Carbon isotopes, stratigraphy and environmental change: the Middle/Upper Cambrian Positive Excursion (SPICE) in Port-au-Port Group, Western Newfoundland, Canada

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Abstract

In many basins, Upper Cambrian carbonate successions display intervals with a positive carbon isotope excursion (CIE) of up to +5‰. In North America, this marks the boundary between the Sauk II-III super-sequences. A Steptoean Positive Carbon Isotope Excursion (SPICE) locality previously identified in the Port-au-Port peninsula, western Newfoundland, has been revisited and an additional potential SPICE locality found. In both locations, a CIE is found to be associated with a prominent bioherm and sandstone layer within a sequence of carbonate rocks. At March Point, columnar stromatolites occur while at Felix Cove thrombolites can be seen. In the latter, the sandstone immediately overlies the thrombolites coincident with the CIE, while at March Point a dolomitized grainstone occurs above the stromatolites. The sandstone at this locality post-dates the CIE. Although lower than the SPICE in some localities, a positive CIE is present in both sections, March Point (+1.1 ‰) and Felix Cove (+1.8 ‰). Additionally, $\delta^{13}C_{org}$ rises from –30.0 ‰ to –22.0 ‰ at March Point, and from -27 ‰ to –24.0 ‰ at Felix Cove and, in accordance with previously published work, we suggest that this could be the SPICE. Comparison of the stratigraphy and petrography between the two localities suggest that both depositional and diagenetic factors could have influenced the nature of the interpreted SPICE in Newfoundland. It is also possible that the local carbon isotopic signature may have been influenced by a semi-restricted depositional and early diagenetic environment, related to the paleogeographic configuration, rather than the global marine excursion.

Keyword: SPICE, Port au Port Group, Stable Isotopes

Introduction

Upper Cambrian (Steptoean Stage) carbonate successions are found worldwide, including examples in North America, Siberia, Kazakhstan, China Australia and Oman (Figure 1), with a positive carbonate carbon isotope ($\delta^{13}C_{carb}$) excursion (CIE) of up to +5‰, lasting nearly 4 Ma (Saltzman et al. 2000, 2004, Kouchinsky et al. 2008, Woods et al. 2011, Neilson et al. 2016). This excursion has also been observed in the $\delta^{13}C$ of organic-rich ($\delta^{13}C_{org}$) mudstones and shales (Ahlberg et al. 2009, Saltzman et al. 2011). This CIE was first reported from the John's Wash Limestone of Utah by Brasier (1993), followed by sections described in the House Range - Utah; McGill - Nevada; Wind Rover Range and Gros Ventre Range - Wyoming (Saltzman et al. 1995). The term Steptoean Positive Carbon Isotope Excursion (SPICE) was proposed by Saltzman et al. (1998), who suggested a global occurrence comparing data from South China, Kazakhstan, Australia and Laurentia (Shingle Pass, Nevada) (Saltzman et al. 2000). This positive carbon isotope excursion is coeval with a trilobite mass extinction horizon (Palmer 1965, Sepkoski 1982, Yochelson 1984, Saltzman et al. 1995, 1998, 2000, Bond and Grasby 2017). Saltzman et al. (2004, 2011) and Bond and Grasby (2017) suggested that the positive excursion represents a perturbation in the global carbon cycle that occurs on the boundary between the Sauk II and Sauk III second order super-sequences from the Sauk megasequence (Sloss 1963).

Other CIE's of similar magnitude and duration have been described from the Late Ordovician, late Silurian, Upper Devonian, early Mississippian, and early late Permian (Gruszczynski et al. 1989; Brenchley 1994; Joachimski et al. 2002; Saltzman 2002, Saltzman et al. 2011). Each positive CIE may correspond to different causes, but in general they are thought to reflect an increased burial of isotopically lighter organic carbon (resulting in higher $\delta^{13}C$ in the residual pool) related to increased organic productivity, with organic preservation due to high sedimentation rates and/or anoxic conditions (Arthur et al. 1987, Derry et al. 1992, Schidlowski 1992, Schrag et al. 2002).

The SPICE was first described in Western Newfoundland in the Petit Jardin Formation (Felix and overlying Man O' War members) at Felix Cove by Saltzman et al. (2004). In this unit, $\delta^{13}C$ values of carbonates rise from –1‰ to 0‰ V-PDB, reaching a peak $\delta^{13}C$ of +2.2‰ just above a quartz sandstone layer that marks the Sauk II – Sauk III boundary. Although the presence of an excursion has been reported in the Port au Port rocks (Saltzman et al. 2004), the magnitude of the SPICE excursion in the Petit Jardin Formation is smaller than observed around the world (Glumac and Walker 1998).

This raises questions about whether the presence of the global SPICE excursion in the Port au Port Peninsula rocks is real, or whether it is just a local environmental or diagenetic shift. In an attempt to address this issue, two Western Newfoundland stratigraphic sections were logged in detail, followed by petrographic analysis of the carbonates, and $\delta^{13}C$ analysis of both carbonate and organic carbon samples.

Geologic Setting

The study area is located on the southern coast of the Port au Port Peninsula, western Newfoundland (Figure 2). The SPICE was identified in Felix Cove (48°31'49.2"N / 58°47'12"E), a section previously studied by Saltzman et al. (2004) and another potential SPICE locality identified at March Point (48°30'42.1"N / 59°05'31.1"E),

The Port au Port Group forms part of the autochthonous Cambrian-Ordovician sequence of the tectono-stratigraphic Humber zone of the northern Appalachian orogeny (Williams 1976, 1979). It is interpreted as shallow-marine deposits from the outer part of a stable carbonate platform that surrounded the Iapetus Ocean (Williams 1976, 1979, Palmer and James 1979). These mixed carbonate-siliciclastic deposits record the gradual transition from early Cambrian siliciclastic deposition to predominantly carbonate sedimentation in the Early Ordovician (Chow 1985, Chow and James 1987b, Cowan and James 1993). The Group is composed of three formations, namely the March Point, Petit Jardin (Cape Ann, Campbells, Big Cove, Felix and Man O' War Members) and Berry Head Formations.

Transgressive-regressive Grand Cycles are identified through the Port au Port Group (Chow 1985, Chow and James 1987a, 1987b) (Figure 3). The marine transgression at the beginning of the Grand Cycles resulted in a shallow subtidal-intertidal environment, where relatively muddy carbonates were deposited (shaley packages and parted limestone; Chow and James 1987b). These deposits pass upwards into more open marine oolitic shoals, probably deposited near the platform edge (carbonate packages; Chow and James 1987b). As sea level dropped at the top of the cycles, the environment returned to a more restricted water circulation situation, although according to Chow and James (1987b) extensive evidence of subaerial exposure at the top of cycle B is absent. Carbon isotope data, previously collected in the Port au Port Group at Felix Cove, show a strong positive $\delta^{13}C_{carb}$ excursion between the Felix and Man O' War Members (Figure 1), which has been interpreted as the SPICE (Saltzman et al. 2004).

Methodology

The field work was performed along two main outcrops on the Port au Port Peninsula – March Point and Felix Cove. Detailed sedimentological logging on a cm scale (1:50) and systematic sampling was carried out at 1m resolution, from the base of accessible units in the Petit Jardin Formation to the top of each exposed Petit Jardin or Berry Head Formation section. The stratigraphic section logged in the March Point locality (MP) was 270m thick, and in the Felix

Cove locality (FC), 40m thick. A third outcrop was found, in which the diagnostic sedimentological characteristics of the SPICE layer in the Port-au-Port peninsula are exhibited (West Felix Cove 48°31'51.6"N / 58°47'49.1"E), but logging was not carried out at this location.

Representative layers were selected for thin sections (March Point: 45; Felix Cove: 8), carbonate $\delta^{13}C$ and $\delta^{18}O$ analyses (March Point: 41; Felix Cove: 16), and organic carbon ($\delta^{13}C_{org}$) (March Point: 14; Felix Cove: 4). Polished thin sections were prepared at the Mineral and Rock Analyses Laboratory (LAMIR) at the Universidade Federal do Paraná (UFPR) and at Petrografia BR, after impregnation with blue resin for porosity identification. Petrographic analysis was performed at the Universidade Federal do Rio Grande do Sul (UFRGS). For carbonate identification, the thin sections were stained with a solution of alizarin red.

Carbonate stable isotope ($\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$) analysis was carried out at LAMIR/UFPR in Brazil and at the BGS in the UK. For isotope analyses, carbonate samples were collected using a microdrill (0.5mm diamond drill), in order to avoid mixing of primary and diagenetic constituents whenever possible. At LAMIR, the amount of material drilled was around 0.3 mg, while a larger amount of powder was required by the BGS for the analysis (10mg). At LAMIR, the isotope ratios were determined using a GasBench II attached to a Thermo Scientific Delta Advantage continuous flow isotope ratio mass spectrometer, following the Spötl and Vennemann (2003) and Paul and Skrzypek (2007) routine with a reproducibility <0.1‰ (1σ). At BGS, isotopic analysis was carried out using a vacuum extraction technique and a VG Optima mass spectrometer with overall analytical reproducibility better than <0.1‰ (1σ) for $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$. The main difference in the carbonate isotope methodology of the two laboratories is the time of carbonate-acid reaction. At the BGS a quick reaction at low temperature (16°C) was performed over two hours in order to release CO_2 from calcite with minimal contribution from any CO_2 derived from secondary dolomite. However, at LAMIR, the time taken for reaction was between one to two hours at a temperature of 72°C. The isotope composition of samples is reported in the standard δ notation, defined as the relative difference, in parts per thousand (‰) without any further conversion. Each laboratory used their own in house standards previously calibrated to Vienna Pee Dee Belemnite (V-PDB).

For organic carbon isotope ($\delta^{13}C_{org}$) analysis at the BGS, the samples were reacted with 5% HCl overnight to remove carbonate, and dried down at 40ºC. After being cleaned, homogenized, and dried, c. 15–25 mg of decarbonized sediment were used for determination of carbon isotope ratios using a carbon isotopic ratio Carlo Erba 1500 on-line to a VG TripleTrap (with a secondary cryogenic trap for very low carbon content samples) and Optima dual-inlet mass spectrometer. $\delta^{13}C_{org}$ values were calculated to the V-PDB scale using a within-run laboratory standard (BROC1) calibrated against NBS-19 and NBS-22. Replicate analysis of well-mixed samples embraces a precision of $\pm$ <0.1‰ (1 σ).

Results

The stratigraphic interval that comprises the purported SPICE in Felix Cove (as identified by Saltzman, 2004, at 22.5 m, Figure 4a) comprises several sets of fining-upward oolitic grainstones (20-40 cm thickness), followed by a layer of pillow-shaped thrombolite, around 25 cm thick, with a clotted center tending to a more regular shape at the edges (Figure 4b). The sedimentary layers that underly the thrombolite layer contain trilobites of the *Crepicephalus* Zone (*Terranovella dorsalis* and *Crepicephalus iowensis* in the FC1 and FC2 collections of Westrop, 1992). Westrop (1992) also records the occurrence of the trilobite *Dytremacephalus strictus* in the thrombolite layer itself (R. Levesque, Geological Survey of Canada, location 96635), indicating that it belongs to the *Aphelaspis* Zone (Figure 3). These bioherms are overlain by a thin glauconitic sandstone layer (~25 cm thickness) before returning upwards to grainstones and parted limestone sets. These sets show different degrees of dolomitization, but it is still possible to identify primary constituents. Saltzman et al. (2004) note that Elvinia Zone fauna (A.R. Palmer, Institute for Cambrian Studies collection ICS-1406) were found approximately 8 m above the quartz sandstone. The trilobite data confirms the CIE as being the SPICE. A similar lithological succession is observed in West Felix Cove (Figure 4c).

In the March Point section, the interval that comprises the positive carbon excursion, between 222m and 226 m, consists of a layer of columnar stromatolites (Figure 4d), around 20 cm thick, either forming as separated columns or laterally continuous mats. These are overlain by a thin dolomitized glauconitic grainstone, 20 cm thick (Figure 4e). A meter-thick glauconitic, fine-grained sandstone (Figure 4f) occurs 3-4 m above. Below the stromatolite layer, the oolitic grainstone sets are extensively dolomitized. No well constrained faunal information is available for this layer.

The uncompacted bioclastic sandstone that overlies the bioherms in Felix Cove is cemented by calcite with very minor replacive dolomite (Figure 5a) although in West Felix Cove the dolomite content is considerably higher, showing small relict calcite areas (pinkish stain) (Figure 5b). Quartz grains are well rounded and well sorted, medium coarse – coarse sand, with 465 µm diameter average (Table 1). The glauconitic grainstone that overlies the stromatolites at March Point is extensively dolomitized (Figure 5c) including the glauconite peloids (Figure 5d). The glauconitic sandstone layer, 3-4 m above it, contains very poorly sorted, sub-rounded to angular silt to medium sand grains (89 µm diameter average) which is also partially cemented by dolomite (Figure 5e and f) and is very compacted. The sets of oolitic grainstones that underlie the potential SPICE layer in

March Point are extensively dolomitized although the ooids outlines may be partially preserved (Figure 6a-c). For several meters above the potential SPICE layer, carbonate-clastic sandstones (composed of quartz grains and carbonate particles) occur (Figure 6d), replaced by dolomite.

The isotope data ($\delta^{13}C_{carb,}$ $\delta^{18}O_{carb,}$ $\delta^{13}C_{org}$ and %C) analysis for the March Point section are presented in Table 2 and Figure 7. The $\delta^{13}C_{org}$ data are relatively stable below the base of the Felix Member, with values between –29.5‰ and –24.8‰. Above this point, however, the values become more variable, between –30‰ and –21.3‰, showing a general enrichment in ^{13}C organic carbon up section, with a maximum within the Felix Member. The total organic carbon level (%C), however, is generally very low, ranging between 0.04% and 0.3%, except for layers at 170 and 180m, with 1.9% and 2.1% respectively. The $\delta^{13}C_{carb}$ data show significant depletion at the top of the Campbells Member (–4.1‰), and a maximum (+1.1‰) at the boundary between the Felix and Man O' War Members. Above this, the $\delta^{13}C_{carb}$ general trend is towards lower values between –2 and –1‰. In the March point section the best defined carbonate carbon excursion occurs over a thickness of approximately 5 m (Figure 7). $\delta^{18}O_{carb}$ values are not directly related to the $\delta^{13}C_{carb}$ values (r^2 = 0.21, n = 41), although they show similar trends. However, $\delta^{18}O_{carb}$ becomes less variable in the Felix Member, showing a more positive peak, around –4.5‰, which coincides with the positive shift in $\delta^{13}C_{carb}$ at the boundary between the Felix Cove and Man O' War Members.

In the Felix Cove section, only part of the Petit Jardin Formation is exposed, starting within the Felix Member. The $\delta^{13}C_{carb}$, $\delta^{18}O_{carb}$, $\delta^{13}C_{org}$ and %C data are given in Table 2 and Figure 8. Near the lowermost part of the outcrop exposed in the Felix Member, the $\delta^{13}C_{carb}$ value is around –2.0‰, reaching a high of +1.8‰ near to the transition between the Felix and Man O' War Members (Figure 8). This section corresponds to the same interval studied by Saltzman et al. (2004). The data present a general upward increase in $\delta^{13}C_{carb}$ values (Figure 8). Compared to $\delta^{13}C_{carb}$, the $\delta^{18}O_{carb}$ data shows a relatively stable trend, as observed for the Felix Member in the March Point section, with a negative trough (though only of one data point) of –9.0‰ just before an interval of higher values that reach –5.4‰. A weak correlation between $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ occurs for the Felix Cove section (r^2= 0.57, n= 16). As in the March Point section, %C is low, ranging between 0.04% and 0.17%. The stratigraphic thickness of the excursion upwards from 22.25 m, is about 15 m (Figure 8).

Discussion

In the Port au Port Peninsula, particular lithologies were found to be related to the peak $\delta^{13}C$ values in outcrop. This positive $\delta^{13}C$ excursion was observed and identified by Saltzman et al. (2004) at Felix Cove and, based on trilobite data presented by Westrop (1992), identified as the SPICE. The positive $\delta^{13}C$ excursion occurs at a time when there was an influx of glauconitic quartzose sand believed to be as a result of a decrease in water depth (regression). This was followed by a rise in sea level and deepening (Saltzman et al. 2004), reflected in the resumption of carbonate deposition. Detailed logging of the SPICE section at Felix Cove has shown that the positive peak is characterized by a lithological sequence of bioherms, overlain by glauconitic sand rich layers, also observed by Saltzman et al. (2004). A very similar lithological sequence has also been identified during this study approximately 0.8 km west of Felix Cove (West Felix Cove) although limited data is available.

In the March Point section (approximately 25 km further west, Figure 2), a similar lithological sequence of bioherms and glauconitic sandstone occur in the interval and is accompanied by a positive carbon isotope excursion (Figure 7). No biostratigraphic data are available for the upper part of the Felix Member. Westrop (1992) provides data for the underlying Big Cove Member but this lies well below where the SPICE would be expected in that section.

Although there are similarities in the lithological sequence between these localities, there are also differences. Folk (1951) suggested that textural and compositional maturity of the sediment are products of the degree of reworking, energy and distance of transport. The fine, poorly sorted, slightly immature sandstones at March Point (Figure 5e and f, Table 1) contrast with the "clean", coarse and mature sandstone observed at Felix Cove (Figure 6a and b). Also, the position of the distinctive glauconitic sandstone is different. At Felix Cove it directly overlies the thombolites while at March Point it occurs 3-4m m above it. At March Point, the stromatolite is overlain by a dolomitized glauconitic grainstone prior to deposition of the glauconitic sandstone. Moreover, even though it is unlikely that the morphology of specific microbial buildups was related to particular environments, lateral differences do exist. The bioherm morphology at March Point comprise columnar stromatolites, (Figure 4e) while thrombolites are observed in this layer at Felix Cove (Figure 4a-c). The interval at March Point can therefore only be identified as a potential SPICE locality.

The Felix Cove section indicates that the lead up to the SPICE occurred in a shallow marine environment, with bioclastic grainstone shoals (e.g. echinoderms) and bioherms. The influx of coarse, well rounded, quartz sandstone marks the base of the positive carbon excursion and start of a regression. The sandstone layer is followed by several sets of fining upward oolitic bioclastic graisntones, up to the Felix/Man O' War member transition, where parted limestone and shale become abundant. These deposits have been interpreted by Chow and James (1987b) as subtidal to intertidal. Comparatively, in the March Point section the positive carbon excursion (potential SPICE) occurs within a set of a glauconitic grainstones. The fine, angular, carbonate-clastic sandstone occurs a few metres above the peak of the positive $\delta^{13}C_{carb}$ excursion rather than at its beginning, near to the transition between Felix and Man O' War members. This suggests that the sandstones at the two locations are diachronous and may have been deposited in different environments with the start of the regression being slightly later at March Point than at Felix Cove.

While the SPICE interval is 200 m thick in Nevada (Saltzman et al. 1998) and 80 m in the Southern Appalachians (Glumac and Walker 1998), it is only 15 m thick in the Felix Cove section and the potential SPICE only 5 m thick in the March Point section (Figure 9). This has already been noted by James and Stevens (1986), who found a thickness of less than 20 m, similar to our observations at Felix Cove. However we observed a much thinner interval in the March Point section. Additionally, the $\delta^{13}C_{carb}$ of the SPICE has a relatively lower magnitude than observed in other suggested localities around the world. Globally, the SPICE is described as a $\delta^{13}C_{carb}$ positive shift of around +5‰ (Saltzman et al. 2000, 2004, Kouchinsky et al. 2008, Woods et al. 2011) in carbonates. The results presented here reach a $\delta^{13}C_{carb}$ peak of about +1.13 ‰ for the March Point section and +2.2 ‰ (Saltzman et al. 2004), and +1.8 ‰ (this work) for the Felix Cove section, with an average shift of about +2 ‰, half of the typical global value. There are other locations which have lower values, for example in the Southern Appalachians and South China (~+3‰; Fan et al. 2011).

At March Point, dolomitisation is significant in the immediate lead up to and around the potential SPICE interval and this may have affected the isotopic results. To minimize the effect of this, the data around the potential SPICE interval itself were collected at the BGS (Figure 7) using a quick acid reaction time. This was performed over two hours at low temperature (16°C) to release CO_2 mainly from calcite and minimize the contribution from dolomite. At March Point, the higher $\delta^{13}C_{carb}$ values are accompanied by an increase in $\delta^{18}O_{carb}$ (up to c. -4‰, Figure 7). A similar pattern in $\delta^{18}O_{carb}$ values is recorded from early dolomites in the Lower-Middle Triassic Moenkopi Formation (Marenco et al. 2008). The early, relatively heavy Moenkopi Formation dolomites were contemporaneous with inner-middle shelf limestones which showed much lighter $\delta^{18}O_{carb}$ values of -9 to -6‰. The $\delta^{18}O_{carb}$ data observed here may therefore reflect a contribution from early dolomitisation which may be more likely to have retained the original carbon isotopic signature due to a lack of subsequent recrystallisation.

Considering the wider effects of diagenesis, the more negative $\delta^{18}O_{carb}$ data observed in both sections could be the result of burial and interaction with hot or meteoric diagenetic fluids (Scholle 1977, Moore 2002). Thus, the large depletion in $\delta^{18}O_{carb}$ values (down to -9‰, Figures 7 and 8) could be interpreted as a diagenetic effect, marked by resetting of the original isotope ratios (Brand and Veizer 1980). Despite different diagenetic patterns around the SPICE and potential SPICE intervals, both sections show similar $\delta^{18}O$ values at that level (between –4.5 and –5.75 ‰, Figures 7 and 8). These values are heavier than most of the samples that lie stratigraphically below or above the potential SPICE at March Point. This may suggest that the original signature has been preserved better around the SPICE and potential SPICE interval.

A positive excursion was observed in $\delta^{13}C_{org}$ data from Avalonia (Woods et al. 2011), Australia, China and North America (Iowa) (Saltzman et al. 2011). In Newfoundland this is also observed although an offset between $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ occurs in the March Point section and, to a lesser degree, in the Felix Cove section (Figure 10). The isotope offset between $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ curves has been noted previously in Queensland, Australia and Iowa, USA by Saltzman et al. (2011). There, $\delta^{13}C_{org}$ was found to track the $\delta^{13}C_{carb}$ curve on the rising limb, with $\delta^{13}C_{org}$ shifting back to lighter values before peak SPICE in the inorganic data. Although the pattern is clear at March Point, the reduced thickness of the Felix Member exposed at Felix Cove makes it more difficult to identify there. The highly variable trend in $\delta^{13}C_{org}$ below the potential SPICE at March Point is most likely due to the low %C values in most of the samples.

The SPICE is a global phenomenon and represents the characteristics of open ocean seawater at that time. However, as shown earlier, the Petit Jardin Formation was deposited in a more marginal marine environment (Chow and James, 1987b) rather than open marine. Gilleaudeau and Kah, (2013) have shown that carbonates deposited in epicratonic seas are typically 2-4 ‰ lighter in $\delta^{13}C$ than those deposited in open-marine pericratonic environments. Gilleaudeau and Kah (2013) suggest that general mechanisms for this include ^{13}C-depletion due to marine upwelling, ^{13}C-depletion from terrigenous plant material (even in pre-Silurian environments from early bryophytes) or ^{13}C-depletion from in situ organic remineralisation.

Local tectonics may also have played a part in reducing the extent of the CIE. It has been suggested that local tectonics influenced the sedimentation patterns observed in the Port-au-Port peninsula in the inner flexural wedge of the Laurentian cratonic margin (Cowan and James, 1993; Lavoie et al, 2012). Even for relatively adjacent locations such as Felix Cove and March Point (c. 25 km apart), local tectonics could have accounted for the variations in input and timing of the clastics observed related to the SPICE and potential SPICE (Figure 9) and could have generated local, more restricted environments. These environments would have had differences in energy (Knight and Boyce 2009) which again could have affected the geochemical signature (Gilleaudeau and Kah, 2013).

As the platforms evolved due to closure of Iapetus, Western Newfoundland and its surroundings, located in southern Laurentia, became progressively more restricted whereas SPICE outcrops situated on the west/northwest of Laurentia maintained open circulation (Figure 11). Likewise, deposition in the southern Appalachians also occurred in a similar progressively restricted environment. The CIE in the southern Appalachians, like the SPICE and potential SPICE in Newfoundland, is thinner with a reduced magnitude.

The isotopic signal observed in the Petit Jardin Formation therefore, could reflect superposition of a regional and local signature onto ocean chemistry as a result of semi-restricted/restricted water circulation in the Newfoundland area due to SL changes and closure of the Iapetus Ocean (Cowan and James 1993, Patterson and Walter 1994, Saltzman et al. 2004). Hence, despite recording a positive excursion plausibly related to the SPICE, the Petit Jardin Formation may have imparted its own isotopic signature onto the SPICE, driven by local tectonic, sedimentary and diagenetic processes.

Conclusions

Two upper Cambrian sections in the Port-au-Port peninsula, Western Newfoundland have been studied and compared in detail (March Point and Felix Cove) These are predominantly carbonate in lithology but contain specific sandstone horizons that occur in close proximity to bioherms. At March Point, this bioherm is of stromatolitic character and a pooly sorted glauconitic sandstone layer occurs 3-4 m above it. At Felix Cove, the bioherm is thromboltic and directly overlain by a coarse glauconitic sandstone. The sandstones are therefore diachronous.

Carbon isotope data (from both carbonate carbon and organic carbon) show a positive excursion (at the level which marks the boundary between Sauk II and III. Saltzman et al. (2004) presented data for the section at Felix Cove which has been dated by trilobite fauna and identified as the SPICE. New data from a potential SPICE horizon at March Point is presented in this work but no biostratigraphic data are available.

The $\delta^{13}C_{carb}$ excursion presented here and by Saltzman et al. (2004) is reduced in magnitude compared to other global occurrences of the SPICE. This may be driven by local tectonic, sedimentary and/or diagenetic processes. A restricted environment would result in a less well developed excursion rather than the expected global CIE due to ocean chemistry. The stratigraphic and isotope variations observed in the Port-au-Port peninsula associated with the SPICE suggest that local as well as global conditions were important in determining its character.

Acknowledgments

This work is a part of the PhD of the first author, developed at Universidade Federal do Rio Grande do Sul (UFRGS) and University of Aberdeen (UoA). The authors gratefully acknowledge support from Shell Brasil through the “BG05: UoA-UFRGS-SWB Sedimentary Systems” project at UFRGS and the strategic importance of the support given by ANP through the R&D levy regulation. BGS and LAMIR staffs are also acknowledged for assisting with stable isotope analysis. We also would like to tank Dr. Duncan McIlroy for all his help during the field work, and

Dr. Marc Laflamme, Dr. Pedro Jose Marenco and an anonymous reviewer for their help in improving the manuscript.

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Table 1. Quartz grain size for March Point and Felix Cove sections.

	March Point		Felix Cove		
Hight	*222.3 m*	*222.5m*	*23 m*	*23.4 m*	*24 m*
Average	88	89	473	466	456
Maximum	338	224	734	815	858
Minimum	37	36	116	227	138
Median	75	78	504	439	409
n	31	31	31	31	31

Table 2. March point section isotopic results.

Sample description	Sample height (m)	$\delta^{13}C_{org}$ (‰)**	%C	$\delta^{13}C_{carb}$ (‰)*	$\delta^{18}O_{carb}$ (‰)*	Laboratory
Glauconitic grainstone	9.25	-		-0.96	-8.09	LAMIR
Grainstone	56.75	-		-1.79	-5.51	LAMIR
Grainstone	59.00	-		-1.32	-5.70	LAMIR
Grainstone	67.00	-		-0.41	-7.63	LAMIR
Grainstone	83.50	-		-1.80	-7.37	LAMIR
Grainstone	86.50	-		-1.26	-7.28	LAMIR
Grainstone	106.00	-		-2.46	-6.74	LAMIR
Grainstone	109.50	-		-3.84	-7.62	BGS
Grainstone interbedded with mudstone	115.25	-		-1.77	-6.55	LAMIR
Glauconitic grainstone	122.5	-29.2	0.2	-	-	BGS
Reddish grainstone interbedded with shale	126.00	-		-2.16	-8.01	LAMIR
Shale	132.50	-28.41	0.4	-	-	BGS
Shale	133	-27.9	0.3	-	-	BGS
Shale	133.50	-29.47		-	-	BGS
Grainstone interbedded with mudstone	136.25	-		-3.18	-7.38	BGS
Shale	136.5	-30.8		-	-	BGS
Grainstone interbedded with mudstone	137.00	-		-4.16	-7.57	LAMIR
Grainstone	140.25	-		-2.54	-8.19	LAMIR
Shale	145.00	-27.48	0.1			BGS

Glauconitic bioclastic grainstone	152.25	-		-1.29	-8.00	LAMIR
Glauconitic bioclastic grainstone	152.50	-		-0.82	-7.84	BGS
Shale	153.25	-28.71	0.1	-	-	BGS
Shale	154.25	-26.61	0.1	-	-	BGS
Shale	155.25	-27.50	0.1	-	-	BGS
Shale	157.25	-28.40	0.1	-	-	BGS
Shale	157.25	-28.70	0.1	-	-	BGS
Mudstone interbedded with shale	160.25	-26.68	0.3	-	-	BGS
Mudstone interbedded with shale	162.25	-27.07	0.1	-	-	BGS
Mudstone interbedded with shale	166.75	-26.79	0.04	-	-	BGS
Glauconitic grainstone	167.00	-		-0.90	-7.94	LAMIR
Glauconitic grainstone	167.50	-27.88	0.3	-	-	BGS
Glauconitic grainstone	167.75	-27.35	0.1	-	-	BGS
Mudstone	168.75	-27.82	0.3	-	-	BGS
Glauconitic grainstone	170.75	-28.01	1.9	-	-	BGS
Glauconitic grainstone interbedded with mudstone	174.00	-27.70	0.5	-	-	BGS
Glauconitic grainstone interbedded with mudstone	175.50	-		-1.16	-5.90	BGS
Mudstone	175.50	-27.97	0.2	-	-	BGS
Glauconitic grainstone interbedded with mudstone	176.50	-		-1.49	-6.72	LAMIR
Glauconitic grainstone interbedded with mudstone	176.50	-24.77	0.3	-	-	BGS
Parted limestone dolomitized	179.00	-		-0.84	-7.19	LAMIR
Dolomitized parted limestone	179.00	-		-0.82	-6.50	LAMIR
Dolomitized parted limestone	179.75	-25.67	0.4	-	-	BGS
Glauconitic grainstone	180.50	-27.36	2.1	-	-	BGS
Dolomitized oolitic grainstone	183.75	-30.02	0.2	-	-	BGS
Dolomitized oolitic grainstone	184.50	-		-1.72	-6.87	LAMIR
Dolomitized oolitic grainstone	189.50	-		-1.53	-6.56	LAMIR

Mudstone	194.00	-22.47	0.3	-	-	BGS
Dolomitized oolitic grainstone	194.25	-27.21	0.5	-	-	BGS
Dolomitized oolitic grainstone	194.75	-26.68	0.5	-	-	BGS
Dolomitized oolitic grainstone interbedded with mudstone	198.50	-28.24	0.1	-	-	BGS
Parted limestone	199.50	-28.55	0.04	-	-	BGS
Dolomitized oolitic grainstone	200.25	-		-1.61	-6.76	LAMIR
Dolomitized oolitic grainstone	201.50	-28.17	0.1	-	-	BGS
Dolomitized oolitic grainstone	206.00	-21.31	0.8	-	-	BGS
Dolomitized oolitic grainstone	208.00	-		-1.29	-6.66	LAMIR
Dolomitized oolitic grainstone	215.50	-		-0.68	-6.93	LAMIR
Dolomitized oolitic grainstone	218.50	-		-0.46	-5.27	BGS
Parted limestone	218.50	-22.55	0.5	-	-	BGS
Dolomitized oolitic grainstone	222.75	-		+1.13	-5.08	BGS
Dolomitized oolitic grainstone	223.60	-		+0.52	-4.58	BGS
Dolomitized oolitic grainstone	223.75	-		+0.79	-5.76	BGS
Parted limestone	224.75	-25.79	0.1	-	-	BGS
Parted limestone	225.50	-		-0.31	-4.75	BGS
Parted limestone	226.25	-		-0.18	-4.04	BGS
Parted limestone	226.25	-25.55	0.1	-	-	BGS
Parted limestone	226.75	-26.3	1.1	-	-	BGS
Glauconitic grainstone	230.00			-1.74	-7.73	BGS
Glauconitic grainstone	230.00	-26.24		-	-	BGS
Mudstone	230.75	-		-1.35	-8.18	BGS
Mudstone	231.50	-		-1.83	-8.47	BGS
Mudstone	233.50	-		-1.05	-7.95	BGS
Mudstone	235.00	-		-1.19	-8.08	BGS
Glauconitic grainstone	236.00	-		-1.73	-8.32	BGS

Glauconitic grainstone	236.00	-		-1.67	-8.62	BGS
Glauconitic grainstone	236.75	-		-2.01	-7.86	BGS
Grainstone	239.25	-		-1.07	-6.57	LAMIR
Grainstone	239.25	-23.05		-	-	BGS
Dolomitized oolitic grainstone	244.50	-		-1.38	-3.32	LAMIR

**Overall analytical reproducibility for ^{13}C and ^{18}O (1σ): BGS - 0.1‰; LAMIR: not determined*
***Overall analytical reproducibility for $^{13}C_{org}$ (1SD): BGS - ±<0.1‰*

Table 3. Felix Cove section isotopic results.

Sample description	**Sample height (m)**	**$\delta^{13}C_{org}$ (‰)****	**%C**	**$\delta^{13}C_{carb}$ (‰)***	**$\delta^{18}O_{carb}$ (‰)***	**Laboratory**
Grainstone	1.00	-		-2.0	-7.3	BGS
Grainstone	6.50	-		-1.3	-5.9	BGS
Shale	9.00	-26.6	1.0	-	-	BGS
Grainstone	13.00	-		-1.2	-7.0	BGS
Grainstone	16.80	-		-1.2	-7.5	BGS
Shale	17.25	-26.4	0.1	-	-	BGS
Shale	17.50	-27.5	0.17	-	-	BGS
Dolomitized oolitic grainstone	19.00	-		-0.5	-6.5	BGS
Dolomitized oolitic grainstone	22.25	-		-1.1	-9.0	BGS
Dolomitized oolitic grainstone	23.40	-		+0.4	-5.4	BGS
Dolomitized oolitic grainstone	24.00	-		+0.9	-5.4	BGS
Dolomitized oolitic grainstone	24.00	-		+0.87	-5.55	BGS
Dolomitized oolitic grainstone	25.50	-		+0.8	-5.4	BGS
Dolomitized oolitic grainstone	26.00	-		+1.02	-5.57	BGS
Shale	26.60	-23.5	0.01	-	-	BGS
Dolomitized oolitic grainstone	27.25	-		+0.9	-5.7	BGS
Dolomitized oolitic grainstone	27.50	-		+1.59	-5.76	BGS
Dolomitized oolitic grainstone	29.75	-		+1.83	-5.34	BGS

Shale	30.75	-25.7	0.04	-	-	BGS
Shale	33	-25.0	0.04	-	-	BGS
Dolomitized oolitic grainstone	35.25	-		+1.70	-5.46	BGS
Shale	36.00	-26.1	0.19	-	-	BGS
Mudstone	36.50	-		+1.10	-5.30	BGS

**Overall analytical reproducibility for $^{13}C_{carb}$ and ^{18}O (1σ): BGS - 0.1‰*

***Overall analytical reproducibility for $^{13}C_{org}$ (1σ): BGS - ±<0.1‰*

Figure 1. Record of the SPICE excursion and global chronostratigraphic framework (after Saltzman et al. 2004).

Figure 2. Study area in the Port au Port Peninsula. Location of the logged sections are shown by black rectangles: 1) March Point and 2) Felix Cove.

Figure 3. Schematic stratigraphic log of the Port au Port Group (after Chow, 1986). Each of the Grand Cycles (A, B and C) consists of a lower shaley half-cycle mainly composed of parted limestone (interbedded shale and mudstone) and an upper carbonate half-cycle of oolitic grainstone / bioherms. Estimated Sauk II-III sequence limit is indicated (Chow and James 1987b, Saltzman et al. 2004).

Figure 4. Outcrop photos of SPICE-bearing layers: (a) Felix Cove outcrop at 22.5 m showing the massive sandstone (S) that overlies the thrombolite layer at 22.25 m. Some intervals in the thrombolite contains vugs parallel to bedding that may also occur in the sandstone (arrow); (b) Detail from Felix Cove of thrombolite at 22.25 m; (c) West Felix Cove outcrop with pillow thrombolites (T) and the overlying sandstone (S); (d) Detail from March Point of columnar stromatolite at 222.5 m; e) Detail of the dolomitized glauconitic grainstone (DG) above the stromatolite (STR); f) View of the outcrop with the dolomitized glauconitic grainstone (DG) overlying the stromatolite.

Figure 5. Felix cove section: (a) Photomicrograph of the sandstone at 22.5m (peak SPICE), with quartz (Qz), crinoid bioclasts (Cr) and a few glauconite grains (G) and peloids (P), cemented by calcite (pinkish stain), with minor dolomite replacement (uncrossed polarizers) (b) Photomicrograph of the equivalent sandstone layer in West Felix Cove cemented by dolomite replacing calcite (pinkish stain), with minor dolomite replacement (uncrossed polarizers); March Point section: (c and d) Photomicrographs of dolomitized (D) glauconitic (G) bioclastic (Cr) peloidal grainstone at 222.6m (peak SPICE). (d) Detail of the glauconite (G) glauconite peloid partially replaced by dolomite (D) in (c); (e and f) Photomicrographs of glauconitic (G) sandstone partially cemented by euhedral dolomite rhombs (D) at 226.5m.

Figure 6. Photomicrographs of March Point dolomitized layers. (a) Dolomitized grainstone at 189.5 m; (b) Dolomitized grainstone at 208 m with ghost of ooids (black arrows); (c) Dolomitized grainstone at 215.5m; (d) Quartzose (Q) arenite cemented by dolomite (D) at 239.5 m.

Figure 7. March Point isotope results, showing $\delta^{13}C_{org}$, $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ isotopic data. Dolomitized samples indicated in red.

Figure 8. Felix Cove isotope results, showing $\delta^{13}C_{org}$, $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ isotopic data. Dolomitized samples are indicated in red.

Figure 9. Comparison between the expression of the SPICE in the March Point (1) and Felix Cove (2) sections. The grey shaded area indicates the correlation based on the carbonate carbon signature.

Figure 10. $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ data for A) March Point Sections and B) Felix Cove Section. The comparison between the curves shows a peak of organic excursion a few meters below (but nearly coincident with) the peak of the carbonate carbon excursion in the March Point section, while in Felix Cove both peaks occurs at same level.

Figure 11. Laurentia paleogeographic map (Blakey 2016), showing its evolution between 510 Ma and 485 Ma. The red square indicates the position of western Newfoundland, yellow square indicates the position of southern Appalachians (Glumac and Walker 1998), and black squares indicates the positions of other SPICE localities in the United States (Nevada, Utah, Iowa and Minnesota) (Saltzman 2004). Detail of Newfoundland (NF) paleogeography and paleolatitudes are indicated on the map.