Fluids associated with hydrothermal dolomitization in St. George Group, western Newfoundland, Canada

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Abstract

Dolomite reservoirs are increasingly recognised as an important petroleum exploration target, although the application of a hydrothermal dolomite exploration model to these reservoirs remains controversial. The St. George Group of western Newfoundland consists of a sequence of dolomitised carbonates, with significant porosity development (up to 30%) and petroleum accumulations. Fluid-inclusion microthermometry and bulk fluid leach analyses indicated that fluids responsible for matrix dolomitization (associated with intercrystalline porosity) and later saddle dolomitization are $CaCl_2 \pm MgCl_2$ rich high salinity (up to 26 eq. wt% NaCl) brines. Integration of fluid inclusion data with thermal maturation histories from the St. George Group show that these dolomites formed at temperatures higher than the ambient rock temperature, and are therefore hydrothermal in origin. Bulk leach analyses show that dolomitization is associated with influxes of post-evaporitic brines (± Cl enriched magmatic fluids) late in the diagenetic history of these carbonates. This dolomitization is possibly Devonian in age, during a period of significant magmatic activity, extensional tectonics and development of hypersaline basins. Petrographic and geochemical similarities between Paleozoic hosted hydrothermal dolomitization in western Newfoundland, eastern Canada and the

48 northeastern United States are consistent with a regional scale hydrothermal
49 dolomitization event late in the diagenetic history of these carbonates.
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Introduction

Hydrothermal dolomites (HTD) reservoirs have increasingly been recognised as an important exploration target (Davies and Smith, 2006). These dolomites have been reported from a large number of locations worldwide e.g. the Paleozoic basins of eastern Canada and the United States (Smith, 2006; Lavoie and Chi, in press; Lavoie et al., in press a), Devonian carbonates of the Western Canada sedimentary basin (Qing and Mountjoy, 1994; Al-Aasm, 2003), Jurassic basins along rifted Atlantic margins (Wierzbicki et al., 2006) and Carboniferous carbonates of the Iberian Belt, Spain (Gasparrini et al., 2006). Hydrothermal dolomitization is defined as dolomitization occurring under burial conditions by high salinity fluids at temperatures higher than the ambient temperature of the host formation (Davies and Smith, 2006). Davies and Smith (2006) suggest that transtensional seismic platform sags associated with major structural features (extensional and/or strike-slip faults) which act as a focus for the HTD fluids should be targeted in exploration programs. However, the interpretation of these dolomites as hydrothermal remains controversial and has been criticized by a number of authors (Machel and Lonnee, 2002, 2008; Lonnee and Machel, 2006; Friedman, 2007). These criticisms centre on a number of questions and uncertainties which remain associated with the HTD exploration model, including determining the absolute timing of dolomitization, the source of Mg^{2+} rich saline brines and the possible driving mechanisms for hydrothermal circulation (Machel and Lonnee, 2002; Davies and Smith, 2006; Lavoie and Chi, in press). From an exploration standpoint these questions need to be addressed in order to determine if the HTD exploration model described by Davies and Smith (2006) is valid and useful.

Over the past few years a large number of interpreted HTD reservoirs have been described from the Paleozoic Appalachian Basins of eastern Canada and the northeastern United States (Montanez and Read, 1992; Lavoie and Morin, 2004; Lavoie et al., 2005; Lavoie and Chi, 2006; Smith, 2006; Azmy et al., 2008, 2009; Conliffe et al., 2009; Lavoie and Chi, in press; Lavoie et al., in press a). A number of possible sources have been suggested for the Mg^{2+}-rich fluids responsible for hydrothermal dolomitization, including the drawdown of postevaporite residual brines from overlying Silurian evaporites (Coniglio et al., 1994) and brines circulating through mafic volcanic and ophiolitic basement rocks (Lavoie and Morin, 2004; Lavoie and Chi, 2006; Lavoie and Chi, in press; Lavoie et al., in press b). However, there is still considerable uncertainty about the source of Mg^{2+}-rich fluids. This study aims to constrain the origin and timing of the fluids responsible for replacement and saddle dolomitization in the Lower Ordovician St. George Group, Western Newfoundland. This sequence of dolomitized carbonates has been described as a potential HTD petroleum reservoir (Cooper et al., 2001; Azmy et al., 2008, 2009; Conliffe et al., 2009). The dolomites of the St. George Group are commonly associated with intracrystalline and vuggy porosity (Knight et al., 2007, 2008), and these porous horizons are currently the driver for renewed petroleum exploration (Cooper et al., 2001). Recent drilling on the Port au Port Peninsula have encountered horizons with significant porosity in the Aguathuna (9.8% porosity and 21 mD permeability over 9.8m), Catoche Formation (15 m of 8.7% average porosity) and Watts Bight Formation (up to 30% porosity, with a mean 14% over 44.5m), which are associated with dolomitization of the predominantly low porosity and permeability rocks of the St. George Group carbonates.

This is the first study in the Appalachian Basin to integrate petrography with detailed and comprehensive fluid inclusion and bulk fluid inclusion (anion and cation) analyses. Fluid inclusion analyses provide important constraints on the temperature of dolomitization and combined with stable isotope analyses can help to define the nature and origin of the dolomitizing fluids. Anion ratios (especially Cl/Br) are particularly useful in determining the source of fluids (e.g. Walter et al., 1990; Kesler et al., 1995), as Cl and Br act conservatively in solution and, with the exception of halite dissolution, water-rock interaction does not alter Cl/Br ratios (e.g. Rittenhouse, 1967; Carpenter et al., 1978). These data are combined with information on the thermal maturity and burial history of the St. George Group, and are used to determine the source of these fluids and whether they are truly hydrothermal (according to the criteria of Machel and Lonnee, 2002 and Davies and Smith, 2006). Economically this has important implications for the HTD exploration model that is currently being used from Western Newfoundland to the Appalachian Basin in eastern USA.

Geological Setting

The Lower Paleozoic shelf rocks of western Newfoundland comprise a succession of Cambrian to Devonian siliciclastic and carbonate sediments that outcrop over 400km from Cape Norman in the north to the Port au Port Peninsula in the south (Fig. 1). These shallow- to deep-marine successions were deposited on the southern margin of Laurentia during the Late-Proterozoic break-up of Rodinia and record the evolution of the margin from a long-lived (~50Ma) passive margin (Labrador, Port au Port and St. George

Groups) to an active foreland basin (Table Head Group) (James et al., 1989; Stenzel et al., 1990; Cooper et al., 2001; Waldron and van Staal, 2001; van Staal, 2005).

The St. George Group consists of a ~500 to 600m succession of subtidal and peritidal carbonates which were deposited as part of a broad low-energy passive margin platform during the Lower to earliest Middle Ordovician. The group has been subdivided into the Watts Bight, Boat Harbour, Catoche and Aguathuna formations (Knight and James, 1987; Fig. 2). These represent two long-lived Tremadoc and Arenig sequences, which were termed megacycles by Knight and James (1987). The lower megacycle consists of the Watts Bight Formation and most of the Boat Harbour Formation, and is bounded at the top by a regional disconformity, the Boat Harbour Disconformity (BHD; Fig. 2). The upper megacycle comprises of the top of the Boat Harbour Formation, and the Catoche and Aguathuna formations. A regional unconformity with karst features, the St. George Unconformity, marks the top of the St. George Group.

Each of these megacycles is attributed to eustatic sea level fluctuations and local tectonics (Knight and James, 1987). These large-scale cycles have a thin lower peritidal interval, a thick middle subtidal succession and a thick upper peritidal cap (Knight and James, 1987; Fig. 2). The peritidal units consist of meter-scale, upward shallowing cycles of thinly bedded peloidal mudstones to packstones which commonly include horizons of stromatolitic, thrombolitic and microbial boundstone mounds (Knight et al., 2007, 2008). The subtidal layers are more thickly bedded (~5m) and are comprised of intensely bioturbated peloidal wackestones to mudstones, parallel laminated peloidal packstones to grainstones and large thrombolitic boundstone mounds (Knight et al., 2007, 2008).

Dolomitization and diagenesis of the St George Group

Petrographic examination of the St. George Group carbonates has led to the recognition of at least three main generations of dolomite in all the units, occurring as both replacements and cements and recording multiple phases of dolomitization (Azmy et al., 2008, 2009; Greene, 2008; Conliffe et al., 2009). The earliest dolomite (D1) replaces precursor calcite (C1) and early meteoric calcite cements (C2). D1 is a fine grained (4 to 40μm) dolomicrite which is fabric-retentive and suggests that dolomitization started shortly after inception of burial, at low temperatures during the early stages of diagenesis. Trace element geochemistry and stable isotope analysis suggested a mixed of marine and meteoric source for D1 dolomitizing fluids, possibly in a mixing zone environment (Azmy et al., 2008, 2009).

Later-stage replacement dolomites (D2) consist of coarse, (50 to 300μm) equant sub- to euhedral dolomite rhombs with characteristic cloudy cores and clear rims (Fig. 3a). The $\delta^{18}O_{fluid}$ of D2 ranges from -2 to 5‰ VSMOW), which are typical of influxes of basinal brines (Goldstein and Reynolds, 1994). Petrographic studies of the St. George Group dolomites have shown that significant intercrystalline porosity (up to 10%) resulted from D2 dolomitization (Azmy et al., 2008, 2009; Conliffe et al., 2009).

The latest dolomite generation (D3) consists of pore- and fracture-filling to locally replacive coarse sub- to anhedral crystals (>0.5mm). D3 dolomite in the St. George Group is commonly Fe-rich (up to 20000ppm) and has the most enriched $\delta^{18}O$ signature of dolomitizing fluids (3 to 8‰ VSMOW), which is consistent with late, deep burial or hydrothermal fluids (Tucker and Wright, 1990; Goldstein and Reynolds, 1994; Azmy et al., 2008, 2009; Conliffe et al., 2009). A translucent, coarse blocky calcite cement (C3) is

the last diagenetic phase recorded in the St. George Group carbonates and partly to completely fills pores and fractures still open after D3 precipitation (Fig. 3b). Although some dissolution and vuggy porosity has been reported associated with D3 dolomitization (Azmy et al., 2008, 2009) these vugs are rarely interconnected, and D3 and C3 cements are generally associated with a reduction in the effective porosities of these early dolomites (Azmy et al., 2008, 2009; Conliffe et al., 2009).

Methodology

Samples for analyses were collected from outcrops at Isthmus Bay on the Port au Port Peninsula and Barbace Cove on the Port aux Choix Peninsula, as well from a number of exploration drillholes (RND 001 and RND 002 on the Port au Port Peninsula and PC79-02 on the Port aux Choix Peninsula (cf. Azmy et al., 2008; Greene, 2008, Azmy et al., 2009; Conliffe et al., 2009). The analyzed samples were carefully selected from a suite of samples that were collected at high resolution intervals of ~ 2m (± 0.5m) and represent a complete succession (~ 525m) of the St. George Group (cf. Azmy et al., 2008, Greene, 2009; Azmy et al., 2009, Conliffe et al., 2009). The sample locations are the same as those presented in Knight et al. (2007, 2008) and the numbering scheme used by these authors is retained here. Based on petrographic and geochemical investigations doubly polished wafers (~ 100µm thick) for fluid inclusion analyses were prepared from representative samples of D2, D3 and C3. Microthermometric fluid-inclusion analyses were performed using a Linkam THMSG600 heating-freezing stage calibrated with synthetic H_2O and CO_2 fluid inclusion standards (Syn Flinc, USA) at temperatures between -56.6 and 374.1°C. Precision on the measurements is ± 0.2°C at –56.6°C and ±

1°C at 300°C. Homogenization temperatures were recorded first in order to minimise the effects of stretching in relatively soft minerals such as calcite. Following procedures outlined by Shepherd et al. (1985) the initial melting temperatures (T_i), hydrohalite melting (T_m(hh)), last ice melting (T_m(ice)) and the temperature of homogenization (T_h) were measured in two-phase (liquid + vapour) inclusions hosted in dolomite and calcite. Hydrohalite melting temperatures facilitate estimates of fluid compositions based on microthermometric data, particularly when combined with charge balance calculations from crush leach analyses. However care must be taken in interpreting these ratios as no phase diagrams are available which accurately describe the H_2O-NaCl-$CaCl_2$-$MgCl_2$ system, and the small size of these inclusions which led to the recording of hydrohalite melting being challenging. Salinities were calculated from the T_m(hh) and T_m(ice) using a program by Chi and Ni (2006) for the system of H_2O-NaCl-$CaCl_2$. X_{NaCl} was calculated using the equation of Oakes et al. (1990).

Following fluid inclusion microthermometry, specific dolomite and calcite phases were selected and cut from a polished mirror-image slab of each fluid inclusion wafer for crush-leach analyses. Care was taken to select samples dominated by one population of primary fluid inclusions. These samples were prepared for crush-leach analysis following the procedure of Banks and Yardley (1992) and Gleeson and Turner (2007). The samples were crushed and sieved to give a 1-2 mm grain size fraction. After crushing, the samples were hand picked under a binocular microscope to obtain 2 g of a clean mineral separate. The samples were washed in 18.2 mΩ water and heated overnight on a hot plate, then dried in an oven. Finally ~1 g of sample was ground to a fine powder in an agate mortar and pestle. The powder was transferred to an unreactive vial and 5 mL of clean water

was added. These samples were shaken, and filtered through 0.2 micron filters. The resultant leachate was analysed for anions (Cl, Br, F and sulphate) using a Dionex DX600 ion chromatograph (IC) at the University of Alberta. The detection limits for all anions was 0.008 ppm. Replicate analyses of standards and samples yielded data with a reproducibility of 5%. Na, K and Li were analysed on the same leachate using atomic adsorption spectroscopy (AAS). The detection limits for these cations was 0.002 ppm.

As the total number of inclusions in each sample is unknown the ion concentrations measured in the leachates do not represent the concentrations in the basinal fluids. In order to back-calculate the ion concentrations in the fluids, the crush leach data were normalized to the salinity values as measured by microthermometry using the technique described in Banks et al. (2002). In addition, a charge balance calculation (see Shepherd et al., 1985) was carried out for each sample. In a solution with a neutral charge the number of positively charged ions (cations) should equal the number of negatively charged ions (anions) and should yield a charge balance of 1. Any deviation from this value can indicate contamination from the host mineral and/or certain cations and anions have been omitted from the analysis. Our charge balance calculations use Cl, Br, F, SO_4, Na, K and Li compositions of the carbonate-hosted leachates. However Ca, Mg, CO_3 and HCO^{3-} are excluded from the analyses due to possible contamination from the host carbonates. Therefore the charge balances presented below are incomplete and are solely used to identify variations in fluid compositions.

Results of Fluid Inclusion Analyses

A number of fluid inclusion microthermometric studies have been published on the St. George Group carbonates (Azmy et al., 2008, 2009; Conliffe et al., 2009) but there has been no comprehensive fluid inclusion study of hydrothermal dolomites in Western Newfoundland. This study combines previously published fluid inclusion data from the Aguathuna (Azmy et al., 2008), Boat Harbour (Azmy et al., 2009) and Watts Bight (Conliffe et al., 2009) formations with new microthermometric data from D2 and D3 dolomite, and C3 calcite in the Catoche, Boat Harbour and Watts Bight formations (Table 1).

Fluid inclusion petrography and classification

The fluid inclusions in dolomite (D2 and D3) were hosted in clusters in the core of dolomite crystals or in discrete zones within dolomite rhombs and inclusions were commonly elongate in the direction of growth. Inclusions in C3 calcite were found in clusters in the core of crystals and can be very large with respect to their host crystals (up to 50µm; Fig. 3f). Therefore inclusions in dolomite and calcite are considered primary in origin and represent samples of fluid trapped during growth (Goldstein, 2003). Primary fluid inclusion assemblages in D2 and D3 dolomite are characterised by a consistent degree of fill (liquid/vapour ratio) indicating little or no post-entrapment reequilibrium (leaking or necking down of inclusions). In contrast some primary inclusion in C3 calcite show evidence of post-entrapment leaking and/or stretching (e.g. microfractures at edge of inclusions). Care was taken only to record microthermometric data from inclusions which displayed small T_h variations within an individual inclusion assemblage, usually less than 10ºC, suggesting that post-entrapment effects are not important (Goldstein and Reynolds, 1994).

D2 dolomite

The fluid inclusions in D2 dolomite are biphase (liquid + vapour; L + V) and range in size from 2 to 20µm. The initial melting temperatures (T_i) ranged from -55.3 to -48°C (Table 1), corresponding to the eutectic temperature for the H_2O-NaCl-$CaCl_2$ ± $MgCl_2$ system (Shepherd et al., 1985). Very low melting temperatures were recorded in one sample from the Catoche Formation (MG13); this is attributed to metastable melting phenomenon in the H_2O-NaCl-$CaCl_2$-$MgCl_2$ system. An additional phase change occurred at ~-40 to -30°C in some samples from the Catoche and Watts Bight formations. This is interpreted as hydrohalite ($NaCl.2H_2O$) melting and indicates that these fluids are $CaCl_2$ rich (Oakes et al., 1990), yielding Ca:Na ratios of 7:1 to 9:1 for the Catoche Formation and 2:1 to 6:1 for the Watts Bight Formation. Ice melting temperatures (T_m(ice)) ranged from -26.7 to -6.2°C, which yield a wide range of fluid salinities of (10.1 to 24.8 eq. wt% NaCl + $CaCl_2$; Fig. 4).

Inclusions in D2 dolomite homogenize (T_h) to the liquid phase between 60 and 121°C. However there are significant variations in homogenization temperatures between sample in each formation (Fig. 4), with samples from the Aguathuna and Watts Bight formations having lower T_h (74 ± 3°C and 83 ± 12°C respectively) than samples from the Catoche Formation (107 ± 13°C) and the Boat Harbour Formation (102 ± 15°C).

D3 dolomite

The fluid inclusions in D3 dolomite are two-phase (L + V) and range in size from 2 to 20µm. The eutectic temperature of -66 to -50.2°C indicates the presence of $CaCl_2$ ± $MgCl_2$ in solution. Hydrohalite melting temperatures were recorded in some larger inclusions in D3 and range from -31.5 to -30.2°C. Assuming a pure $CaCl_2$-NaCl fluid

composition this corresponds to a Ca:Na ratio of ~ 2:1. T_m(ice) ranged from –1 to -31.3ºC, with calculated salinities from 1.7 to 26.2 eq. wt% NaCl + $CaCl_2$. Inclusions homogenize (T_h) to the liquid phase between 69 and 140°C (mean = 111°C, standard deviation = 15°C), with no significant variations found between the formations.

C3 calcite

Fluid inclusions in C3 calcite display a wide range of size (2 to 50µm) and degree of liquid fill (0.6 to 0.95). Low T_i of -62 to -49°C again suggests that Na, Ca and Mg are the dominant cations in solution. The majority of inclusions in C3 calcite have salinities of 17 to 24 wt% NaCl + $CaCl_2$ and have T_h values of 64 to 182°C.

Results of Bulk Fluid Analyses

Following detailed petrographic and microthermometric analyses, fourteen samples (nine D2, three D3 and two C3) were selected for bulk fluid analyses. The results of the leachate analysis are summarized in Table 2, and the calculated charge balances and molar element ratios are presented in Table 3.

D2 dolomite

The crush leach analyses of the D2 dolomite samples suggest that there are two geochemically-distinct fluids in this paragenetic phase; one is found in samples above the BHD (Aguathuna and Catoche formations) and the other in those below the BHD (Boat Harbour and Watts Bight formations.

The charge balances of D2 dolomite leachates from above the BHD range from 0.5 to 0.8. Leachate analyses of D2 samples from below the BHD have a charge balance of 1 or a slight excess in cations (1.0 to 1.5). The anion analyses of samples from above and

below the BHD are also markedly different. D2 samples from carbonates above the BHD have Cl/Br ratios of 167 to 284, significantly less than 655 (composition of modern day seawater from the compilation of Fontes and Matray, 1993). In contrast those below the BHD have Cl/Br ratios that are equal to or slightly above that of seawater (661 to 935) and slightly elevated Na/Br ratios (677 to 972). The absolute concentrations of Cl and Br indicate that D2 dolomites above the BHD plot below the Seawater Evaporation Trend (SET), while those from below the BHD lie on or slightly to the left of the SET.

The Na/Br and K/Br ratio of leachates (Fig. 7) show that three samples from the Catoche Formation (on the Port a Choix Peninsula) are depleted in K (below the SET). In contrast those from the Aguathuna, Boat Harbour and Watts Bight formations from the Port au Port Peninsula have relatively high K/Br ratios (15.5 to 80.5), higher than the SET and suggesting an addition of K to the fluids. In addition a single sample from the Watts Bight Formation (WBA3) has elevated Li concentrations (Li/Na of 0.0015).

D3 dolomite

The leachate-analyses from D3 dolomites are similar to those of D2 dolomites above the BHD, and no significant variations have been observed between samples from above or below the BHD. A charge balance calculation yields values of 0.5 to 0.6. The Cl/Br ratios from all three D3 samples are 305, and are lower than modern day seawater (Fig. 5). Halide compositions have been calculated for two D3 samples plot below the SET, indicating mixing between high salinity brines and a dilute fluid. These fluids have low K and Li values (Li values below the detection limit), consistent with limited water-rock interaction during fluid transport.

C3 calcite

Only two C3 calcite samples were analysed, one from the Boat Harbour Formation and one from the Watts Bight Formation. Both samples have Cl/Br ratios lower than modern seawater (371 and 538 respectively). Bulk fluid analyses of C3 calcite from the Boat Harbour and Watts Bight formations show significant variations (Table 3; Fig. 7), with variable SO_4/Br, Na/Br and K/Br ratios.

Discussion

Hydrothermal Origin of St. George Group Dolomites

In order to determine whether dolomites are truly hydrothermal or not, the homogenization temperature of dolomites has to be evaluated in light of the burial and thermal history of the dolomite host (Davies and Smith, 2006). If the homogenization temperatures are significantly (5 to 10°C) higher than maximum burial temperatures it can be safely concluded that these dolomites are hydrothermal. However if the homogenization temperatures are the same as, or lower than, maximum burial temperatures then these dolomites cannot be confidently classified as hydrothermal in origin, and may, in fact, be deep burial dolomites which formed at, or below, ambient temperatures (geothermal or hydrofrigid dolomites; Machel and Lonnee, 2002). This rigorous definition of "hydrothermal dolomites" is important in avoiding the misinterpretation of dolomites as hydrothermal dolomites, as demonstrated by Machel and Lonnee (2002) and is necessary for the application of the HTD exploration model (as proposed by Davies and Smith, 2006).

Maximum burial temperatures from the St. George Group in western Newfoundland have been indirectly estimated from conodont alteration indices (CAI), acritarch alteration

indices (AAI) and random graptolite reflectance data (GRo) (Nowlan and Barnes, 1987; Williams et al., 1998). A general trend of increasing maturity from the Port au Port Peninsula in the south to Cape Norman in the north has been documented. The AAI values from the Watts Bight Formation (lowermost unit of the St. George Group) on the Port au Port Peninsula are 2.3, combined with the low AAI and low GRo from the overlying Ordovician and Carboniferous strata (Williams et al., 1998) indicates that maximum burial temperatures on the Port au Port Peninsula are <75°C. The St. George Group on the Port au Choix Peninsula is characterised by higher AAI (>3) and GRo (>1.11%), corresponding to burial temperatures of ~120 to 130°C. Nowlan and Barnes (1987) argued that these higher temperatures may be related to elevated geothermal gradients during the passage of north-western Newfoundland over a hot spot during the Mesozoic. However no evidence of elevated geothermal gradients was observed in overlying Carboniferous strata (William et al., 1998). Therefore, these temperatures must have been reached during the Paleozoic and are due to normal orogenic processes (i.e. deep burial and high geothermal gradients).

When pristine, fluid inclusion homogenization temperatures reflect the minimum trapping temperature, and therefore the minimum temperature of dolomitization. In order to determine the extent to which these temperatures underestimate the true dolomitization temperature isochores have been constructed for fluids with T_H of 70 and 100°C and salinities of 8 and 16 eq. wt% NaCl (Fig. 8) using the program FLUIDS (Bakker, 2003). If dolomitization occurred at a depth of 2-3km (maximum burial depth on the Port au Port Peninsula; Williams et al., 1998), trapping pressures range from 530 to 795 bars for lithostatic pressures and 196 to 294 for hydrostatic pressures (Fig. 8). At these pressures

the T_H underestimates the true trapping temperatures by 19-35°C for lithostatic pressures and 7-13°C for hydrostatic pressures. Therefore it can be concluded that although the fluid inclusion homogenization temperatures provide minimum trapping temperatures, these data may severely underestimate the true temperature of dolomitization, particularly at deeper levels (> 2km).

The T_H values from D2 and D3 dolomites on the Port au Port Peninsula (Fig. 9) are equal to, or greater than, the maximum burial temperatures estimated by Williams et al. (1998). Therefore D2 and D3 dolomite in the St. George Group on the Port au Port Peninsula can be described as hydrothermal in origin according to the criteria of Machel and Lonnee (2002), particularly if the underestimation of true temperatures of dolomitization based on fluid inclusion homogenization temperatures is considered. In contrast, maximum burial temperatures estimated from the St. George Group on the Port aux Choix Peninsula are equal to or greater than the fluid-inclusion homogenization temperatures in the dolomites (Fig. 9). This may be due to the burial of these dolomites to temperatures which exceed the homogenization temperatures at some point after dolomitization, as has been suggested by Smith (2006) for Ordovician dolomites in New York. Without a precise control on the timing of dolomitization, it cannot be stated unequivocally that the St. George Group dolomites on the Port aux Choix Peninsula are hydrothermal in origin, they may instead have formed at, or below, ambient rock temperatures during deep burial.

Origin of Hydrothermal Fluids

Numerous studies have shown that crush leach analyses, combined with microthermometric data, are useful in the determination of the source of dolomitizing

fluids (Banks et al., 2002; Gleeson and Turner, 2007). Fluid inclusion analyses show that dolomitizing fluids in western Newfoundland are high salinity $CaCl_2$-$MgCl_2$-rich brines (Table 1), similar to other hydrothermal dolomites in eastern Canada and northeastern United States (Coniglio et al., 1994; Lavoie and Morin, 2004; Lavoie et al., 2005; Lavoie and Chi, 2006; Smith, 2006; Lavoie and Chi, in press; Lavoie et al., in press a). However significant variations were recognised in the composition and source of the hydrothermal fluids responsible for D2 and D3 dolomitization, and the precipitation of C3 calcite.

D2 Dolomite

The charge balance calculations for D2 dolomites range from 0.5 to 1.5, with samples from above the BHD having lower charge balances (<1) that those from below the BHD (>1). This may indicate compositional variations between D2 dolomitizing fluids from above and below the BHD. Compositional variation is also indicated by microthermometric data. Hydrohalite melting temperatures, combined with T_m(ice), from D2-hosted inclusions in the Catoche Formation (above the BHD) yield salinities of 20.8 to 22.3 eq. wt% NaCl and X_{NaCl} of 0.1 to 0.13 (Fig. 10a). In contrast, the fluids present in D2 dolomite from the Watts Bight Formation (below the BHD) have a range in compositions from high salinity (up to 25 eq. wt% NaCl) Ca-rich (X_{NaCl} of 0.14) fluids to lower salinity (12.4 eq. wt% NaCl), less calcic (X_{NaCl} of 0.28) brines (Fig 10b). This is consistent with fluid mixing between bittern brines similar to those identified in the D2 dolomite from above the BHD and a lower salinity NaCl-rich fluid.

The halide geochemistry of entrapped fluids in D2 dolomites above the BHD is consistent with genesis from evaporated seawater. These fluids are enriched in Br relative to Cl, with Cl/Br ratios significantly less than that of modern seawater (Fig. 5). This

418 suggests that these fluids formed from seawater that has evaporated to such a degree that
419 halite has precipitated from the solution, which resulted in the residual fluid (or bittern
420 brine) becoming enriched in Br (Carpenter, 1978). This is confirmed by the absolute
421 concentrations of Cl and Br in these samples, which show that these fluids originated as
422 bittern brines which may been partially diluted by meteoric waters (Fig. 6).
423 The Cl/Br ratios of D2 dolomites below the BHD are greater than modern seawater (661
424 to 935; Fig. 5). This suggests that these fluids are not post-evaporitic brines (Chi and
425 Savard, 1997) and fluids with Cl/Br ratios greater than seawater are generally assumed to
426 have a component which is derived from the dissolution of halite (Walter et al., 1990;
427 Kesler et al., 1995). However, fluids associated with halite dissolution are commonly Mg
428 poor, as co-precipitation of Mg^{2+} with NaCl is negligible (McCaffery et al., 1987), and
429 are, therefore, unlikely to be associated with the dolomitization of significant volumes of
430 rock. Therefore an alternative source for the substantial volumes of Mg^{2+} for
431 dolomitization must be sought for these fluids. Dissolution of Mg-rich salts, including
432 polyhalite ($K_2MgCa_2(SO_4)_4 \cdot 2H_2O$) and carnallite ($K_2MgCl_3 \cdot 6H_2O$) is a possible source
433 of Mg^{2+} to these fluids (Warren, 2000). A number of previous studies have identified
434 chert nodules in these carbonates, the former possibly being of evaporitic in origin,
435 particularly where associated with the BHD (Pratt, 1979) and in the Aguathuna
436 Formation (Pratt and James, 1986). However, the rarity of these nodules indicates that
437 dissolution was of magnesium-rich salts was minor at most. Other possible sources for
438 magnesium-rich fluids include structural Mg^{2+} expelled during interactions with clay
439 minerals (e.g. illitization of clay minerals; Boles and Franks, 1979; Warren 2000) and

mafic to ultramafic igneous units. However no such water rock interactions were evident in the cation analyses of these fluids (see below).

Lavoie and Morin (2004) and Lavoie and Chi (2006, in press) noted that some Lower Silurian hydrothermal dolomites in Eastern Canada were spatially associated with Lower Ordovician ultramafic slivers and within-plate mafic volcanic units. Moreover, an empirical link between foreland basins and tectono-magmatic events at the continental margin of Laurentia with hydrothermal dolomitization has been proposed for the carbonates of the Middle-Upper Ordovician (Taconian foreland), Silurian (Salinic foreland) and Lower Devonian (Acadian foreland) (Lavoie and Chi, in press; Lavoie et al., in press a). Although magmatic fluids generally have low Mg:Ca rations (<0.47; Smith et al., 1995; Graser et al., 2008), they are capable of dolomitization at the elevated fluid temperatures encountered in hydrothermal dolomites (Hardie 1987; Lavoie et al, in press a). Magmatic processes may also enhance convective circulation of dolomitizing fluids in sedimentary basins, and Lavoie and Chi (in press) considered that magmatic activity associated with active foreland basins (e.g. Western Newfoundland during the Ordovician) are likely to be associated with the development of HTD reservoirs. Therefore, magmatic fluids are considered a possible source for Mg^{2+}-rich fluids associated with hydrothermal dolomitization below the BHD.

D3 Dolomite

Dolomitizing fluids associated with D3 saddle dolomites from both the Port au Port and Port aux Choix peninsula are characterised by similar microthermometric characteristics and bulk fluid geochemistry. Primary fluid inclusions in D3 dolomites are $CaCl_2$ rich fluids (X_{NaCl} of 0.22 to 0.34) with a narrow range of T_H values (111 ± 15°C). These fluids

are similar to high salinity (up to 30 eq. wt% NaCl) $CaCl_2$-rich mineralizing fluids associated with MVT mineralization in the Appalachian Basin, including the Daniels Harbour Pb-Zn mine in Western Newfoundland (Lane, 1990; Appold et al., 1995). All bulk fluid analyses from the Aguathuna, Catoche and Boat Harbour formations have Cl/Br ratios of 305, suggesting that these fluids also originated as bittern brines. However, absolute Cl and Br concentrations indicate that these fluids formed from the mixing of brines with dilute fluids, such as meteoric water (Fig. 6), consistent with the wide range of salinities of D3 fluids (1.7 to 26.2 eq. wt% NaCl). Bulk fluid analyses of sphalerite from the Daniel Harbour mine also show evidence of mixing between high salinity bittern brines and low salinity, possible meteoric, fluids (Kessler et al. 1996). The similarities in the microthermometric characteristics and bulk fluid composition support the link between D3 dolomitization and MVT mineralization in Western Newfoundland.

C3 Calcite

Fluids associated with C3 calcite precipitation are also Ca-rich brines, with Cl/Br ratios lower than modern seawater (371 to 538) indicating that these fluids formed from evaporated seawater. However microthermometric analyses show that these fluids have a wide range X_{NaCl} (0.1 to 0.54) and salinities of 17.9 to 22.8 eq. wt% NaCl (Fig. 10d), consistent with either mixing between Ca-rich and Na-rich fluids or multiple episodes of late-stage calcite precipitation. Based on bulk fluid analyses, which show that included fluids in C3 calcite from the Boat Harbour and Watts Bight formations are geochemically distinct, it is likely that C3 calcite represent a number of separate episodes of calcite precipitation in Western Newfoundland. This is consistent with trace element

geochemistry and CL petrography from C3 calcites (Azmy et al., 2008, 2009; Conliffe et al. 2009).

Evidence for Water-Rock Interactions along the Flow Path

Unlike geochemically conservative anions, the concentrations of reactive cations (Na, K and Li) are easily altered during interaction with the host rocks (Banks et al., 2002) and therefore are useful in determining the extent and type of water-rock interactions. In Figure 7 it is shown that D2 samples from the Port au Port Peninsula (Aguathuna, Boat Harbour and Watts Bight formations) are enriched in K relative to samples from Catoche Formation on the Port aux Choix Peninsula. Although the exact cause of this K enrichment is unclear, it is possibly due to water-rock interactions (e.g. albitization of K-feldspars; Banks et al., 2002). The variability of K enrichment from the Port au Choix to the Port au Port Peninsula may reflect variations in the local geology; with dolomitizing fluids on the Port au Port Peninsula flowing along fault conduits through the clastic sediments of the Goose Tickle Group (see Cooper et al., 2001, pg 412).

With the exception of a single sample from the Watts Bight Formation, all other samples have relatively low Li (Li/Na of <0.0006). Micas are a major reservoir for crustal Li (Banks et al., 2002), and therefore the low Li content of these fluids suggests that the effects of any interaction with clay minerals is generally minimal when compared with other studies (e.g. Gleeson and Turner, 2007; Vandeginste et al., 2009).

The dolomitizing fluids associated with D3 dolomite precipitation are depleted in K and Na relative to the evaporitic composition of modern-day seawater, which may be related to albitization of Ca-bearing feldspars, as has been observed in previous studies (e.g. Gleeson and Turner, 2007). This is in contrast to D2 dolomites from the Port au Port

Peninsula, and suggests that D3 dolomitizing fluids on the Port au Port Peninsula had a different evolution or flow path from that of D2 dolomitizing fluids.

Implication for the HTD exploration model in Palaeozoic Appalachian Basins

Although petroleum fluid inclusions have not been recorded in D2 or D3 dolomite, D2 dolomite rhombs are commonly coated by a bituminous material (Conliffe et al. 2009), indicating that petroleum migration may have occurred after D2 dolomitization, and therefore the St. George Group dolomites are potential hydrocarbon reservoirs. Significant accumulations of petroleum in dolomite reservoirs have been recorded in the Palaeozoic Appalachian Basins of eastern Canada and the northeastern United States (e.g. the Upper Ordovician Trenton Black River Group in south-central New York, the Lower Ordovician Garden Hill oil field on the Port au Port peninsula in western Newfoundland and the Lower Devonian Galt gas field on Gaspé Peninsula, Quebec) and an HTD exploration model for these reservoirs has been proposed by a number of studies (e.g. Cooper et al., 2001; Smith, 2006). However the application of the HTD exploration model in the Appalachians remains controversial and the definition of dolomite reservoirs as hydrothermal has been the subject of a number of criticisms (Machel and Lonnee, 2002, 2008; Lonnee and Machel, 2006; Friedman, 2007). The recognition of hydrothermal dolomite reservoirs must be based on integration of fluid inclusion homogenization temperatures with documented geothermal and/or burial histories (Machel and Lonnee, 2002; Davies and Smith, 2006). Most fluid inclusion homogenization temperatures from matrix and saddle dolomites in the Appalachians range from 80 to 170°C and are greater than maximum burial temperatures, consistent with the description of these dolomites as hydrothermal in origin (Lavoie et al., 2005;

Smith, 2006; Lavoie and Chi, in press; this study). Therefore, both matrix and saddle dolomites are here considered to be hydrothermal in origin, although they are not necessarily cogenetic.

HTD dolomite reservoirs in the Appalachian Basins are characterised by multiple phases of dolomitization, with early matrix dolomitization (similar to D2 dolomitization) followed by later saddle dolomite precipitation (D3 dolomite). Saddle dolomite is commonly associated with Mississippi-Valley type mineralization in the Appalachian Orogen (Kesler and van der Pluijm 1990). In addition, fluid inclusions and geochemical evidence highlights similarities between fluids responsible for dolomitization, which have a $MgCl_2$-$CaCl_2$-NaCl brine composition and similar stable isotope characteristics (Smith, 2006; Azmy et al., 2008, 2009; Conliffe et al., 2009; Lavoie and Chi, in press). The simplest interpretation of the geological and geochemical similarities between these hydrothermal dolomites in the Appalachians is that they are either coeval, or at least represent hydrothermal dolomitization via comparable processes. Therefore, a HTD exploration model may be applicable in Western Newfoundland, throughout the Appalachian and Michigan Basins and in other active foreland basins.

The exact timing of these hydrothermal fluid influxes in Western Newfoundland is unknown. Kesler and van der Pluijm (1990) argued that MVT mineralization in the Appalachians, including mineralization at Daniels Harbour, predates late Devonian deformation and therefore hydrothermal dolomitization must have occurred between the Middle Ordovician and the Middle Devonian. Rb-Sr dating of the MVT mineralization at Daniels Harbour, Western Newfoundland proved inconclusive (Nakai et al., 1993). However Rb-Sr dating of MVT deposits in elsewhere in the Appalachians yielded

Devonian ages (347 ± 20 Ma and 377 ± 29 Ma; Nakai et al., 1993), and based on the geological and geochemical similarities between MVT deposits throughout the Appalachian Basin (Kesler and van der Pluijm, 1990; Kesler et al. 1996) MVT mineralization in Daniels Harbour (and D3 dolomitization) may also be Devonian in age. D2 matrix dolomitization predates D3 dolomitization, and therefore it must have occurred between the Middle Ordovician and the Devonian. Smith (2006) argued that matrix dolomitisation in the Middle-Upper Ordovician Trenton-Black River (TBR) groups in New York was early in the burial history, as most of the faults associated with dolomitisation were active during the Ordovician and were sealed off by the Upper Ordovician Utica Shale that stratigraphically overlies the TBR. In the Appalachian basin, only minor evaporite nodules have been recorded in Ordovician strata and therefore the large volume of Mg^{2+} for the proposed early matrix dolomitization has to originate form a non-evaporite source. Late Silurian evaporites are preserved in the Michigan basin (Coniglio et al., 1994), but given the interpreted early origin of the dolomitization for the Trenton carbonates (Davies and Smith, 2006), they likely did not source the magnesium for the dolomitization. The potential for fluids derived from or having chemically exchanged with the underlying Precambrian basement is currently touted by some research groups (Selleck, 2006). . The same fundamental problem of Mg^{2+} source for the St. George Group D2 and D3 dolomites exists if an Ordovician dolomitization event is assumed. However, in Western Newfoundland, the Devonian basins show evidence of periodic episodes of evaporation (Burden et al., 2002), providing a possible source of post-evaporitic brines that could have provide the magnesium for both D2 and D3 dolomitization if a Devonian age for dolomitization is confirmed. These Mg-rich brines

could have been drawn into the underlying sediments via brine reflux, where dense hypersaline brines displace the less dense waters in underlying sediments and seep downwards into the basin. Saline fluids would have subsequently been entrained in hydrothermal convection cells (driven by Devonian igneous activity associated with the Acadian orogeny), possible with some input of magmatic fluids. HTD reservoirs in western Newfoundland are spatially associated with major extensional faults, which were active in the Devonian (e.g. the Garden Hill discovery in the footwall the high angle Round Head Fault; Cooper et al., 2001), and both matrix and saddle dolomites are commonly associated with local fault networks (Knight et al., 2007). Therefore, these major extensional faults are considered to be the main conduits for dolomitising fluids in the St. George Group carbonates (as suggested by Cooper et al., 2001). Some significant differences (petrography, abundance of dolomite phases, Sr isotopes) have been recorded between hydrothermal dolomite reservoirs in the Ordovician of eastern Canada (e.g. between heavily tectonized western Newfoundland successions and the little deformed Anticosti Basin; Lavoie et al., 2005; Azmy et al., 2009), these could be attributable to the very different tectonic framework or possibly to a different timing of dolomitization that proceeded from different fluids. Analyses of Mg isotopes from interpreted hydrothermal dolomites of various ages and tectonic settings are currently being carried out, with the ultimate goal to identify the source of magnesium needed for the huge volume of high temperature dolomites in the Appalachian Basin (Lavoie et al., in press b). Nonetheless, the hydrothermal dolomitization model proposed here is analogous to models proposed in the northeastern United States (e.g. Smith, 2006) and eastern Canada (Lavoie and Chi, in

press), and points to regional scale hydrothermal dolomitization throughout the Appalachian Basin.

Conclusions

On the basis of fluid inclusion microthermometry and bulk fluid inclusion (anion and cation) analyses, matrix and saddle dolomites in western Newfoundland can be classified as hydrothermal in origin (according to the definition of Machel and Lonnee, 2002 and Davies and Smith, 2006). Bulk fluid analyses indicated that the majority of dolomitizing fluids were post-evaporitic in origin, with some input of Cl enriched fluids below the BHD, which eliminates the mass balance problems envisioned by Machel and Lonnee (2002). We propose that dolomitization was associated with the drawdown of post-evaporitic brines from overlying basins via brine reflux (possibly Devonian). These fluids were then entrained in hydrothermal convections cells driven by magmatic activity (possibly with some input of magmatic fluids), and major extensional faults were the main conduits for dolomitising fluids. The secondary porosity development associated with hydrothermal dolomitization would have facilitated the accumulation of petroleum, and similar settings must be considered prime targets for future HTD exploration, both in Western Newfoundland and elsewhere in the Appalachian Basin. These data also show that the HTD exploration model may be applicable in other post-orogenic extensional basins, with associated drawdown of post-evaporitic brines and magmatic driven hydrothermal fluid flow along extensional faults.

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Figures

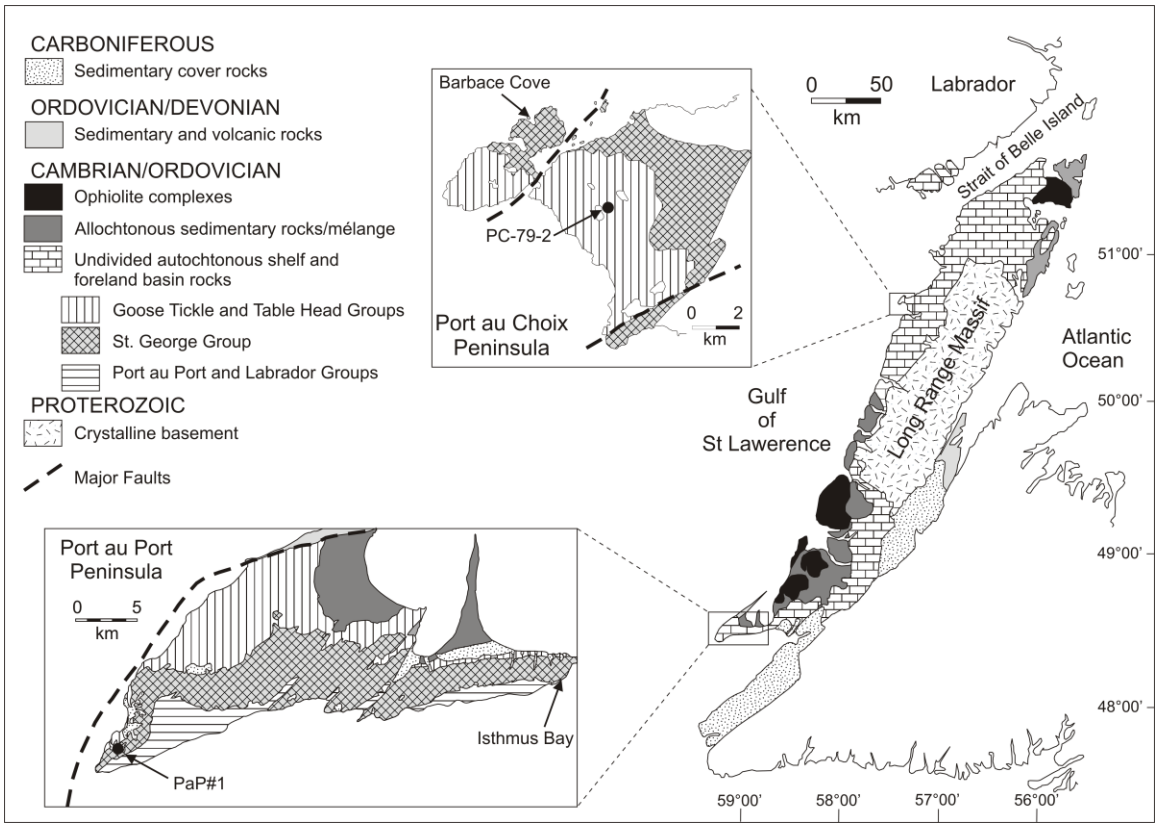

Figure 1: Simplified map of the geology of Western Newfoundland, with insets showing the geology of the Port au Port and Port aux Choix peninsulas (adapted from Zhang and Barnes, 2004 and Knight et al., 2007)

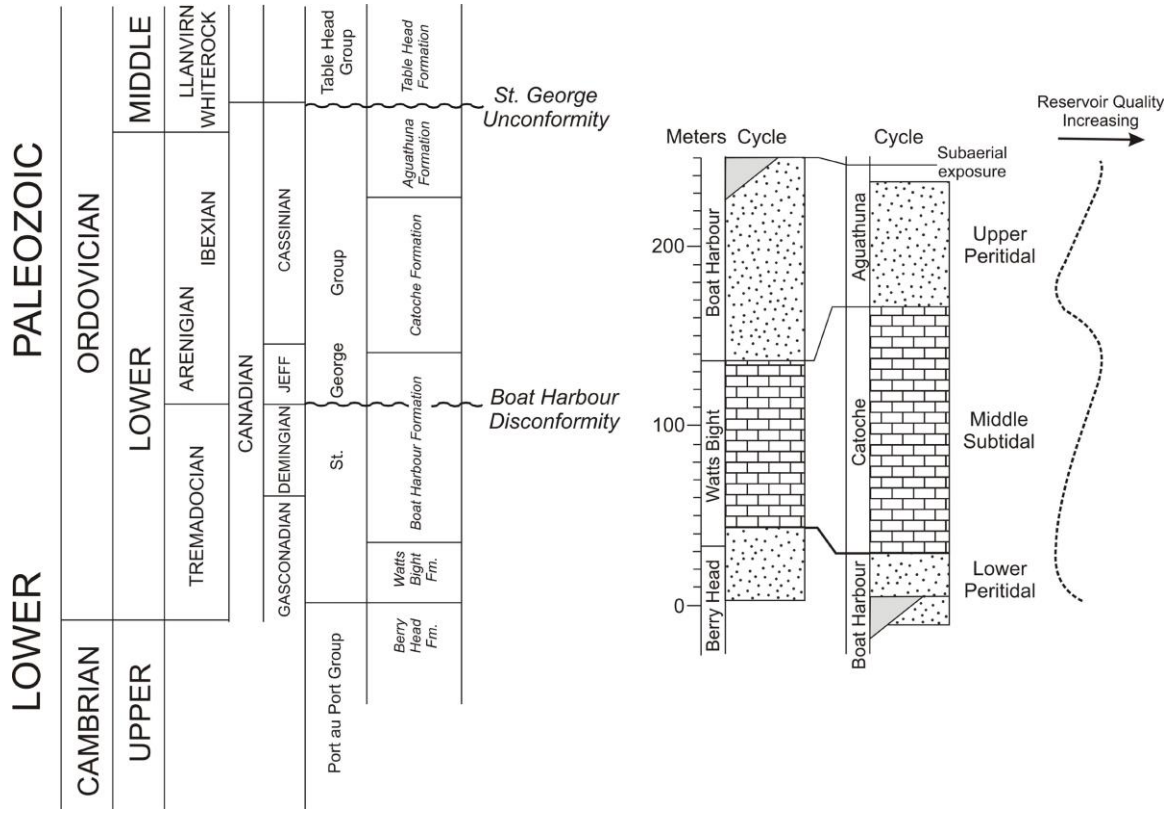

Figure 2: Generalized stratigraphic section of the St George Group, including distribution of subtidal and peritidal cycles (from Knight and James, 1987)

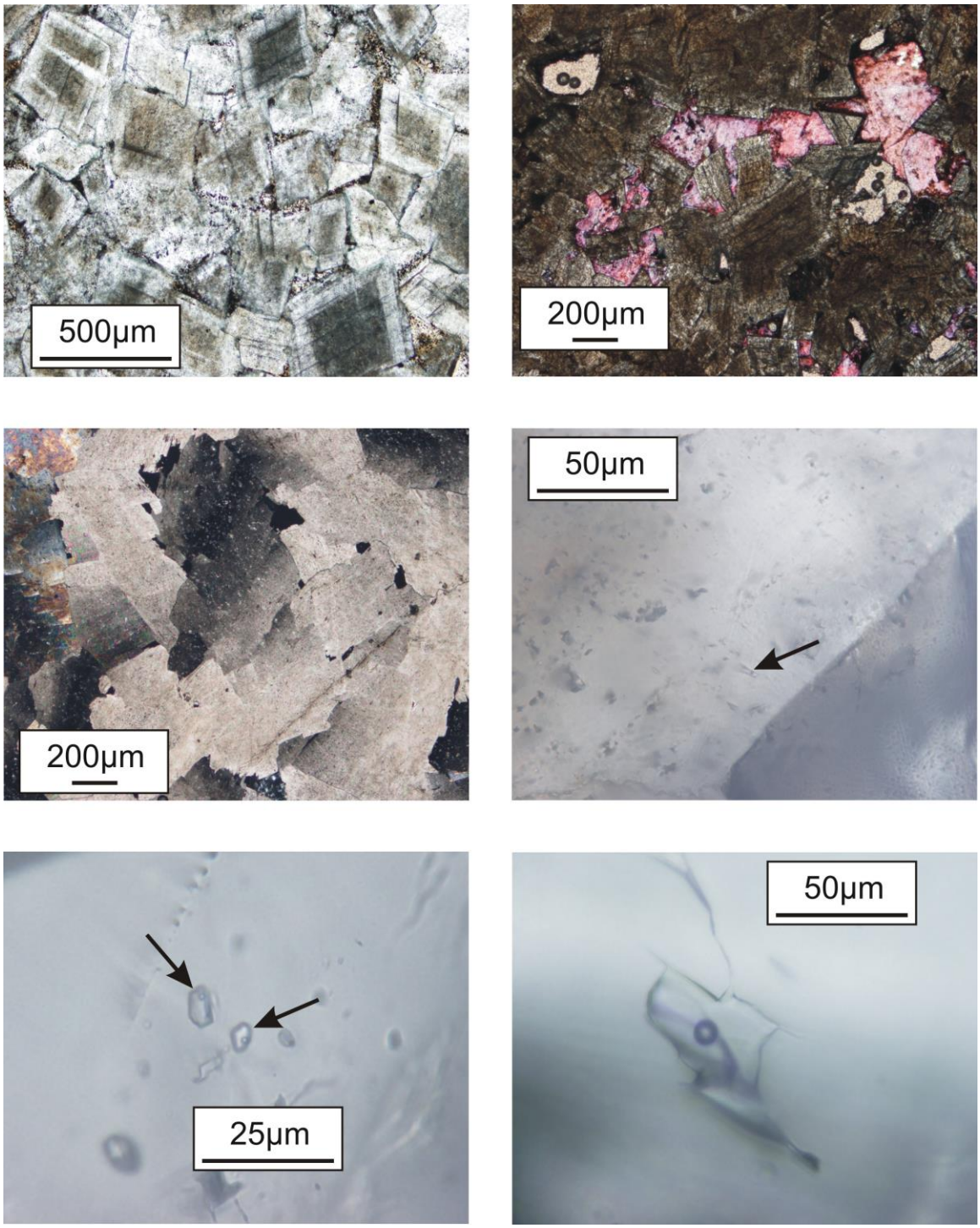

Figure 3: Photomicrographs from the St. George Group Carbonates. (a) Zoned D2 dolomite rhombs; (b) Stained thin section showing Fe-poor (pink) and Fe-rich (purple) C3 infilling pores between D2b rhombs; (c) D3 saddle dolomite, showing undulose extinction; (d) Biphase inclusions in D2 dolomite rhomb. Note inclusion is elongate in the direction of growth of the dolomite rhomb; (e) Biphase inclusions in D3 dolomite; (f) Large biphase inclusion in C3 calcite

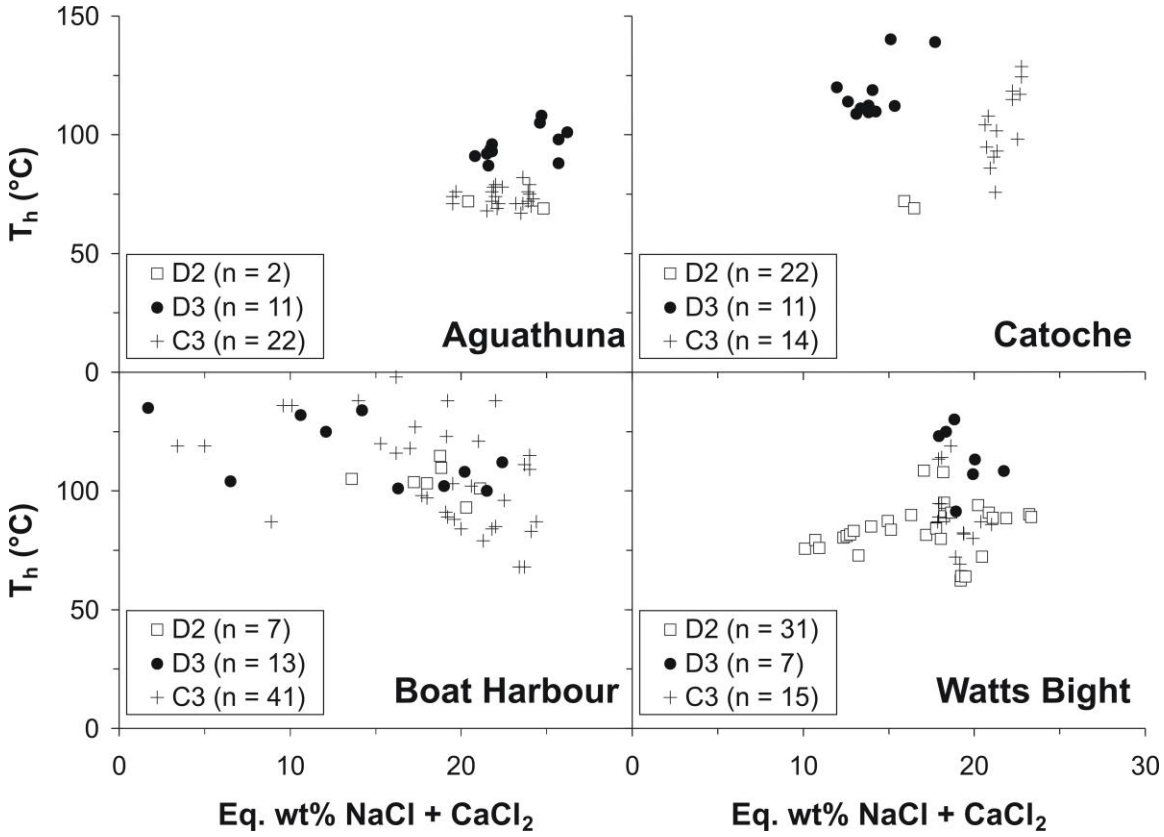

Figure 4: Bivariate plot of homogenization temperature vs. salinity for fluid inclusions in the D2 and D3 dolomites and C3 calcite of the Aguathuna, Catoche, Boat Harbour and Watts Bight formations

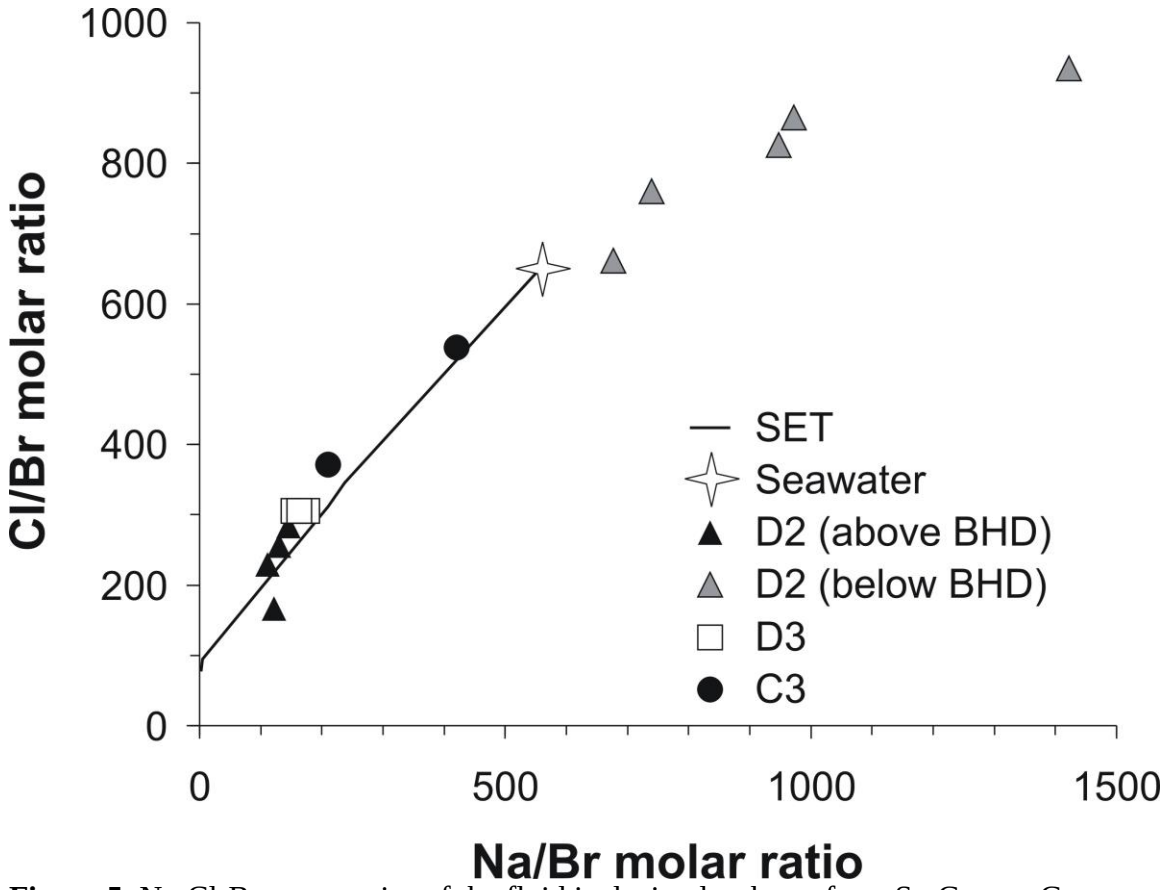

Figure 5: Na-Cl-Br systematics of the fluid inclusion leachates from St. George Group carbonates. Seawater evaporation trajectory (SET) after McCaffrey et al., 1987. With the exception of D2 samples from below the BHD, samples sit on or close to the SET.

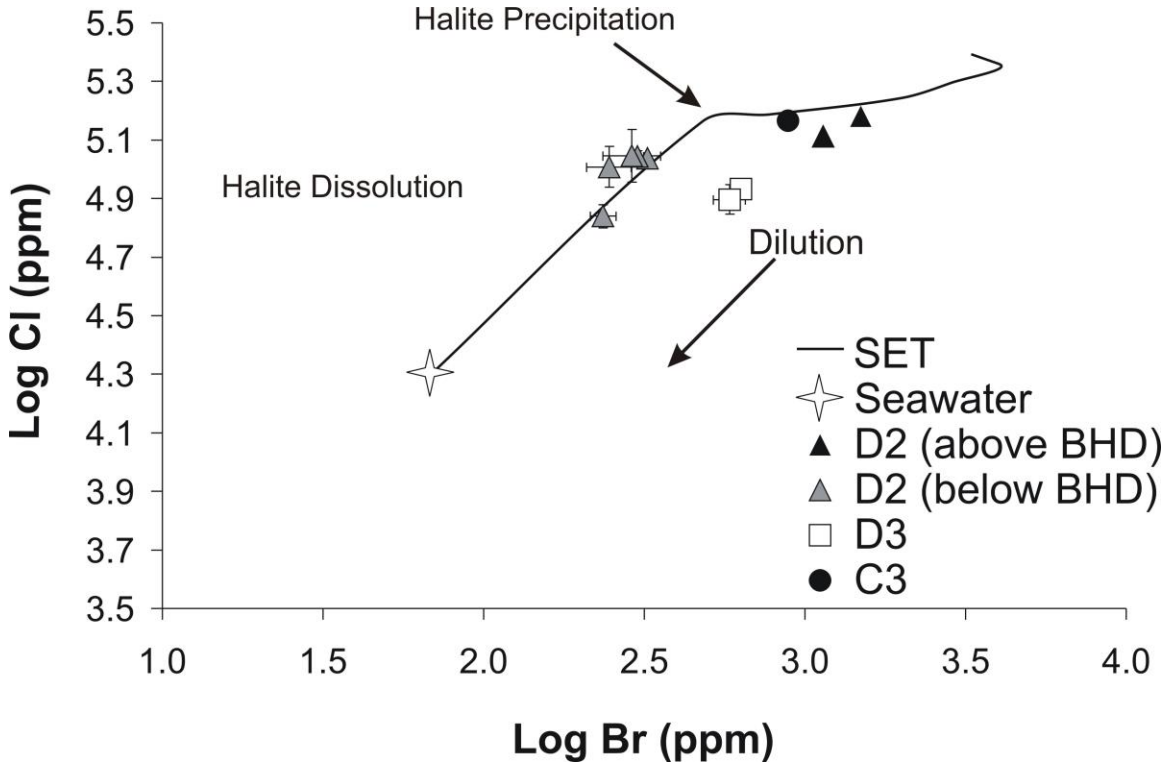

Figure 6: Calculated halogen compositions for D2 (above and below the BHD), D3 and C3 samples. Points are calculated using the mean salinity for each sample, with error bars representing the range of compositions possible using microthermometric data. The data for the Seawater Evaporation Trajectory are from the compilation of Fontes & Matray (1993)

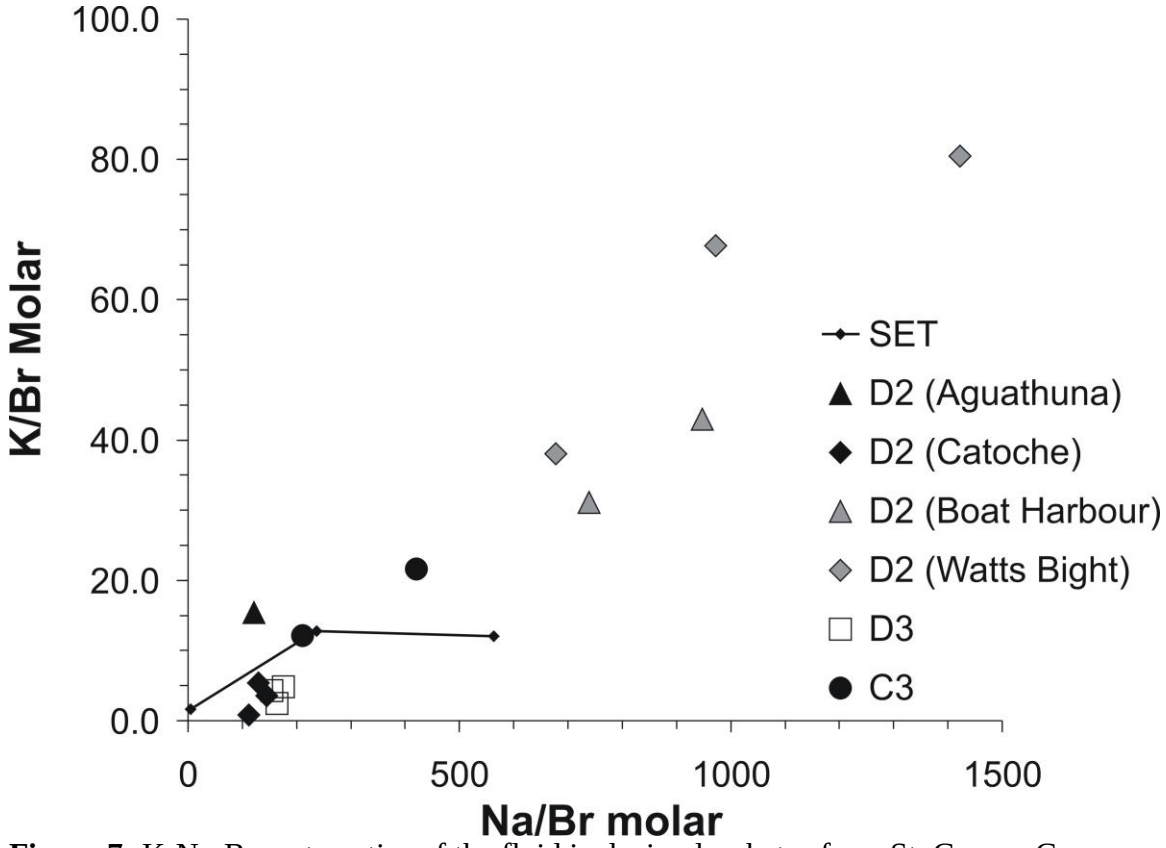

Figure 7: K-Na-Br systematics of the fluid inclusion leachates from St. George Group carbonates, showing wide variety of K/Br and Na/Br ratios between samples. The data for the SET come from Fontes & Matray (1993)

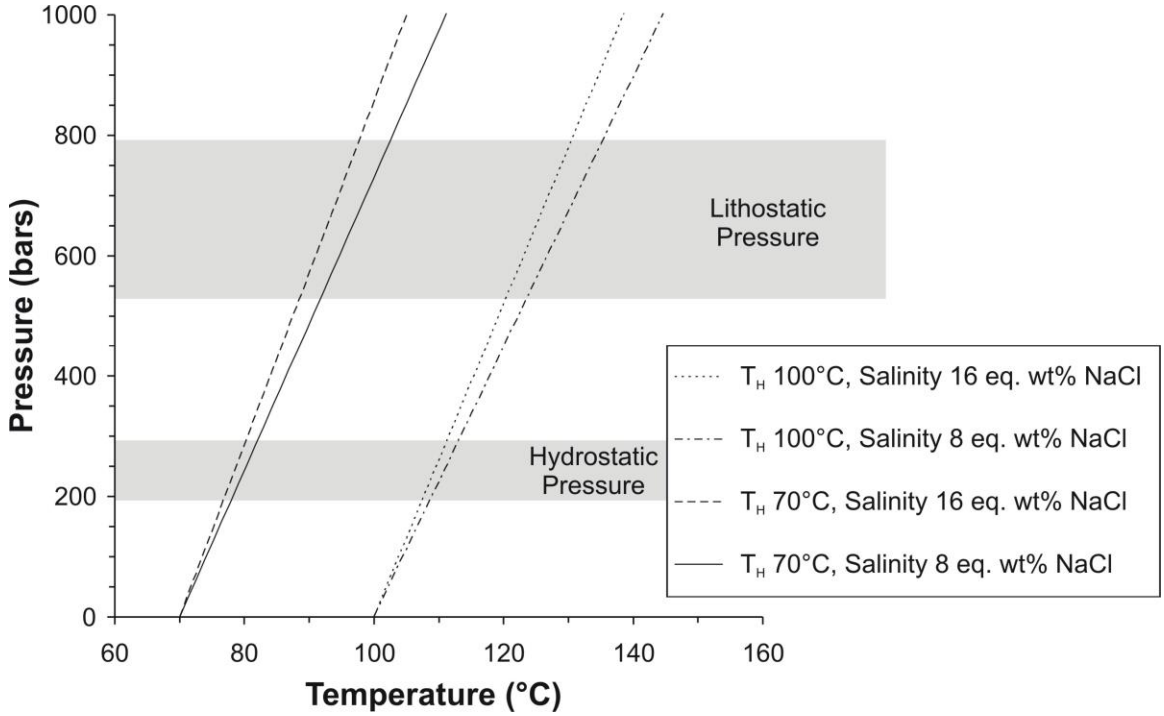

Figure 8: Calculated fluid inclusions isochores for 8 and 16 eq. wt% NaCl fluids trapped at 70 and 100°C. Isochores constructed using the FLUIDS software package (Bakker, 2003). Trapping pressures of 530 to 795 bars for lithostatic pressures and 196 to 294 for hydrostatic pressures calculated using maximum burial depths of 2-3km (Williams et al., 1998)

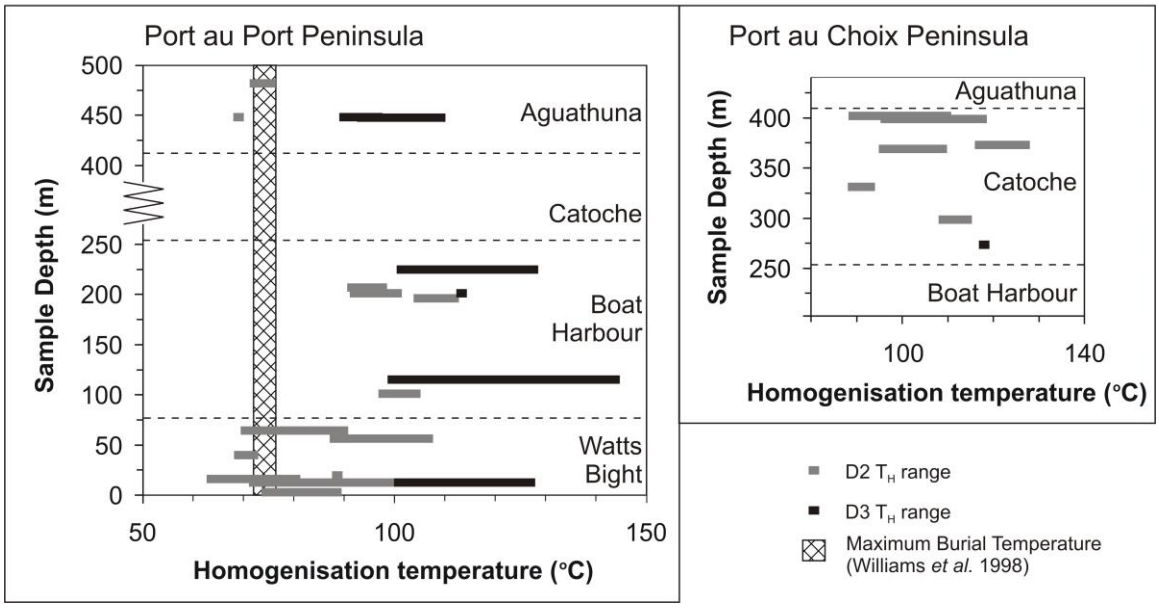

Figure 9: Fluid-inclusion homogenization temperature for D2 and D3 dolomites vs. maximum burial depth from the Port au Port and Port aux Choix Peninsulas. Maximum burial temperatures indirectly estimated CAI, AAI and GRo (Nowlan and Barnes, 1987; Williams et al., 1998)

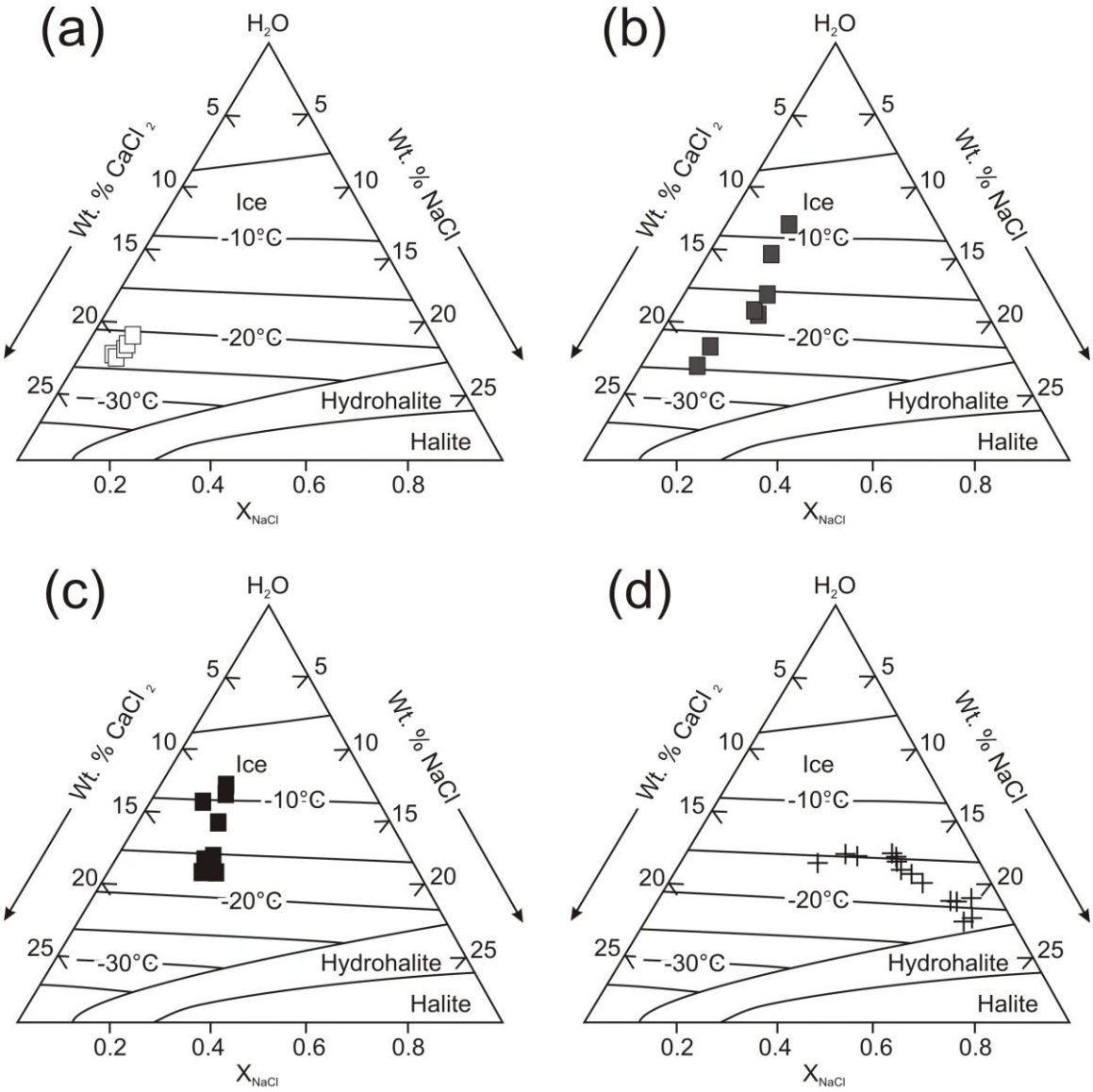

Figure 10: Fluid inclusion compositional data (calculated from T_m(hh) and T_m(ice)) plotted on the NaCl- $CaCl_2$-H_2O ternary plot after Oakes et al. (1990) (a) D2 above BHD; (b) D2 below BHD; (c) D3; (d) C3

882 **Table 1:** Summary of the microthermometric data from D2, D3 and C3 carbonates in the St.
883 George Group. [1] Azmy et al. (2008). [2] This study. [3] Azmy et al. (2009). [4] Conliffe et al.
884 (2009).

	Sample ID	T_i (ºC)	T_m(hydrohalite) (ºC)	T_m(ice) (ºC)	Salinity (eq. wt% NaCl)	T_h (L) (ºC)
Aguathuna[1]						
D2	R1-116			-17.4	20.4	69 to 78
D3	R1-147.8	-66 to -53		-31.3 to -17.4	20.4 to 26.2	87 to 101
	R1-148	-62 to -58		-26.2 to -17.4	21 to 24.7	91 to 108
C3	R1-102	-60 to -53		-24.5 to -16.1	19.5 to 24.2	67 to 79
	R1-116	-62 to -50		-24.4 to -20	22.4 to 24.1	64 to 82
Catoche[2]						
D2	MG401					109 to 114
	MG41	-55.3		-20.7 to -13.6	17 to 21.5	87 to 95
	MG44	-50.1		-15.2 to -12.2	15.9 to 18	85 to 121
	MG13	-84.3 to -75				93 to 122
	MG17	-54.2 to -55	-43.9 to -39.9	-24.8 to -18	19.7 to 23.1	114 to 134
D3	MG108	-54.4 to -51.8	-31 to -30.8	-14.6 to -7.8	12 to 17.7	109 to 140
C3	MG401	-55.2 to 51.2		-24 to 19.7	20.6 to 22.8	72 to 129
Boat Harbour[2,3]						
D2	BH-35A			-16.4 to -14	17.2 to 18.8	103 to 117
	BH-38A					90 to 102
	BH-42					90 to 99
	BH-A13	-50 to -48		-18.2 to -9.6	13.6 to 21.1	93 to 105
D3	BH-38A	-57 to -52		-20.1 to -8.3	12.2 to 22.4	100 to 134
	BH51-VC			-4.5 to -1	1.7 to 6.5	104 to 135
	BH-A19-2			-10.2 to -7.1	10.6 to 14.2	132 to 134
C3	BH-34			-25.4 to -19.4	22 to 24.4	68 to 87
	BH-35A	-53 to -50		-24 to -14.3	18 to 24	84 to 115
	BH-46	-49		-19.5 to -12.2	16.2 to 22	103 to 182
	BH-51-VC-2	-52 to -49		-20.2 to -5.7	8.9 to 22.5	79 to 123
	BH-A13			-18.1 to -2	3.4 to 21	119 to 138
	BH-A19-2	-57 to -49		-21.2 to -2	3.4 to 22	118 to 168
Watts Bight[2,4]						
D2	WB-9	-55.2 to -53.8	-31.9	-8.8 to -6.2	10.1 to 12.9	76 to 83
	WB17	-51.4		-15.3 to -13.7	17.1 to 18.2	82 to 109
	WB24			-16 to -9.1	13.2 to 18.6	70 to 95
	WBA2		-39.1 to -38.5	-25 to -22.1	21.9 to 23.3	87 to 90
	WBA4	-54.5 to -51.3	-33.7 to -33.2	-17.4 to -8.4	12.5 to 19.5	62 to 90
	WBA6A					60 to 108
	WBA10A	-55 to -53.1	-33.5 to -32.4	-20.1 to -9.9	14 to 21.8	69 to 94
D3	WBA6A	-52 to -50.2	-31.5 to -30.2	-21.3 to -14.7	17.8 to 21.7	91 to 130
C3	WB-9					99 to 127
	WB17	-55.2 to -52.3		-16.8 to -14.8	17.9 to 19.2	68 to 95
	WB24			-20.1 to -19	20.4 to 21	84 to 87
	WBA2	-51.3 to -51		-18.2 to -17	19.4 to 19.9	80 to 84
	WBA6A	-51.1		-15.6 to -14.7	17.9 to 18.6	114 to 119

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886 **Table 2:** Leachate analyses from the St. George Group carbonates. All the data are in
887 ppm, samples that were analysed but yielded data below the detection limits of the
888 techniques are indicated by "< detection limit value".

Sample ID	Formation	Mineral	Cl	Br	F	SO_4	Na	K	Li
RI162	Aguathuna	D2	41.10	0.55	0.21	2.89	19.41	4.19	<0.004
MG13	Catoche	D2	438.85	4.31	<0.008	1.44	138.32	1.64	0.02
MG17	Catoche	D2	215.10	1.89	<0.008	2.91	70.95	4.97	0.01
MG33	Catoche	D2	163.50	1.30	<0.008	1.18	54.15	2.24	0.01
BH35	Boat Harbour	D2	47.21	0.13	0.26	1.31	35.06	2.69	0.01
BHA13	Boat Harbour	D2	44.46	0.12	0.10	1.90	32.38	3.82	<0.004
WB9	Watts Bight	D2	56.71	0.19	0.17	1.89	37.63	3.58	0.01
WBA3	Watts Bight	D2	62.61	0.19	0.52	3.80	39.43	2.81	0.02
WBA4	Watts Bight	D2	43.30	0.10	0.27	2.57	42.64	4.09	0.01
RI202	Aguathuna	D3	85.88	0.63	<0.008	0.81	32.03	1.48	<0.004
MG114	Catoche	D3	128.83	0.95	<0.008	1.21	42.09	1.99	<0.004
BHD34.1	Boat Harbour	D3	107.35	0.79	<0.008	1.01	37.22	0.97	<0.004
BH34.2	Boat Harbour	C3	171.91	1.04	<0.008	0.31	63.10	6.18	<0.004
WB20	Watts Bight	C3	40.38	0.17	0.12	1.67	20.42	1.78	<0.004

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891 **Table 3:** Molar ratio data for the minerals sampled from the St. George Group
892 carbonates. The charge balance calculation is discussed in the text

Sample ID	Formation	Mineral	Charge Balance	Cl/Br (molar)	SO_4/Br (molar)	K/Na (molar)	Na/Br (molar)	K/Br (molar)	Li/Na (molar)
RI162	Aguathuna	D2	0.8	167	6.3	0.37	122	15.5	-
MG13	Catoche	D2	0.5	229	0.4	0.02	112	0.8	0.0006
MG17	Catoche	D2	0.5	256	1.8	0.12	130	5.4	0.0004
MG33	Catoche	D2	0.5	284	1.1	0.07	145	3.5	0.0004
BH35	Boat Harbour	D2	1.2	827	12.2	0.13	948	38.0	0.0005
BHA13	Boat Harbour	D2	1.2	865	19.7	0.20	972	31.1	-
WB9	Watts Bight	D2	1.0	661	11.7	0.16	677	42.9	0.0006
WBA3	Watts Bight	D2	1.0	761	24.6	0.12	739	67.7	0.0015
WBA4	Watts Bight	D2	1.5	935	29.6	0.16	1422	80.5	0.0006
RI202	Aguathuna	D3	0.6	305	1.53	0.08	176	4.3	-
MG114	Catoche	D3	0.5	305	1.53	0.08	154	4.8	-
BHD34.1	Boat Harbour	D3	0.5	305	1.53	0.04	163	2.5	-
BH34.2	Boat Harbour	C3	0.6	371	0.4	0.17	210	12.1	-
WB20	Watts Bight	C3	0.8	538	11.9	0.15	420	21.6	-

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