermal fluids.

429 **5.6 Reservoir potential in the Watts Bight Formation**

430 Hydrothermal dolomites and associated limestones have been demonstrated to be one of
431 the most significant targets for hydrocarbon exploration in eastern North America (e.g.
432 Lavoie et al. 2005; Smith 2006; Azmy et al. 2008). Hydrothermal dolomitization during
433 early burial is an important process in the development of secondary porosity and
434 permeability in potential hydrocarbon reservoirs (e.g. Smith 2006; Wierzbicki et al. 2006;
435 Lavoie and Chi in press). Therefore, petrographic and geochemical investigations of
436 diagenesis in these dolomites provide a better understanding of the timing and origin of
437 diagenetic fluids, key controls on porosity evolution and distribution in potential reservoir
438 rocks (Smith 2006; Wierzbicki et al. 2006).

439 This study demonstrates that the pore network and diagenetic evolution of the Watts
440 Bight Formation recorded significant porosity development associated with the migration
441 of hydrothermal fluids and hydrothermal dolomitization. In many locations in Western
442 Newfoundland sucrosic dolomites (similar to D2) in the St. George Group are spatially
443 associated with faults e.g. Daniels Harbour, Port au Choix (Knight et al. 2008). At
444 Isthmus Bay the upper porous level is associated with a normal fault, now filled in with
445 C3 calcite. Although no major faults have been reported from the lower porous level,
446 hydrothermal fluids may have infiltrated along microfractures that have been recognised
447 during petrographic analysis of Watts Bight dolomites. The exact timing of the
448 hydrothermal dolomitization in western Newfoundland is unknown a Devonian age has
449 been suggested by Cooper et al. (2001). This age is supported by Devonian Rb-Sr ages

450 from sphalerite in the Daniel's Harbour MVT deposit in western Newfoundland (Lane
451 1990) which provides an upper age limit for D2 and D3 dolomitization. Potential
452 hydrocarbon charges postdate hydrothermal dolomitization as D2 rhombs are commonly
453 coated by a bituminous material; the original hydrocarbons might have utilized the
454 enhanced porosity and permeability of dolomite horizons in the Watts Bight Formation.
455 Cooper et al. (2001) demonstrated that potential source rock in western Newfoundland
456 entered the oil window in the Late Devonian, by which time extensional faulting would
457 have juxtaposed the source rocks of the Green Point Formation and the dolomites of the
458 St. George Group. Lateral and vertical variations in the porosity distribution in the Watts
459 Bight Formation, due to the transition between porous hydrothermal dolomites and non-
460 porous dolomites and limestones, would have facilitated the development of diagenetic
461 traps and potential diagenetic reservoirs for hydrocarbon accumulations, as has been
462 noted in other hydrothermal fields in eastern North America (e.g., Davies and Smith
463 2006; Wierzbicki et al. 2006).

464 **6. Conclusions**

465 Petrographic, fluid inclusion, stable isotope and trace element data indicate that there are
466 at least three types of dolomite in the Watts Bight Formation, representing early
467 diagenetic to late-stage hydrothermal dolomites. Early replacement micritic dolomites
468 (D1) are fine grained and indicate that dolomitization began during the earliest stages of
469 diagenesis. The $\delta^{18}\text{O}$ of D1 dolomitizing fluids (-6.4 to -8.4‰ VSMOW) fall between the
470 estimated $\delta^{18}\text{O}$ of the Tremadoc sea and meteoric waters and support a mixing-zone
471 dolomitization, as has been suggested elsewhere in the St. George Group.

472 Later-stage replacement dolomites (D2) are associated with enhancement in
473 intercrystalline porosity and permeability through the development of intercrystalline
474 pores, while latest stage saddle dolomite (D3) and late burial calcite cements,
475 significantly occluded the pores in some horizons. The D2 dolomite crystals are often
476 coated by a bituminous material which suggests possible hydrocarbon charge after D2
477 dolomitization. Fluid-inclusion microthermometric data imply that D2 and D3 dolomites
478 were formed from warm, saline fluids of hydrothermal origin. The $\delta^{18}\text{O}_{\text{fluid}}$ of D2 ranges
479 from -4.5 to 3.6 ‰ VSMOW and for D3 dolomites $\delta^{18}\text{O}_{\text{fluid}}$ ranges from 1.4 to 8.4 ‰
480 VSMOW, suggesting an influx of $\delta^{18}\text{O}$ heavier basinal brines.

481 The high porosity and permeability associated with D2 dolomites has been recorded in
482 other cored sections from the Watts Bight Formation and combined with tight limestone
483 beds, presence of favourable source rocks and thermal maturation, may suggest that the
484 Watts Bight Formation carbonates are possible potential hydrocarbon reservoirs and
485 suitable targets for future hydrocarbon exploration in Western Newfoundland.

486 **Acknowledgements**

487 This project was financed by the PPSC (Pan-Atlantic Petroleum Systems Consortium),
488 and by ISPSG (Irish Shelf Petroleum Studies Group, Ireland). Support from the Earth
489 Science Sector of Natural Resources Canada and by the Department of Natural Resources
490 and Mines of Newfoundland and Labrador is warmly acknowledged. Nicolas Pinet is
491 thanked for reviewing an early draft of this paper. This is Geological Survey of Canada
492 contribution 20080544

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621 **Figure Captions**

622

623 **Figure 1:** Geological map of the Port au Port peninsula showing locating of the Isthmus
624 Bay section (modified from Knight *et al.* 2008).

625

626 **Figure 2:** Simplified lithostratigraphy of the St. George Group, Port au Port peninsula
627 with detailed section of the Watts Bight Formation showing the distribution of dolostones
628 and limestones (adapted from Knight *et al.* 2008).

629

630 **Figure 3:** Photomicrographs of the Watts Bight Formation. (a) Stained thin section
631 showing D1 dolomite replacing C1 micrite peloidal and intraclasts; (b) Photomicrograph
632 of D2a and D2 dolomite; (c) Stained thin section showing Fe-poor (pink) and Fe-rich
633 (purple) C3 infilling pores between D2b rhombs; (d) Stained thin section with D2b
634 rhombs showing dissolution (dedolomitization) and infilling with Fe-rich C3 calcite; (e)
635 D2b dolomite; (f) Same view as (a) under cathodoluminescence showing zoned
636 orange/red luminescence of D2 dolomite and yellow fluorescence of C3 infilling pores.

637

638 **Figure 4:** Photomicrographs showing distribution of fluid inclusions. (a) Biphasic
639 inclusions in D2 dolomite rhomb. Note inclusion is elongate in the direction of growth of
640 the dolomite rhomb. (b) Large biphasic inclusion in C3 calcite. Microfractures around
641 edge of inclusion may indicate leaking of trapped fluid.

642

643 **Figure 5:** Histogram of homogenization temperatures for fluid inclusions in the D2 and
644 D3 dolomites and C3 calcite of the Watts Bight Formation.

645

646 **Figure 6:** Bivariate plot of homogenization temperature vs. salinity for fluid inclusions in
647 the D2 and D3 dolomites and C3 calcite of the Watts Bight Formation.

648

649 **Figure 7:** Oxygen vs. Carbon isotope values for dolomite (D1, D2a, D2b, D3) and calcite
650 (C1, C3). The square represents isotopic values for best preserved carbonate precipitated
651 from Tremadoc seawater (Shields *et al.* 2003).

652

653 **Figure 8:** Scatter diagram showing the $^{87}\text{Sr}/^{86}\text{Sr}$ values in the Watts Bight dolomites (D1
654 to D3). The shaded area represents the range of $^{87}\text{Sr}/^{86}\text{Sr}$ values for the Tremadoc (Veizer
655 *et al.* 1999; Shields *et al.* 2003)

656

657 **Figure 9:** Temperature vs. $\delta^{18}\text{O}_{\text{fluid}}$ for various $\delta^{18}\text{O}_{\text{dolomite}}$ derived from the fractionation
658 equation: $10^3 \ln \alpha_{\text{dolomite-water}} = 3.2 \times 10^6 T^{-2} - 3.3$ (Lands, 1983). Hatched areas represent
659 range of temperatures and $\delta^{18}\text{O}$ for various dolomite generations (D1, D2, D3). Values
660 for Tremadoc seawater from Shields *et al.* (2003). See text for details.

661

662

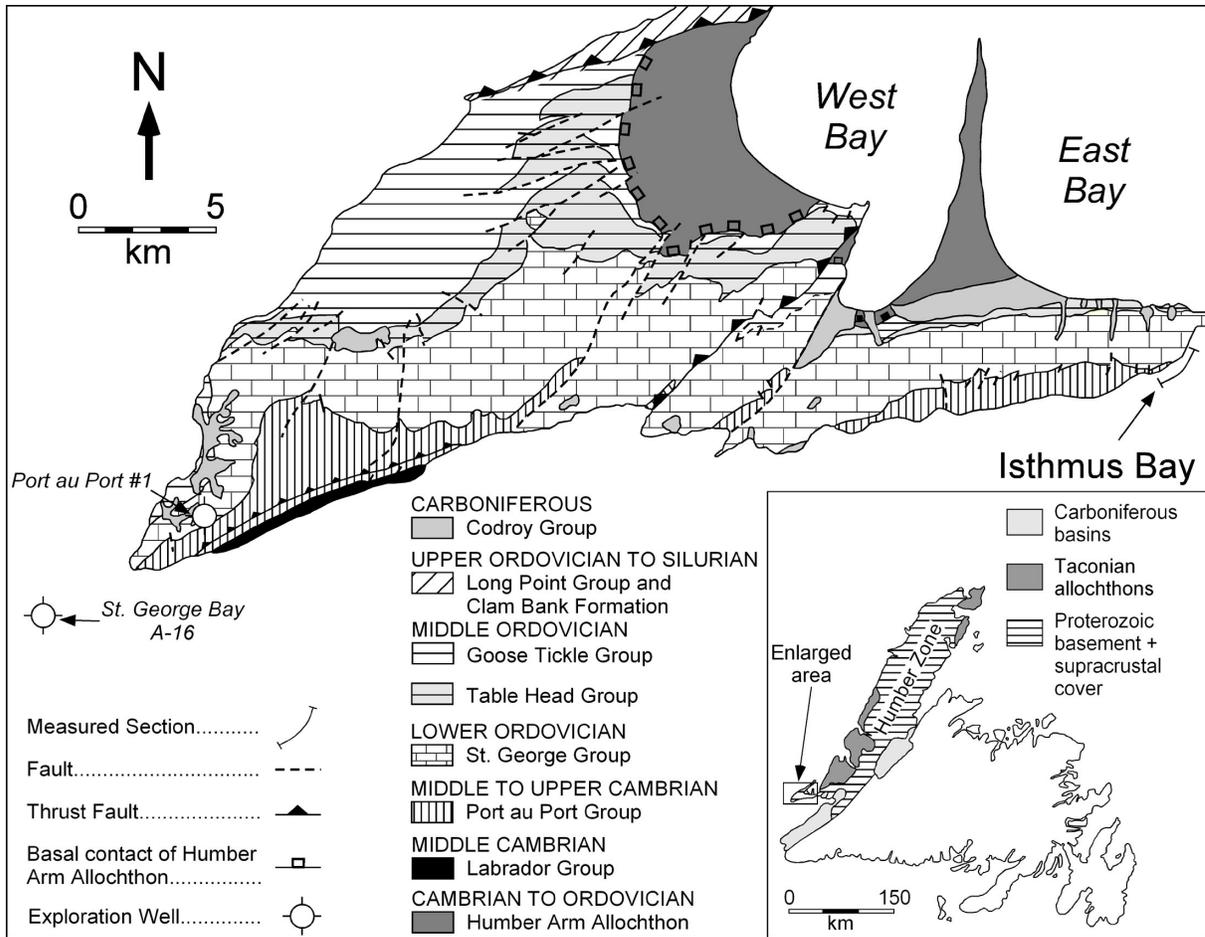
Table 1: Fluid inclusion microthermometric data from the Watts Bight Formation

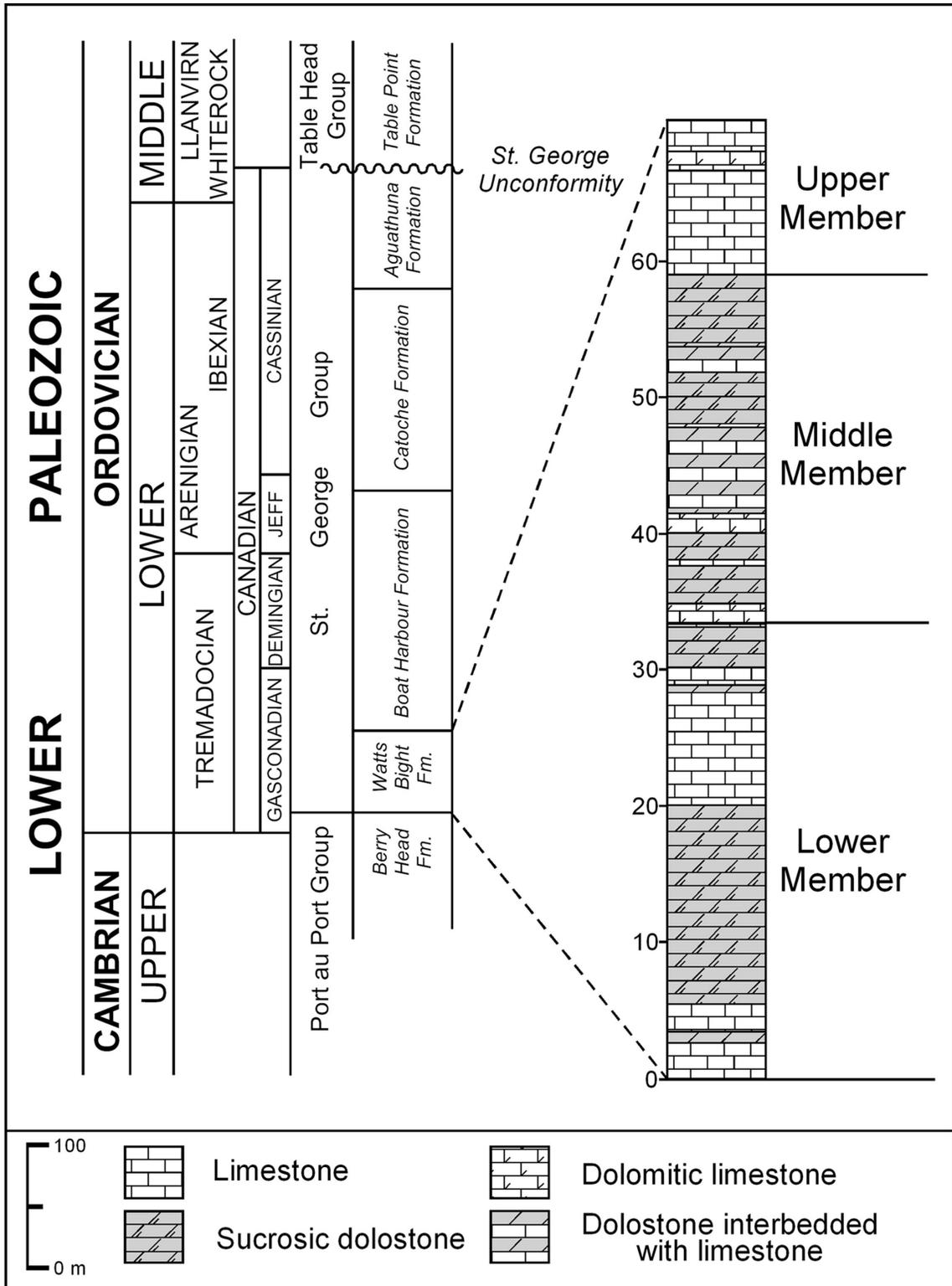
Phase		T_i	T_m (hydrohalite)	$T_m(\text{ice})$	Salinity (eq. wt% NaCl)	X_{NaCl}	T_h (L)
D2	<i>n</i>	11	7	31	31	7	58
	Mean	-53.3	-34.6	-14.3	17.5	0.22	79.7
	Max.	-51.3	-31.9	-6.2	25.6	0.28	108.6
	Min.	-55.2	-39.1	-25.0	9.5	0.14	44.6
	S.D.	1.4	2.9	5.2	4.5	0.06	13.4
D3	<i>n</i>	3	4	8	8	3	7
	Mean	-51.1	-31.1	-16.9	20.1	0.31	114.0
	Max.	-50.2	-30.2	-14.7	23.2	0.34	130.1
	Min.	-52.0	-31.5	-21.3	18.4	0.29	91.4
	S.D.	0.9	0.6	2.2	1.6	0.03	13.3
C2	<i>n</i>	8	11	15	15	11	28
	Mean	-53.3	-30.9	-16.4	19.7	0.32	94.1
	Max.	-51.0	-26.1	-14.7	22.4	0.54	126.7
	Min.	-55.2	-34.6	-20.1	18.4	0.22	68.0
	S.D.	1.7	2.5	1.7	1.3	0.10	17.3

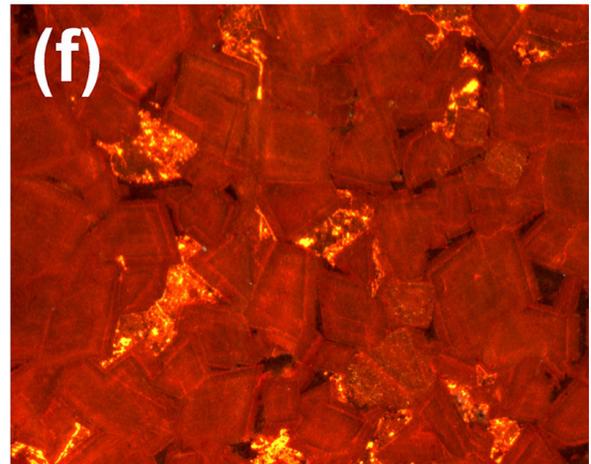
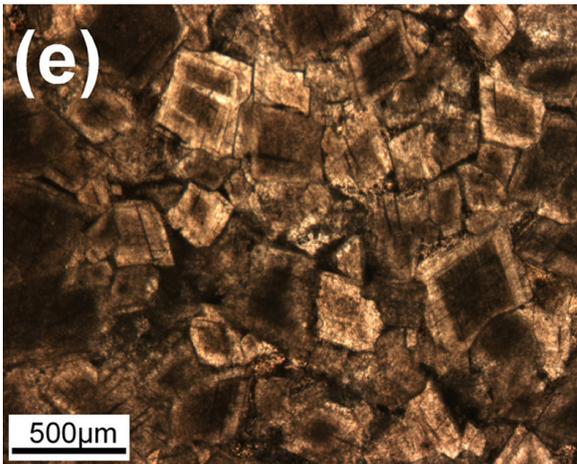
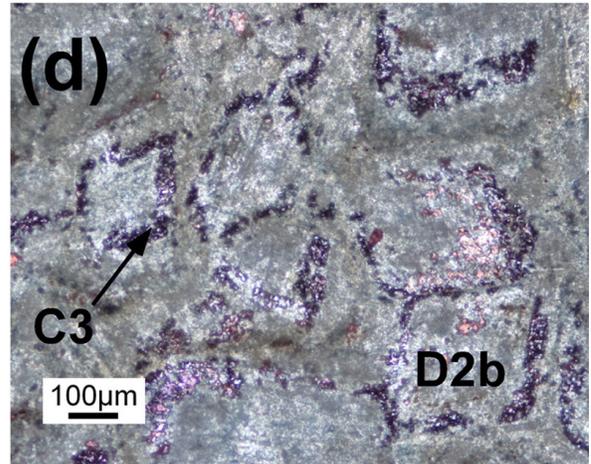
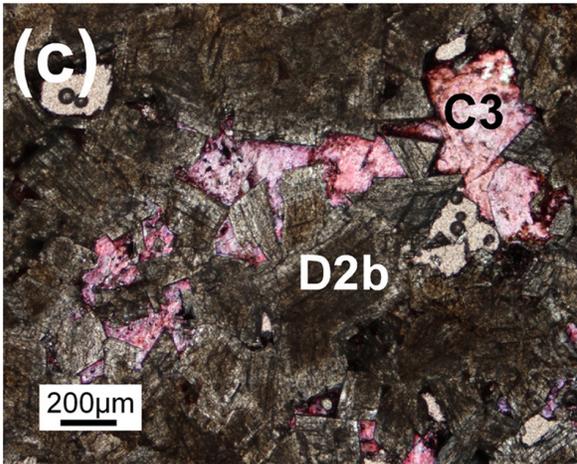
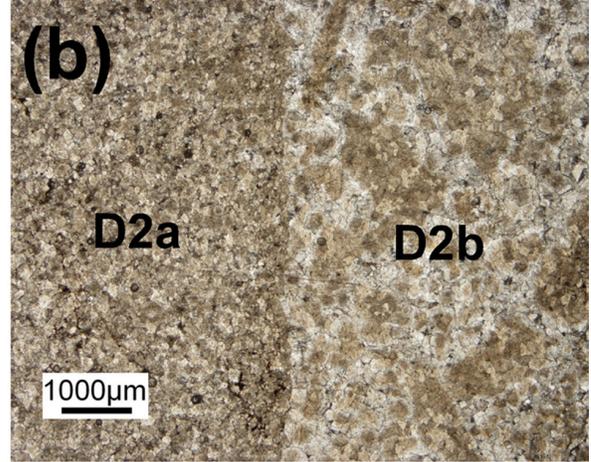
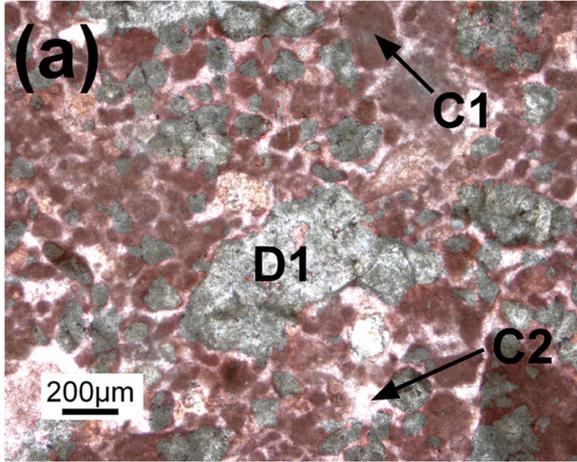
T_i = temperature of first ice melting; $T_m(\text{hydrohalite})$ = temperature of hydrohalite melting; $T_m(\text{ice})$ = temperature of last ice melting; $X_{\text{NaCl}} = \text{NaCl} / (\text{NaCl} + \text{CaCl}_2)$; T_h (L) = homogenisation temperature (to the liquid phase)

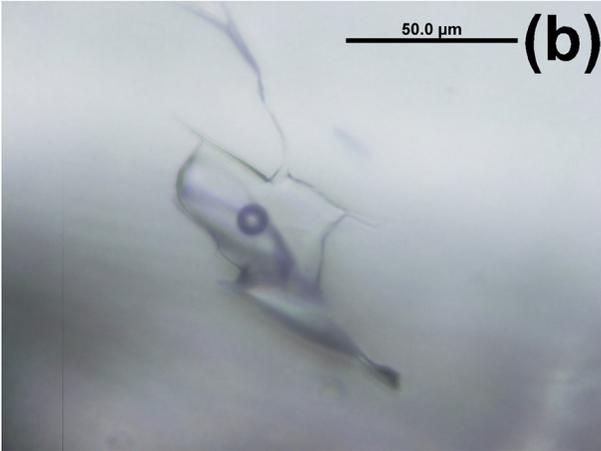
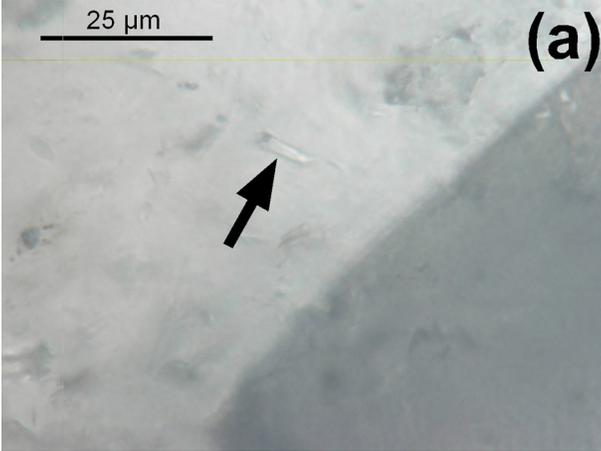
Table 2: Ca, Mg, Sr, Fe, Mn, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data for the Watts Bight Formation

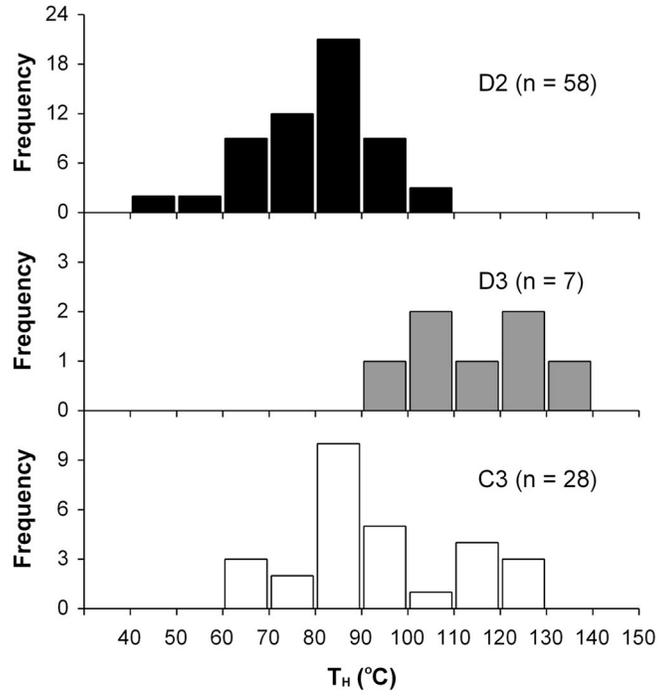
Phase		CaCO₃ (%)	MgCO₃ (%)	Sr (ppm)	Fe (ppm)	Mn (ppm)	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
C1/C2	<i>n</i>	7	7	7	7	7	12	12
	Mean	98.5	1.5	320	168	64	-1.3	-7.8
	Max.	99.2	3.0	390	320	99	-0.3	-7.4
	Min.	97.0	0.8	239	95	35	-2.2	-8.4
	S.D.	0.8	0.8	50	82	23	0.6	0.3
C3	<i>n</i>	3	3	3	3	3	4	4
	Mean	99.0	1.0	155	155	31	-2.5	-7.7
	Max.	99.4	1.2	192	403	37	-1.5	-7.0
	Min.	98.8	0.6	101	21	24	-5.1	-8.5
	S.D.	0.3	0.3	48	215	6	1.7	0.7
D1	<i>n</i>	1	1	1	1	1	2	2
	Mean	64.1	35.9	257	1323	96	-1.0	-5.9
	Max.						-1.0	-5.5
	Min.						-1.0	-6.3
	S.D.						0.0	0.5
D2a	<i>n</i>	8	8	8	8	8	14	14
	Mean	58.3	41.7	79	765	63	-1.3	-9.2
	Max.	62.2	45.6	225	1242	82	-0.6	-6.0
	Min.	54.4	37.8	27	411	45	-1.8	-11.4
	S.D.	3.2	3.2	70	249	14	0.3	1.8
D2b	<i>n</i>	10	10	10	10	10	12	12
	Mean	60.0	40.0	112	537	69	-1.4	-8.2
	Max.	63.7	45.8	183	1126	114	-1.0	-5.5
	Min.	54.2	36.3	32	201	43	-1.9	-11.4
	S.D.	3.0	3.0	58	258	21	0.3	2.0
D3	<i>n</i>	1	1	1	1	1	3	3
	Mean	58.0	42.0	89	357	59	-1.4	-7.9
	Max.						-1.0	-5.6
	Min.						-2.1	-9.6
	S.D.						0.6	2.1

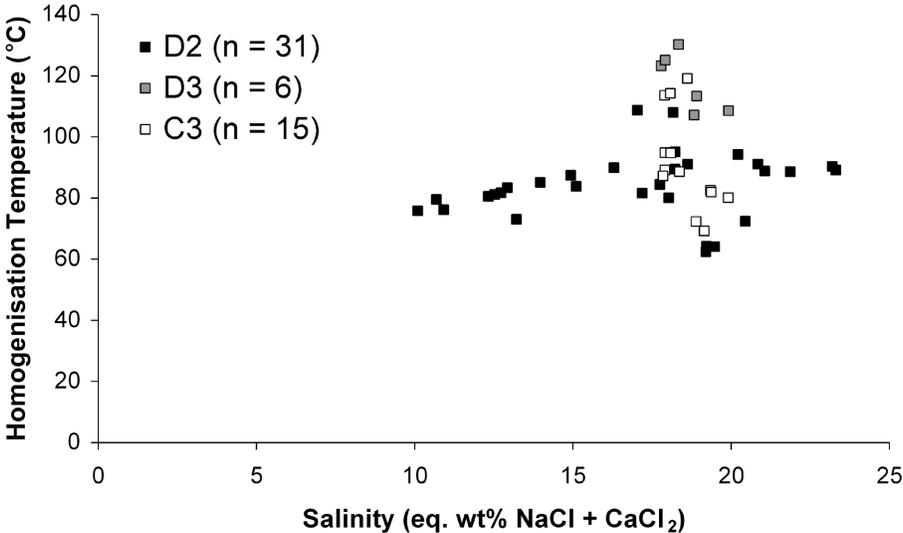


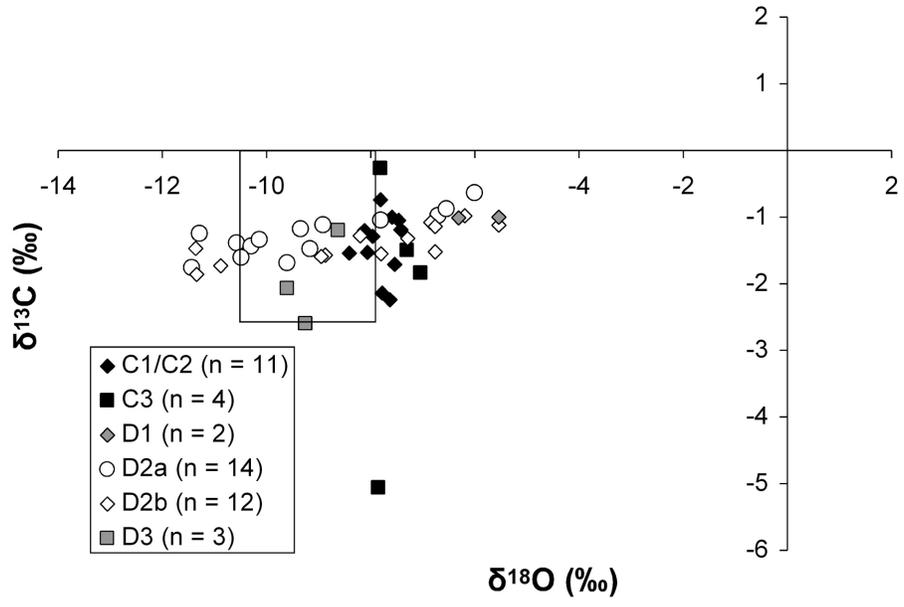


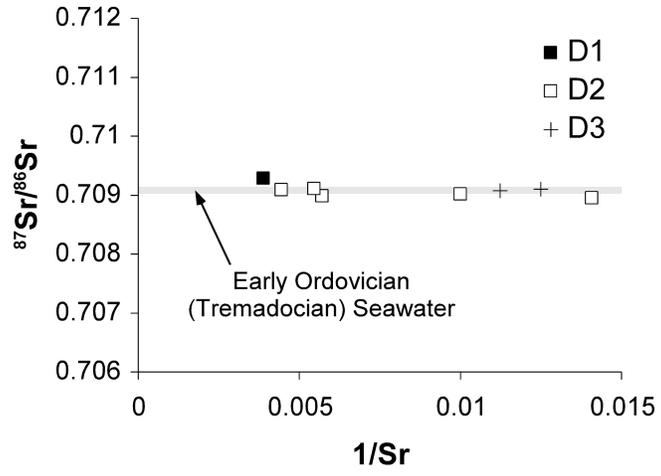


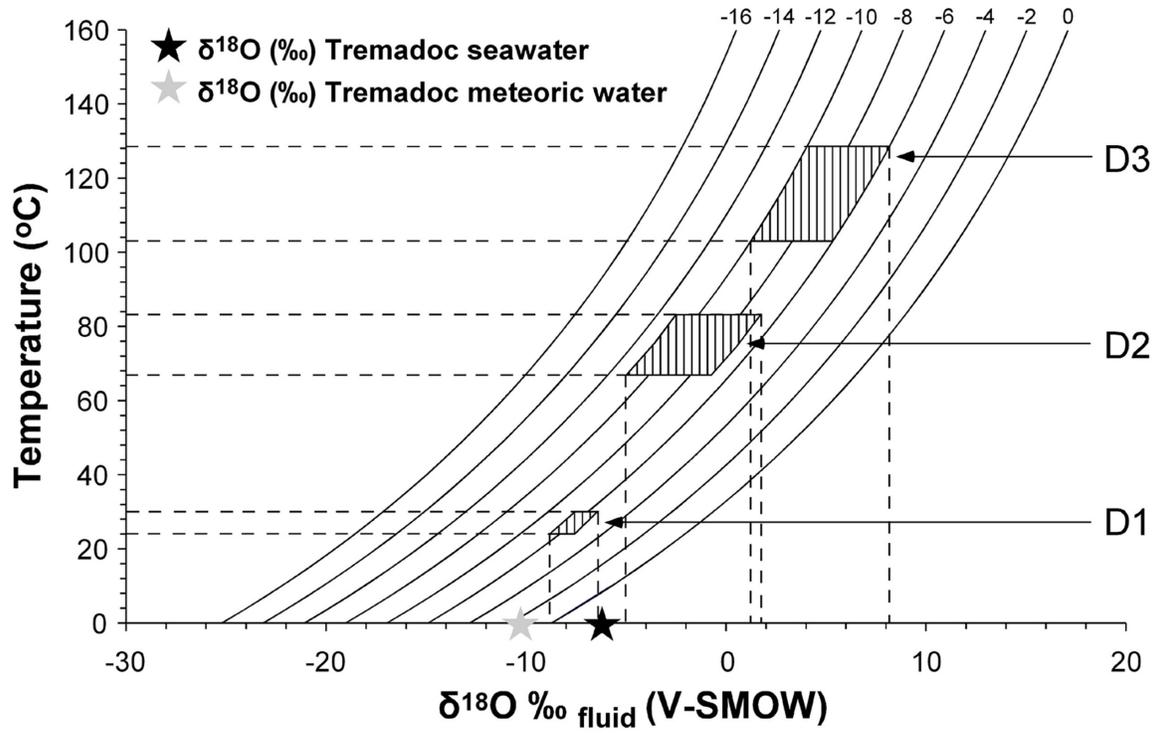












Appendix A. Samples, description, elemental and isotopic compositions, visual porosity estimates and permeability in the Watts Bight Formation.

Sample ID	Phase	Formation	Depth (m)	CaCO ₃ (%)	MgCO ₃ (%)	Sr (ppm)	Mn (ppm)	Fe (ppm)	δ ¹⁸ O (‰ VPDB)	δ ¹³ C (‰ VPDB)	⁸⁷ Sr/ ⁸⁶ Sr	Visual estimate of porosity (%)	Permeability (mD)
WB30	C1/C2	Watts Bight	68	98.50	1.50	239	70	320	-8.41	-1.54		<1	
WB26	C1/C2	Watts Bight	60	99.07	0.93	390	35	128	-8.06	-1.53		0	
WB22	D2a	Watts Bight	58.3	54.37	45.63	32	75	1242	-11.43	-1.76		4	1.30
	D2b	Watts Bight		54.20	45.80	32	74	1126	-11.34	-1.86			
WB21	D2b	Watts Bight	56.8						-7.80	-1.55		<1	
WB24	D3	Watts Bight	55.9	57.97	42.03	89	59	357	-9.60	-2.07	0.709075	1	
WB21	D2a	Watts Bight	54.8						-9.60	-1.69			
WB20	C3	Watts Bight	53.9	98.78	1.22	173	24	21	-7.85	-5.06		0	
WB18	D2a	Watts Bight	50.4	54.82	45.18	41	67	744	-9.16	-1.48		4	1.42
WB17	D2b	Watts Bight	48.1									4	1.28
WB16	D2a	Watts Bight	45.8						-10.48	-1.61		<1	
WB15	C1/C2	Watts Bight	43.5	97.02	2.98	275	99	228	-7.63	-2.24		0	
	D2a	Watts Bight		62.19	37.81	59	52	773	-10.29	-1.44		<1	
WB14	D2a	Watts Bight	42						-6.70	-0.98		<1	
WB13	D2a	Watts Bight	40.2						-8.91	-1.12		0	
WB12	C1/C2	Watts Bight	37.9						-7.78	-2.14		<1	
WB11	D2b	Watts Bight	35.6	57.30	42.70	100	60	326	-8.20	-1.28	0.709015	1	
	D3	Watts Bight							-8.62	-1.20	0.7091		
WB10	D1	Watts Bight	33.6	64.10	35.90	257	96	1323	-6.31	-1.01	0.709283	0	
WB9	D2b	Watts Bight	31.7	60.65	39.35	171	68	586	-6.85	-1.08	0.708953	1	
WB8	C1/C2	Watts Bight	29.8	98.41	1.59	335	81	182	-7.96	-1.29		<1	
WB-7	C3	Watts Bight	27.4	98.94	1.06	101	33	41	-7.30	-1.50		<1	
	D2a	Watts Bight							-6.54	-0.88			
WB6	C1/C2	Watts Bight	25.1	99.18	0.82	346	74	114	-7.81	-0.27		<1	
	C1/C2	Watts Bight							-7.81	-0.74			

Appendix A (continued)

Sample ID	Phase	Formation	Depth (m)	CaCO ₃ (%)	MgCO ₃ (%)	Sr (ppm)	Mn (ppm)	Fe (ppm)	δ ¹⁸ O (‰ VPDB)	δ ¹³ C (‰ VPDB)	⁸⁷ Sr/ ⁸⁶ Sr	Visual estimate of porosity (%)	Permeability (mD)
WB5	D2a	Watts Bight	22.7	60.24	39.76	27	50	411	-11.28	-1.25		3	
WB4	C1/C2	Watts Bight	21.2	99.15	0.85	341	42	108	-7.59	-1.00		1	
WB3	D2b	Watts Bight	18.3						-9.34	-1.18		7	16.50
WB2	D2b	Watts Bight	15.9	62.81	37.19	121	54	492	-7.29	-1.32		3	
WB1	D2a	Watts Bight	14.6	55.25	44.75	38	54	554	-10.57	-1.39		4	
	D2b	Watts Bight		60.81	39.19	32	54	460	-10.88	-1.73			
WBA1	D2b	Watts Bight	13.3						-8.87	-1.57		7	1.95
WBA2	D2b	Watts Bight	11.7									7	10.05
WBA3	D2b	Watts Bight	10						-6.84	-2.29		2	1.90
WBA4	D2a	Watts Bight	8	62.07	37.93	225	82	940	-6.00	-0.64	0.70909	<1	
	D2b	Watts Bight		60.41	39.59	183	61	423	-5.54	-1.12	0.709106		
WBA5	D2a	Watts Bight	5.9	59.78	40.22	142	45	694	-7.80	-1.05		<1	
	D2b	Watts Bight		63.72	36.28	134	43	386	-6.76	-1.14			
WBA6	C1/C2	Watts Bight	4.5	98.30	1.70	313	50	95	-7.42	-1.19		<1	
	D2a	Watts Bight		57.36	42.64	64	77	759	-10.13	-1.34			
	D2b	Watts Bight		57.84	42.16	48	91	633	-11.36	-1.47			5
	D3	Watts Bight							-5.57	-0.99			
WBA7	C1/C2	Watts Bight	0.9						-7.54	-1.71		<1	
	C1/C2	Watts Bight							-8.12	-1.20			
	C3	Watts Bight		99.39	0.61	192	37	403	-7.04	-1.84			
WBA8	C1/C2	Berry Head	0						-7.46	-1.05		<1	
	D2b	Berry Head		63.67	36.33	175	69	201	-6.19	-0.98	0.708984		
WBA9	D2b	Berry Head	-1.6	52.45	47.55	43	49	424	-8.95	-1.59		4	2.00
WBA10	D1	Berry Head	-3.7						-5.54	-1.00		<1	
WBA11	D2b	Berry Head	-5.2	59.03	40.97	120	114	736	-6.76	-1.52		2	