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**In situ geochemical characterization of pyrite crystals in burial
dolomites of St. George Group carbonates**

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**Key words: Pyrites, Sulfur isotope, Secondary Ion Mass Spectrometry (SIMS), Bacterial
Sulfate Reduction, Thermochemical Sulfate Reduction, Bitumen, dolomite.**

ABSTRACT

Secondary Ion Mass Spectrometry (SIMS) was used to measure the $\delta^{34}\text{S}$ of pyrite disseminated in burial dolomite matrix of Boat Harbour formation at Main Brook and Daniel's Harbour (about 130km apart). At Main Brook, $\delta^{34}\text{S}$ values for the pyrite grains show wide variation (-15 to +20 ‰ ($n = 20$), but are mostly negative. Combined with a paucity of two-phase fluid inclusions in the host burial dolomite, the depleted $\delta^{34}\text{S}$ values suggest that the pyrite is a direct product of bacterial sulfate reduction (BSR). Predominantly negative $\delta^{34}\text{S}$ values was also obtained for sampled pyrite at Daniel's Harbour and Port au Choix, however relatively high homogenization temperatures ($>100^\circ\text{C}$) of two-phase fluid inclusions in the host dolomite is incompatible with a BSR process for pyrite formation. More so, Daniel's Harbour is a site for main stage sulfide mineralization (MVT system), hosted in similarly burial dolomite and that has been previously constrained to be associated with thermochemical sulfate reduction (TSR). A relative proximity of the currently studied pyrite samples to this MVT system deposit is thus inconsistent with an in-situ BSR for these pyrites. The analyzed pyrite grains are commonly encased in bitumen, post-date their host burial dolomite and pre-date deep burial saddle dolomite. Taken together, the depleted $\delta^{34}\text{S}$ signature in the pyrite was likely inherited from migrated hydrocarbons in the reservoir. Incursion of an initial pulse of hot sulfate-rich brine into the formation can cause thermal cracking of hydrocarbons, thereby releasing its low $\delta^{34}\text{S}$. Thus the inherited low $\delta^{34}\text{S}$ signature was likely a product of an earlier BSR that occurred in the kerogen or source organic materials in source rock. Subsequently, the main stage sulfide mineralization (Mississippi Valley Type deposit) occurred via in-situ TSR. These findings have an implication for the paragenetic history of sulfide minerals precipitated during MVT-type mineralization episode.

1. INTRODUCTION

The application of ion microprobe (i.e Secondary Ion Mass Spectrometry, SIMS) technique to in situ microanalysis of sulfur isotope ratios in sulfides is becoming increasingly popular (see Riciputi et al., 1996; Kohn et al., 1998; King et al 2014; Mathieu et al., 2015; Magnall et al., 2016; Gadd et al., 2017). This technique is particularly useful for sampling micrometer sized sulfide grains and those characterized by intragranular sulfur isotope zoning (Kohn et al., 1998).

The study of sulfur isotope ($\delta^{34}\text{S}$ ‰VCDT) variability is a key method for constraining the origin of sulfide minerals (e.g., Seal, 2006; Drake et al., 2015; Magnall et al., 2016; Gadd et al., 2017 and references therein), as well as hydrocarbon migration and alteration in sedimentary basins (e.g., Orr, 1977; Cai et al., 2010; King, 2014 and references therein). Notably, mass-dependent fractionation process of the ^{34}S variation in sulfide minerals (e.g., pyrite) is associated with formation of these minerals from their cogenetic sulfate/s (e.g., Canfield, 2001; Seal, 2006). In a sedimentary setting, this can be kinetically achieved by bacterial sulfate reduction (BSR) or thermochemical sulfate reduction (TSR) in the presence of organic materials which act as a reductant (Berner et al., 1985; Machel, 2001) (See Eqns. 1 and 2 below).

Bacteria mediation, which enhances low-temperature reaction rates during redox reactions contributes significantly to isotopic fractionations. Specifically, fractionation of sulfur isotope via BSR yields a significant ^{34}S depletion in the produced sulfide mineral relative to its sulfate source(Seal, 2006). However, the extent of such depletion depends on sulfate availability in and temperature of the local reaction site (Canfield, 2001). Alternative to BSR, the abiogenic TSR occurs at a higher temperature ($>100^{\circ}\text{C}$; Goldstein and Aizenshtat, 1994; Machel, 2001; Cross et al., 2004) and results in a lower degree of ^{34}S fractionation than BSR ($<10\%$ for TSR versus 16 to 66‰ for BSR; Habicht and Canfield, 1997; Canfield, 2001; Seal, 2006; Sim et al., 2011).

65 $2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-$ (BSR,).....1

66 $\text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+$2

67 To better understand the origin of pyrite, this study used ion microprobe (SIMS) to measure the
68 $\delta^{34}\text{S}$ of pyrite grains disseminated in burial dolomite of Boat Harbour Formation at Main Brook
69 and Daniel's Harbour localities, about 130km apart.

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2. DOLOMITIZATION OF ST. GEORGE GROUP

CARBONATES

The St. George Group located in western Newfoundland, Canada (Fig. 1) consists of Lower Ordovician carbonate mega-sequences deposited during the rifting phase of the Iapetus Ocean (Cooper et al., 2001; Knight et al., 2007; 2008). From the base upwards, it consists of the Watts Bight, Boat Harbour, Catoche and Aguathuna Formations (Knight et al., 2007; 2008). The deposition of the mega-sequences is punctuated by 2 major disconformities, namely, Boat Harbour Disconformity (BHD) and the St. George disconformity (Knight et al., 2008).

The St. George Group carbonates have been affected by varying degrees of dolomitization (Azmy et al., 2008; 2009). Dolomitization commenced at the near surface and continued through burial; resulting in multi-phase dolomite that is common to all the formations of St. George Group (Azmy et al., 2008; 2009; Conliffe et al., 2012). In the Boat Harbour Formation, the early dolomite is finely (<4-30 μm) crystalline, fabric retentive and commonly stratiform. The mid-stage burial phase formed in intermediate burial environment (600 – 1000 m, sensu Machel, 2005) is pervasive and characterized by coarser (50-300 μm), euhedral to subhedral crystals with commonly fabric destructive textures (Olanipekun et al., 2014). Similarly, in the overlying Catoche Formation, the burial dolomitization of the carbonates at Port aux Choix Peninsula is extensive (Conliffe et al., 2012).

The late-stage dolomite consists of coarse and anhedral crystals (up to 3 mm) with sweeping extinction (saddle dolomite) and usually occur as cement filling vugs and fractures (Azmy et al., 2008; 2009; Conliffe et al., 2012; Olanipekun et al., 2014).

91 Rising geothermal gradients generated by structural thickening (Silurian - Devonian Acadian
92 orogeny, Cooper et al., 2001) of the crust probably caused warming of basinal fluids and release
93 of metals and sulfur from minerals in the sedimentary units and basement (Lane, 1990). The
94 incursion of this “hot” (140°C) brine through deep seated fractures into the St. George Group
95 carbonate sequence intensified dolomitization (Conliffe et al., 2012; Olanipekun et al., 2014),
96 and also marked the genesis of strata – bound sulfide mineralization (Lane, 1990) in western
97 Newfoundland. This mineralization episode resulted in major economic sphalerite deposit at the
98 Newfoundland Zinc Mines near Daniel’s Harbour in western Newfoundland. See Lane (1990)
99 for more detail on the origin of this sulfide mineralization and its association with
100 dolomitization.

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3. METHODOLOGY

Burial dolomite samples from depths of 154 m and 158 m were taken from drillholes 12P/1-12 (N51°08'23'', W56°10'54'') at Main Brook. They were taken from depth of 172 m from drill hole 12i/6-121 (N51°17'46'', W57°27'22'') at Daniel's Harbour (Fig. 1; Olanipekun et al., 2014), while they were taken from depths of 185 m, 216 m and 218 m from drill hole 12B/11 44 (N48°35'49'', W59°02'16'') at Port au Choix (Conliffe et al., 2012). Polished thin sections were prepared from these samples for microprobe analyses.

Samples were examined in FEI Quanta 400 SEM equipped with energy dispersive X-ray microanalytical system (EDX). This was used to constrain the sulphide mineral phases (pyrite, marcasite, sphalerite) in the samples. Subsequently, sulfur isotope analyses were performed on pyrite grains, using the Cameca IMS 4f Secondary Ion Mass Spectrometer at the MAF-IIC Microanalysis Facility at Memorial University of Newfoundland. All samples were sputter coated with 300 Å of Au, to mitigate charging under primary ion bombardment. They were bombarded with a primary ion beam of 850 -1200 pA of Cs⁺, accelerated through a 10 keV potential, and focused into a ~5–15 µm spot size. Each spot was first pre-sputtered for 120 seconds with a 25 µm square raster applied to the beam then pre-sputtered again using a 10 µm raster for 100 seconds. Negatively charged sputtered secondary ions were transmitted into the mass spectrometer of the instrument through a potential of 4.5 keV. The instrument was operated with a medium Contrast Aperture (150 µm), and Entrance and Exit Slits paired to give flat topped peaks at a mass resolving power (MRP) of 2975 (10% peak height definition). This is sufficient to discriminate ³³SH⁻ (and ³²SH₂⁻) from ³⁴S⁻. In addition, a sample offset voltage of -60eV and Energy Window of 40eV width were deployed to purposely reduce transmission, enabling a higher primary beam current (and concomitantly faster sputter rate).

125 Signals for $^{32}\text{S}^-$, $^{34}\text{S}^-$ and a background position at 31.67 Da were obtained by cyclical magnetic
126 peak switching. Standard counting times and peak sequence used were; 0.5 s at the background
127 position, 2.0 s on $^{32}\text{S}^-$, and 6.0 s on $^{34}\text{S}^-$. Wait times of 0.25 s were inserted before each peak
128 counting position to allow for magnet settling. A typical analysis consisted of accumulating 80 of
129 these peak cycles, which takes less than 15 min (including pre-sputtering time).

130 All peak signals were collected with multiple-dynode electron multiplier (em) and processed
131 through ECL-based pulse-counting electronics with an overall dead time of 11 ns. Background
132 measurements at the nominal mass 31.67 Da were taken during each magnetic switching cycle –
133 and were routinely less than 0.05–0.1 counts per second. Count rates on $^{32}\text{S}^-$ were maintained
134 between 1,000,000 and 1,500,000 counts per second by adjusting the primary beam current
135 appropriately for each sulfide phase of interest.

136 Beyond the excellent spatial resolution, a further advantage of SIMS stems from the gradual
137 nature of material removal by sputtering, with each counting interval producing depth-resolved
138 data on the sample. Inclusions of other sulfide phases, in particular, have the potential to produce
139 excursions in the measured $\delta^{34}\text{S}$ values. However, the depth-resolved characteristic of SIMS
140 allows the detection of inclusions, or other heterogeneities within a mineral, simply by
141 monitoring sharp excursions in $I^{32}\text{S}^-$ with time. These signal time intervals can then easily be
142 eliminated from the measured data.

143 $^{34}\text{S}/^{32}\text{S}$ measured in samples of pyrite were corrected for IMF by comparison to replicate
144 measurements of in-house reference materials UL9B (pyrite; $\delta^{34}\text{S}$ of 15.8‰ VCDT) and KH87
145 (pyrite; $\delta^{34}\text{S}$ of 0.2‰ VCDT). Analyses accumulated in 12 min routinely yield internal
146 precisions on individual $\delta^{34}\text{S}$ determinations of better than ± 0.2 ‰ (1σ), while producing sputter

147 craters only a few μm deep. These precisions closely approach the optimum possible precision as
148 calculated from Poisson counting statistics. Overall reproducibility, based on replicate standard
149 analyses, is typically better than $\pm 0.5\text{ ‰}$ (1σ). All reported $\delta^{34}\text{S}$ values are in reference to Vienna
150 Canyon Diablo Troilite (V-CDT).

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4. PETROGRAPHY

Energy Dispersive X-ray scan of all samples shows that pyrite is the only sulfide present in the studied samples. Other possible sulfides such as marcasite, sphalerite and galena, typically found in burial carbonates were not observed. The pyrite in the studied localities generally occur as anhedral to euhedral grains, with size range of $<5\mu\text{m}$ to $700\mu\text{m}$ (longest dimensions) (Figs. 2 to 5). At Main Brook, they occur mostly as agglomerated nano- to – micrometer ($<1\mu\text{m}$ to $\sim 5\mu\text{m}$) sized crystals with or without void spaces (Figs. 2A and C). The resulting grain of coalesced pyrite crystal aggregate measures $<25\mu\text{m}$ to $\sim 300\mu\text{m}$ (longest dimensions) and is commonly framboidal (Fig. 2C). These crystalline clusters are disseminated within intra-crystalline areas of dolomite crystals as well as in intercrystalline pores of the host dolomite crystals (Fig. 2). The larger ($>200\mu\text{m}$) pyrite grains exhibit blocky texture that lack distinct crystallographic faces (Figs 2 and 5). Notably, many of the pyrite grains are encased in bituminous materials. Pyrite grains ($\sim 40\mu\text{m}$ – $\sim 60\mu\text{m}$) that have planar edges akin to cubic forms are much more common at Daniel's Harbour (Figs. 3 and 4) and Port au Choix than at Main Brook. Less commonly, they occur as coalesced pyrite crystal aggregates ($55\mu\text{m}$ – $500\mu\text{m}$). Pyrites of Daniel's Harbour (Fig. 3A, Figs. 4 A, B, D) and Port au Choix are also nucleated in inter-crystalline pores and, at times, encroach into neighbouring dolomite crystals. Additionally, many of the pyrite grains are also encased in bituminous materials (e.g., Figs. 4A and B).

5. SIMS ANALYTICAL RESULTS AND DISCUSSION

The $\delta^{34}\text{S}$ values from Main Brook pyrite range from -15 to +20 ‰ ($n = 20$). However most (80%) of the data points range from -15 ‰ to +7.91‰ (Table 1). The $\delta^{34}\text{S}$ values vary significantly within about 10 mm² and even within the same pyrite grain (Fig. 5). The $\delta^{34}\text{S}$ values do not vary with grain sizes. On the other hand, $\delta^{34}\text{S}$ of pyrites from the Daniel's Harbour show a tighter cluster and are mostly negative, ranging from -22.15 to -5.71‰ ($n = 12$) while only two data points show positive $\delta^{34}\text{S}$ values of +0.11 and +1.65 ‰. In the same vein, those from Port au Choix are mostly negative, ranging from -26 to -2.10 ‰ ($n = 22$) while only three pyrite grains have positive $\delta^{34}\text{S}$ values of +0.03, +18.3 and +31 ‰.

In diagenetic settings (<200°C), BSR (very efficient at surface temperature to ~ 70°C) and TSR (operational at >100°C) occur in two mutually exclusive thermal regimes (Machel 2001, Seal, 2006). Inferred temperature of formation for the host burial dolomite crystals can be used to classify the currently studied pyrite.

5.1. Main Brook (Distal to main stage MVT sulfide mineralization)

A thorough scan of the sample did not reveal any noticeable two phase fluid inclusions in the mid-stage (600 – 1000 m, sensu Machel, 2005) burial dolomite crystals. This implies that this burial dolomite was formed within a relatively low temperature (<80°C; cf. Goldstein and Reynolds, 1994) setting that is much more conducive to BSR than TSR (Machel, 2001). Further to this, the fact that the analyzed pyrites post-dates or is coeval with this burial dolomitization (Figs. 2 and 6) suggests formation from the same parent fluid as the host dolomite. If so, these pyrites were likely formed in the same relatively shallow to intermediate burial environment as their host dolomite.

The $\delta^{34}\text{S}$ of the pyrite can be used to constrain their origin as either BSR or TSR. Pyrites that form via BSR have $\delta^{34}\text{S}$ values between 16 and 66‰ (but can be as low as 2‰; Detmers et al., 2001) lower than their contemporary sulfates (e.g., Habicht and Canfield, 1997; Canfield, 2001; Sim et al., 2011). The low concentration of dissolved sulfate in meteoric water (Berner, 1985) is a strong evidence that the ultimate source of sulfur in sulfide minerals of sedimentary basins is seawater sulfates which have varied through geologic times (Claypool et al., 1980; Canfield, 2004; Kampschulte and Strauss, 2004). Thus, best preserved $\delta^{34}\text{S}$ value of early Ordovician seawater sulfate was reported to be about 28‰ (Canfield, 2004; Kampschulte and Strauss, 2004, their Fig. 3). This value is similar to that of barite (26.2‰) and celestite (28.2‰) precipitated from basinal brine within the St. George Group (Lane, 1990; his Page 553). Given these values early Ordovician sulfides should have $\delta^{34}\text{S}$ values between +12 and -38‰. About 90% of the $\delta^{34}\text{S}$ values obtained for the analyzed pyrite grains at Main Brook fall within this range (+1.6 and -22.1‰; Table 1) indicating bacterial origin. Notably, some of the pyrite grains in this locality have round edges that suggest modified framboidal shapes (Fig. 2C) and they are most likely co-

genetic with their anhedral counterparts within the same sample. In the same vein, Machel et al., (1997) documented that a depleted $\delta^{34}\text{S}$ in pyrite crystals of Devonian carbonates indicates formation of those pyrites in a shallow to intermediate burial setting. Additionally, many of the carbonate sequences in the St. George Group Formation carbonates are dominated by microbial mud mats (Knights et al., 2008), which commonly contain biogenic materials that can be utilized for sulfate reduction (Eqn. 1; cf. Xiao et al., 2010).

The relatively wide range in $\delta^{34}\text{S}$ values (cf. Drake et al., 2013; Drake et al., 2015) of the pyrites could be a result of Raleigh fractionation. This occurs when the H_2S and iron sulfides, that are formed during progressive reduction of limited available sulfate in diagenetically closed or partially closed setting of a burial environment, become progressively ^{34}S -enriched (e.g., Riciputi et al., 1996; Machel, 2001; Seal, 2006). In addition to this factor, the studied pyrites often occur in a patchy fashion as blocky ($> 100\ \mu\text{m}$) anhedral cement (Fig. 2A). Their exhibited irregular shape and intra-granular pore spaces suggests they form from an agglomeration of a cluster of crystals. In the same vein, grains that show coalescence of framboids are also common (Fig. 2C). These suggest recrystallization to larger sizes. Such recrystallization is thought to be associated with significant variability in sulfur isotope composition (Kohn et al., 1998; Syverson et al., 2015). Nevertheless, a sulfate ‘supply-demand’ dynamics associated with Raleigh fractionation in the local reaction site could exclusively account for a wide variation in the measured $\delta^{34}\text{S}$ values, regardless of the impact of recrystallization (cf. Xiao et al., 2010). This type of local variation in sulfur isotope fractionation is much more pronounced for BSR than for TSR, because the initial sulfur isotope fractionation is much larger for BSR (Riciputi et al., 1996).

5.2. Daniel's Harbour and Port au Choix (Proximal to main stage MVT sulfide mineralization)

At Daniel's Harbour and Port au Choix, earlier detailed micro-thermometric study indicates, respectively, minimum formation temperature (T_h) of ~101 to 114°C (Olanipekun et al., 2014) and ~106 to ~132°C (Conliffe et al., 2012) for the matrix burial dolomite (Olanipekun et al., 2014) that host the studied pyrite grains. Much like the analyzed pyrite of Main Brook, pyrite grains at Daniel's Harbour and Port au Choix post-date or at least are coeval with the burial dolomite (Figs. 3 and 4D, Daniel's Harbour). However, the thermal regime (>100°C) in which the host dolomite formed is un conducive to microbial activity (BSR). Therefore, irrespective of a low $\delta^{34}\text{S}$ signature in the analyzed pyrite of Main Brook and Daniel's Harbour and Port au Choix, it is likely that the sulfur species (H_2S) responsible for the pyrite formation at Daniel's Harbour and Port au Choix was ultimately derived from hydrocarbons in the formation. This is not surprising, given that reduced sulfur species produced as a result of microbial activity (BSR) on organic matter in source rock is commonly retained in migrated hydrocarbons (e.g., Hirner and Robinson, 1989; Cai et al., 2009; Cai et al., 2010).

It is proposed that an initial pulse of the 'hot' (> 100°C) sulfate-rich basinal brine that fluxed through the carbonate sequence caused thermal cracking of hydrocarbon pool in the formation, whereby light molecular hydrocarbons escaped leaving residual bitumen (e.g., Kelemen et al., 2010; Walters et al., 2015; Eqn. 3). This process is accompanied by a release of H_2S and CO_2 (Orr, 1977). The S-O bonds of dissolved sulfates in a brine are very strong and difficult to break (Machel, 2001; Cross et al., 2004) and it is therefore reasonable to suggest that sulfur derived from crude oil will be preferentially sequestered at the initial stage. It is this reduced biogenic sulfur species (H_2S) that is largely responsible for formation of the analyzed pyrite grains in

Daniel’s Harbour and Port au Choix. Thus, the depleted $\delta^{34}\text{S}$ signature exhibited by these pyrite grains was caused by low $\delta^{34}\text{S}$ signature of the hydrocarbons. In like manner, such interpretation was offered for the Cambro-Ordovician Cincinnati Arch Mississippi Valley Type (MVT) district (Kesler et al., 1994).

Subsequent (likely in quick succession) incursion of the ‘hot’ ($>100^\circ\text{C}$) brine resulted in a thermochemical reduction of inorganic SO_4^{2-} (*sensu stricto* TSR) in the fluid phase, concomitant with further oxidation of the reservoir hydrocarbons. The reduced S species generated from this TSR has been previously demonstrated (Lane, 1990) to account for the main stage sulfide mineralization (MVT) in the region. In perspective, the subsequent episode of pyrite formation (by-product of the TSR) which is associated with this main-stage of mineralization did not yield significant fractionation at Daniel’s Harbour ($\sim +24\text{‰}$ for their ‘early’ pyrite; $\sim +26\text{‰}$ for their ‘early’ sphalerite; $\sim 27.2\text{‰}$ for barite and celestite; see Lane, 1990).

For comparison, the observed low $\delta^{34}\text{S}$ signature is in contrast with an enriched $\delta^{34}\text{S}$ signature obtained for analogous Mississippian carbonate-hosted pyrite investigated by King et al. (2014). Similarly, their studied pyrite grains are intricately associated with bitumen and they also used microprobe technique. Reasons for such discrepancy in the $\delta^{34}\text{S}$ signature is that their studied pyrite was interpreted to post-date formation of coexisting solid bitumen and that the sulfur content is sourced from the brine (King et al., 2014). This is clearly in contrast to the findings of the current study. However, the interpretation offered for the low $\delta^{34}\text{S}$ values of the current study

is consistent with that of Richardson et al. (1988) who documented a depleted $\delta^{34}\text{S}$ in main-stage sphalerite (3.7‰ to 9.8‰) and galena (0.3‰ to 4.8‰) mineralization relative to later formed barites (56.6 ‰ to 102.6 ‰). They showed that petroleum-derived H_2S likewise contributed low $\delta^{34}\text{S}$ to the warm (140 - 153°C) brine that formed the sulfide minerals. These mineral deposits are hosted in Mississippian carbonate sequences in Illinois basin (Richardson et al., 1988). Meanwhile, a narrow range in the measured $\delta^{34}\text{S}$ of the studied pyrites is interpreted to be akin to an open system model of sulphate reduction (Magnall et al., 2016).

Alternatively, it may be argued that biodegradation of the reservoir hydrocarbons, with resultant solid bitumen formation, occurred in shallow environment following a tectonic uplift (Kelemen et al., 2010). However, this is unlikely because the petrographic examination shows that the pyrite grains, which are commonly enclosed in the bitumen (Figs. 4A and B), pre-date late stage saddle dolomite (Figs. 4D; Fig. 6) that formed at temperatures higher than 100°C (Olanipekun et al., 2014). In addition, homogenization temperatures obtained from coeval sphalerites range from 114°C to 126°C (Olanipekun et al., 2014). This sphalerite post-dates pyrite grains (Lane, 1990), clearly indicating that pyrite formation occurred in the burial environment. Furthermore, a tectonic uplift typically causes exposure to oxidizing condition associated with meteoric settings within which there is paucity of reduced Fe for pyrite formation..

5.3. Source of Iron (Fe)

In general, Fe constitutes a trace or minor component of carbonate systems relative to siliciclastic sequences. The Fe is mostly contained in clay minerals and some iron oxides and hydroxides which occur as impurities in platform carbonate sequences. Specifically, the Fe content of the Boat Harbour Formation burial dolomites is less than 3000 ppm (Olanipekun et al., 2014; their Table 4), if contamination by pyrite grains is considered. Similarly, visual

297 estimate of volumetric abundance shows the formation contains less than 5 % pyrite. Thus Fe
298 leached from silicate minerals (especially clay minerals), which form trace constituent in the St
299 George Group, can adequately account for the Fe needed to precipitate most of the studied
300 pyrite(cf. Riciputi et al., 1996).

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5.4. Implications

The mechanisms and controls on in-situ TSR processes in sedimentary systems are not clearly understood (see Machel, 2001). Thus, to shed more light on the mechanism of sulfate reduction in sedimentary systems, this study compliments Riciputi et al. (1996) which employed SIMS technique to investigate pyrite and marcasite formation in Devonian Nisku Formation carbonates. These sulfides post-date or are coeval with burial dolomite that exhibit minimum formation temperature (T_h) of ~ 100 to $\sim 150^\circ\text{C}$ (their Fig. 4). Thus these sulfides are expected to be by-products of TSR, however they are mostly characterized by negative $\delta^{34}\text{S}$ (< -10 ‰ CDT, their Table 1). The authors admittedly stated that they “could not envision how reduced sulfur generated during early burial via BSR could survive to the time of sulfide formation” in the burial (> 300 m) environment (Riciputi et al., 1996). Similar to their study, microthermometric study of dolomites at Daniel’s Harbour and Port au Choix (current study) suggests dolomitization occurred in excess of 100°C (Olanipekun et al., 2014, Conliffe et al., 2012). However, the biogenic origin interpreted for a negative $\delta^{34}\text{S}$ of the studied pyrite is such that reduction of sulfur (most likely BSR), that formed the analyzed pyrite, did not occur at the burial environment within which this pyrite phase was formed (cf. Mathieu et al., 2015, their page 64).

This distinction suggests multiple sources of reduced sulfur for the origin of sulfide minerals precipitated during MVT-type mineralization episode/s.

6. CONCLUSIONS

SIMS was used to measure $\delta^{34}\text{S}$ composition of pyrite disseminated in Boat Harbour formation at Main Brook (40% dolomitized) and Daniel's Harbour (100% dolomitized). Even though the studied pyrites from both localities have low $\delta^{34}\text{S}$ values and that they generally have similar texture, they are genetically distinct from each other.

Bacterial Sulfate Reduction (BSR) was interpreted as the mechanism of pyrite formation at Main Brook. Supporting evidences include: negative $\delta^{34}\text{S}$, lack of 2-phase fluid inclusion in host dolomite and existence of framboidal pyrite.

On the other hand, the negative $\delta^{34}\text{S}$ of the analyzed pyrite at Daniel's Harbour was likely contributed by the reduced (originally BSR) organic sulfur released as a result of thermal cracking of reservoir crude oil. Evidences include: micro-thermometric (T_h) value in excess of 100°C in host dolomite, formation in relatively deeper burial and occurrence of bituminous materials that encase pyrite grains. Subsequent flux of sulfate-rich brine resulted in a thermochemical reduction of inorganic dissolved SO_4^{2-} in the brine which yielded the main stage sulfide mineralization (MVT type). This mineralization episode resulted in major economic sphalerite deposit at the Newfoundland Zinc Mines near Daniel's Harbour. The deposit is strata-bound and formed around regional deep seated fracture systems. This regional fracture system is associated with regional compression that occurred during Siluro – Devonian Acadian orogeny (Lane 1990, Cooper et al., 2001). The fracture system is documented to be the conduit for the hot brine responsible for sulphide precipitation at this site (Lane, 1990).

341 Many of the pyrite grains in the dolomite are too small (<15 μm) for a reliable SIMS
342 measurement, thus limiting the number of obtainable $\delta^{34}\text{S}$ values. Thus, a more extensive SIMS
343 analyzed $\delta^{34}\text{S}$ values in pyrite grains in future studies will complement the current study.

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- 468

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469 **LIST OF TABLES**

470 Table 1: List of SIMS analyzed $\delta^{34}\text{S}$ ‰ (VCDT) from pyrite grains from Main Brook, Daniel's
471 Harbour and Port au Choix. SEM is Standard Error of Mean.

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Figure 1: Locality map of the Boat Harbour Formation and the studied drillholes in Western Newfoundland, Canada (modified from Olanipekun et al., 2014). Cores from two drillholes (black circles) were investigated from Main Brook (12P/1-12; 51° 08' 23" N; 56° 10' 54" W), Daniel's Harbour (12i/6 121; 51° 17' 46" N; 57° 27' 22" W) and Port au Choix (12B/11 44; N48° 35' 49", W59° 02' 16") on the Northern Peninsula.

Figure 2. (A) BSE image of pyrite in dolomite matrix. Sample P-158; (B) BSE image of pyrite in dolomite matrix. Sample P-154; (C) Reflected light image of framboidal pyrite in dolomite matrix. (D) Same view as (C) in transmitted light. Sample P-154. Both samples are from Main Brook.

Figure 3. A to D: EDX spectra map showing (A) Backscatter Electron (BSE) image and distribution of Fe; (B) BSE image and distribution of S; (C) distribution of S (navy blue) and C to demonstrate the carbonate mineralogy and disseminated pyrite; (D) distribution of Zn to demonstrate a lack of sphalerite in the dolomite matrix. Figures A to D illustrate that pyrite is the most important sulfide mineral in the sample. It also depicts the distribution of the pyrite in the carbonate matrix. Sample 6-172 from Daniel's Harbour.

Figure 4. (A reflected light, B transmitted light). Pyrite grains encased in bitumen/organic material within dolomite matrix. Respective $\delta^{34}\text{S}$ values are displayed in (A). Py in (A) is pyrite and Py-Bit in (B) is pyrite in bitumen. Inset in A-B shows the lower center pyrite grain (bright yellow) surrounded by dark bituminous material at higher magnification. Sample 6-172, Daniel's Harbour.

(C) Photomicrograph showing two phases (B-Dol 1 and B-Dol 2) of burial dolomite. Deeper burial dolomite (B-Dol 2) crosscuts stylolite, implying formation in relatively deeper burial environment and is the phase (B-Dol 2) that hosts analyzed pyrite grains. Sample 6-136. (D) BSE of a region of interest in the burial dolomite matrix demonstrating paragenesis. It shows pyrite grain (blue arrow) is restricted to burial dolomite matrix while late stage saddle dolomite vein (black arrow) is devoid of pyrite. Sample 6-172. Daniel's Harbour.

Figure 5. A blocky pyrite grain showing intra-grain variation in $\delta^{34}\text{S}$ values. Depth of 158 m (Sample P-158, Main Brook).

Figure 6. Interpreted paragenesis of events within the studied samples.

APPENDIX

Daniel’s Harbour (Sample Id. 6-172)

Photomicrograph of a region of interest showing pyrite grains in host burial dolomite annotated with respective SIMS analyzed $\delta^{34}\text{S}$ (‰) values. (A) is a transmitted light image of the region of interest and (B) is a reflected light image of the gold coated sample. SSW-NNE line is a scratch artifact impressed on the sample for easy location of the region of interest in the SIMS equipment.

Figure 1: Locality map of the Boat Harbour Formation and the studied drillholes in Western Newfoundland, Canada (modified from Olanipekun et al., 2014). Cores from two drillholes (black circles) were investigated from Main Brook (12P/1-12; 51°08' 23" N; 56°10' 54" W), Daniel's Harbour (12i/6-121; 51°17' 46" N; 57°27' 22" W) and Port au Choix (12B/11-44; 48°35' 49" N; 59°02' 16" W) on the Northern Peninsula.

212x172mm (300 x 300 DPI)

Figure 2. (A) BSE image of pyrite in dolomite matrix. Sample P-158; (B) BSE image of pyrite in dolomite matrix. Sample P-154; (C) Reflected light image of framboidal pyrite in dolomite matrix. (D) Same view as (C) in transmitted light. Sample P-154. Both samples are from Main Brook.

299x253mm (300 x 300 DPI)

Figure 3. A to D: EDX spectra map showing (A) Backscatter Electron (BSE) image and distribution of Fe; (B) BSE image and distribution of S; (C) distribution of S (navy blue) and C to demonstrate the carbonate mineralogy and disseminated pyrite; (D) distribution of Zn to demonstrate a lack of sphalerite in the dolomite matrix. Figures A to D illustrate that pyrite is the most important sulfide mineral in the sample. It also depicts the distribution of the pyrite in the carbonate matrix. Sample 6-172 from Daniel's Harbour.

211x215mm (300 x 300 DPI)

Figure 4. (A reflected light, B transmitted light). Pyrite grains encased in bitumen/organic material within dolomite matrix. Respective $\delta^{34}\text{S}$ values are displayed in (A). Py in (A) is pyrite and Py-Bit in (B) is pyrite in bitumen. Inset in A-B shows the lower center pyrite grain (bright yellow) surrounded by dark bituminous material at higher magnification. Sample 6-172, Daniel's Harbour.

(C) Photomicrograph showing two phases (B-Dol 1 and B-Dol 2) of burial dolomite. Deeper burial dolomite (B-Dol 2) crosscuts stylolite, implying formation in relatively deeper burial environment and is the phase (B-Dol 2) that hosts analyzed pyrite grains. Sample 6-136. (D) BSE of a region of interest in the burial dolomite matrix demonstrating paragenesis. It shows pyrite grain (blue arrow) is restricted to burial dolomite matrix while late stage saddle dolomite vein (black arrow) is devoid of pyrite. Sample 6-172. Daniel's Harbour.

267x221mm (300 x 300 DPI)

Figure 5. A blocky pyrite grain showing intra-grain variation in $\delta^{34}\text{S}$ values. Depth of 158 m (Sample P-158, Main Brook).

261x104mm (300 x 300 DPI)

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Figure 6. Interpreted paragenesis of events within the studied samples.

201x250mm (300 x 300 DPI)

Main Brook				Daniel's Harbour			
File name		$\delta^{34}\text{S}$ ‰	SEM	File name		$\delta^{34}\text{S}$ ‰	SEM
1	P158Py1 19 1	-14	0.2	6 172 Py 4 19	1 1	-12	0.4
2	P158Py1 19 2	-8	0.5	6 172 Py 4 19	2 2	-6	0.3
3	P158Py1 19 3	17	0.4	6 172 Py 4 19	3 3	-6	0.3
4	P158Py2 19 1	20	0.3	6 172 Py 4 19	4 4	-9	0.5
5	P158Py3 19 1	-1	0.2	5 6 172 1 1205	5 6 172 1 1205	-7	0.2
6	P158 3 1205 6	-8	0.3	6 6 172 2 1205	6 6 172 2 1205	-6	0.2
7	P158 3 1205 7	-11	0.3	7 6 172 3 1205	7 6 172 3 1205	-10	0.2
8	P158_3_1205@3	1	0.2	P6 172 1 26	8 Py 1	-13	0.2
9	P158_3_1205@4	-15	0.3	9 6 172 1Py 1	9 6 172 1Py 1	2	0.2
10	P158_3_1205@5	15	0.3	10 6 172 1Py 2	10 6 172 1Py 2	0	0.2
11	P_158_1_26_Py_@1	-8	0.3	11 6 172 1Py 3	11 6 172 1Py 3	-22	0.4
12	P_158_1_26_Py_@2	1	0.3	12 6 172 1Py 4	12 6 172 1Py 4	-19	0.3
13	P_158_1_26_Py_@3	6	0.5				
14	P_158_1_26_Py_@4	-12	0.3				
15	P154 1 26 Py1a	7	0.3				
16	P154 2 26 Py1	19	0.2				
17	P154 2 26 Py2	8	0.3				
18	P154 2 26 Py3	-4	0.2				
19	P154	-10					
20	P154	-13					
Port au Choix							
File name		SEM					

		$\delta^{34}\text{S}$	
		‰	
1	JBO_184 5 A1 1	-14	0.2
2	JBO_184 5 A1 2	-18	0.5
3	JBO_184 5 A1 3	-26	1.0
4	JBO_184 5 A1 4	-11	0.3
5	JBO_184 5 A1 5	-9	0.4
6	JBO_184 5 A2 1	-13	0.3
7	JBO_184 5 A2 2	-11	0.4
8	JBO_184 5 A2 3	0	0.4
9	JBO_184 5 A2 5	-13	0.3
10	JBO_184 5 A2 6	31	0.2
11	JBO_184 5 C2 1	-8	0.3
12	JBO_184 5 C2 2	-12	0.3
13	JBO_184 5 C2 3	18	0.2
14	JBO_184 5 C2 4	-10	0.2
15	JBO_216 AL1	-2	0.2
16	JBO_218 A1 1	-20	0.2
17	JBO_218 A1 2	-20	0.3
18	JBO_218 A1 3b	-26	0.8
19	JBO_218 A1 4	-22	1.3
20	JBO_218 A1 5	-17	0.4
21	JBO_218 D1 1	-20	0.2
22	JBO_218 D1 1b	-20	0.2
23	JBO_218 D1 2	-21	0.2
24	JBO_218 D1 3	-23	0.3