

**Light Carbon Stable Isotopes in Aragonite Veins, Lopez Island, WA: Evidence  
for Deep Life**

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A Senior Thesis presented to the faculty of the Department of Geology and Geophysics, Yale University, in partial fulfillment of the Bachelor's Degree.

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## I. Abstract

The San Juan Islands of NW Washington State preserve a record of high-pressure, low-temperature metamorphism formed during structural burial and rapid exhumation between 100 and 84 Ma. Metamorphic assemblages include lawsonite, prehnite, Al-pumpellyite, and aragonite, constraining peak conditions to at least 500 MPa and 100-200° C. We studied aragonite veins at Davis Head, a 50 m-long outcrop on the southern coast of Lopez Island. The outcrop lies within a 3 km-long fault zone, the Lopez Structural Complex, which locally juxtaposes pillow basalts over mudstones. Structural relationships in the region indicate that faulting occurred first, followed by high-pressure metamorphism and the development of pressure-solution cleavage. The Davis Head aragonite veins show variable deformation, indicating emplacement during cleavage formation, and incomplete retrograding to calcite by a solid-solid transformation. Because the transformation occurred without dissolution and re-precipitation, carbonate anions remained intact and would not be isotopically reset. Our work on 57 aragonite veins from Davis Head found anomalously light carbon stable isotopes, with  $\delta^{13}\text{C}$  values between +1 and -50 per mil; six veins had values in the range of -30 to -50 per mil. Further study of ten veins measured preliminary  $\Delta_{47}$  values between +4 and -27 per mil, corresponding to temperatures between 111 and -12°C. Clumped isotope temperatures are strongly correlated with carbon isotopic values. We propose that the aragonite veins were formed by oxidation of isotopically light methane during subduction and accretion. The wide range of carbon isotopic values indicates that the degree of oxidation was heterogeneous across the outcrop. Because oxygen

isotopes suggest that vein-forming fluids were rock buffered, oxidation was likely catalyzed by biogenic sulfate reduction. The correlation between temperature and carbon fractionation suggests that isotopic composition of methane varied over the subduction history of the outcrop, either because the lightest methane was oxidized first or because the intensity of methanotroph activity was temperature dependent. At low surface pressures, bacterial life is known to remain active to temperatures of  $\sim 122^{\circ}\text{C}$ . Biomolecules are stabilized by pressure, so bacterial life should extend to higher temperatures within the Earth's interior. We conclude that the Lopez Island aragonite veins are evidence of such deep life.

## **II. Introduction**

Scientific interest in biological communities in extreme conditions has increased significantly in recent decades (e.g. Bons et al. 1997, Trewin and Knoll 1999, Colwell and D'Hondt 2013). Colonies of bacteria and archaea, usually lithotropic in nature, have been found in environments as diverse as deep-sea hydrothermal vents, glacial ice, and several kilometers deep in the crust. Many of these discoveries coincide with improved understanding of the diverse metabolic and respiratory strategies employed by extremophile bacteria and archaea. Since the 1980's, biologists have begun to realize the astonishingly flexible survival strategies that prokaryotes employ (Nealson and Rye 2003). Whereas eukaryotes invariably respire oxygen and consume certain carbon-based molecules, many lithotrophic prokaryotes survive in inhospitable environments by catalyzing energetically favorable oxidation-reduction reactions and harnessing the chemical

potential energy. These biologically mediated but inorganic reactions often destroy minerals in the microbes' environments and prompt the precipitation of new ones. Thus, it can be said that these prokaryotes "eat and breathe' anything, including the rocks on this planet" (Nealson and Rye 2003).

The other innovation in our understanding of extremophile life is the discovery that certain microbes can survive in pressure and temperature conditions far beyond those at the surface. These conditions present numerous biological challenges, including weakening phospholipid cell membranes, unfolding proteins, and denaturing nucleic acids (Chen and Prohofsky 1993, Meersman 2013). For instance, research by Kaye and Baross (2004) found that bacteria subjected to pressures up to 55 MPa experienced decreased phospholipid saturation and eventually stopped growing. However, the researchers found that certain taxa were better able to withstand these pressure effects, suggesting the capacity to adapt to extreme conditions (Kaye and Baross 2004). These adaptations can be seen in laboratory experiments in which strains of *E. coli* and *Shewanella* MR1 were able to adapt and thrive at lithostatic pressures exceeding 1 GPa (Sharma 2002). Other research indicates that extremophiles can also survive under normally lethal temperatures. The upper temperature limit for life on the surface is thought to be about 110°C; however, due to the stabilizing effects of pressure on biomolecules, certain microbes can survive and even grow up to 122°C at hydrostatic pressures of 20-40 MPa (Takai et al. 2008). Organic enzymes outside of cellular membranes have been recorded in the field at temperatures as high as 140°C (Holden and Daniel 2004). While less research has been done on life at lithostatic pressures, it is logical

that these stabilization effects could increase the upper temperature limit for life in the deep interior.

In 1997, Jeffrey Feehan and his doctoral advisors proposed a biological origin for several calcium carbonate veins with extremely light carbon isotopes in a basaltic outcrop on Lopez Island, Washington State. These unusual isotopic values ranged from -47 to -51 ‰ PDB. Carbon with values below -40‰ is often suspected of having a biological source and has frequently been used to argue for life in the deep past (Neelson and Rye 2003). Mineral assemblages and structural studies indicated that the rocks were accreted by subduction to about 18 km depth before being rapidly exhumed to the surface (Brandon et al., 1988). If Feehan's hypothesis is correct, these veins represent the deepest evidence of life within the crust to date. We resampled the carbonate veins identified by Feehan in order to further explore his assertion that they are biogenic. We first characterized the veins' mineralogy and fluid inclusions through optical examination of thin sections, powder X-Ray Diffraction, and Raman spectroscopy. We then measured the veins' carbon and oxygen stable isotopic chemistry in order to compare them to Feehan's data. Finally, we measured the  $\Delta_{47}$  carbonate isotopologue in the vein minerals to establish the veins' formation temperatures. Our findings support Feehan's original hypothesis that the veins were formed through biological processes at depth. In addition to testing this idea, we also explore the biological mechanisms involved.

### III. Background

*Regional Geology.* The San Juan Islands of northwest Washington State represent a complex thrust fault system formed during a late Cretaceous collisional event. The San Juan-Cascade accretionary wedge (SJC) lies between the western coast of present-day North America and Wrangellia, an outboard exotic terrane that makes up the bedrock of Vancouver Island. The nappes of the SJC are highly varied, ranging in age from Cambrian to mid-Cretaceous and containing a wide range of lithologies (Brandon et al. 1988). Units are bounded by several large, roughly parallel thrust faults dipping to the northeast. Mapping of the thrust zone's stratigraphy, as well as chemical analyses of its geological units, indicate that the SJC thrust zone is made up of at least seven distinct tectonostratigraphic terranes and formations. These formations and the timing of deformation are constrained by fossil and isotopic ages (Brandon et al. 1988).

The terranes of the SJC are further divided into a large number of units related by primary stratigraphic contacts and common metamorphic histories (Brandon 1989). Most of these structural packages can be traced to geological settings along the west coast of North America; for instance, the early Cretaceous blueschist Easton Terrane appears correlative in mineralogy and age to parts of the Franciscan Complex of southern Oregon and northern California (Brown and Blake, 1987). However, the fault zone also includes exotic units such as the mid-Cretaceous Richardson pillow basalts, whose relation to other thrust slices remains poorly understood (Brandon et al. 1988). Widespread assemblages of lawsonite, prehnite, high-Al pumpellyite, and aragonite across the entire thrust zone characterize the

high-pressure, low-temperature metamorphism associated with this tectonic event. The presence of metamorphic aragonite facies places the burial depth of the SJC nappes at 500 MPa, or about 18 km. Apatite and zircon fission-track data constrain the maximum temperatures during burial: apatite tracks are reset but zircons are not, indicating that the rocks reached at least 100°C but not more than 180-200°C (Brandon & Vance 1992).

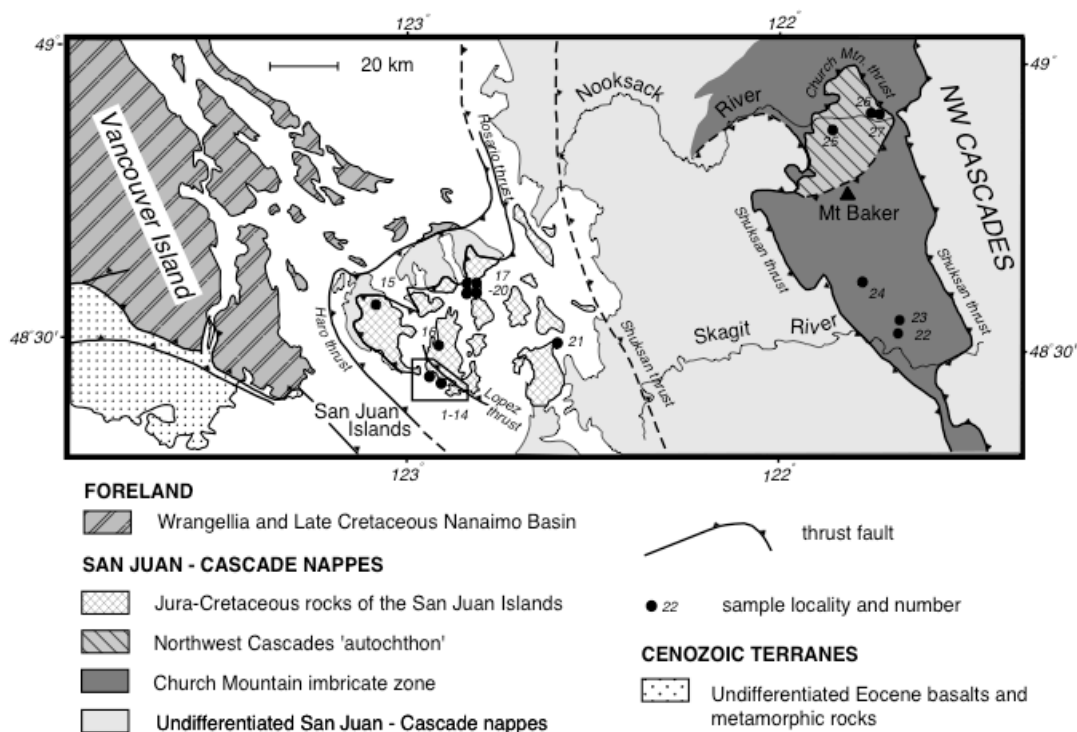


Figure 1: Map of the San Juan Islands. Source: Brandon et al. 1988

*The Lopez Structural Complex.* The Lopez Structural Complex (LSC) is an unusual unit of the San Juan thrust system exposed along the southern coast of Lopez Island. It lies between two relatively coherent units, the Decatur Terrane above and the Constitution Formation below. The Decatur Terrane, the structurally highest layer



of the San Juan thrust zone, is a stratigraphically well-defined sequence of ophiolitic, arc volcanic, and clastic rocks. The Constitution Formation, on the other hand, is made up primarily of sandstones and mudstones but includes ribbon cherts and pillow basalts that appear to be conformable with the sedimentary sequences (Brandon et al. 1988).

Unlike these generally coherent nappes, the Lopez Structural Complex is a thick (2.5 km) zone of highly heterogeneous imbricated rock slices (Brandon et al. 1988). These units include turbidites, brecciated gabbros, and Jurassic pillow basalts probably faulted off the Decatur Terrane; mudstones and sandstones likely from the Constitution Formation; tonalities similar to those of the structurally much lower Turtleback Formation; and a 2.5 km-long exotic slice of Cretaceous pillow basalt (Brandon et al. 1988). It is estimated that the combined horizontal slip of the LSC imbricates and the overlying Lopez Thrust was 26 km (Cowan & Brandon 1994).

All of the imbricate slices of the LSC show evidence of the pervasive late Cretaceous high-pressure, low-temperature metamorphic event that affected most of the San Juan thrust zone. These effects are characterized by the presence of lawsonite-aragonite and aragonite-pumpellyite-chlorite assemblages in the sandstone and basaltic units, respectively (Brandon et al. 1988). The units also show widespread pressure-solution cleavage textures related to solution mass transfer and extensive mass loss during the rapid exhumation of the units (Feehan & Brandon, 1999).

Many units of the San Juan thrust system, including the Lopez Structural Complex, also contain extensive vein systems that broadly follow the geometry of the pressure solution cleavages, indicating that they formed during burial and exhumation of the wedge. These veins are generally thin and make up less than 1% of the total volume of the rock, and are dominated by carbonate phases and quartz (Feehan 1997).

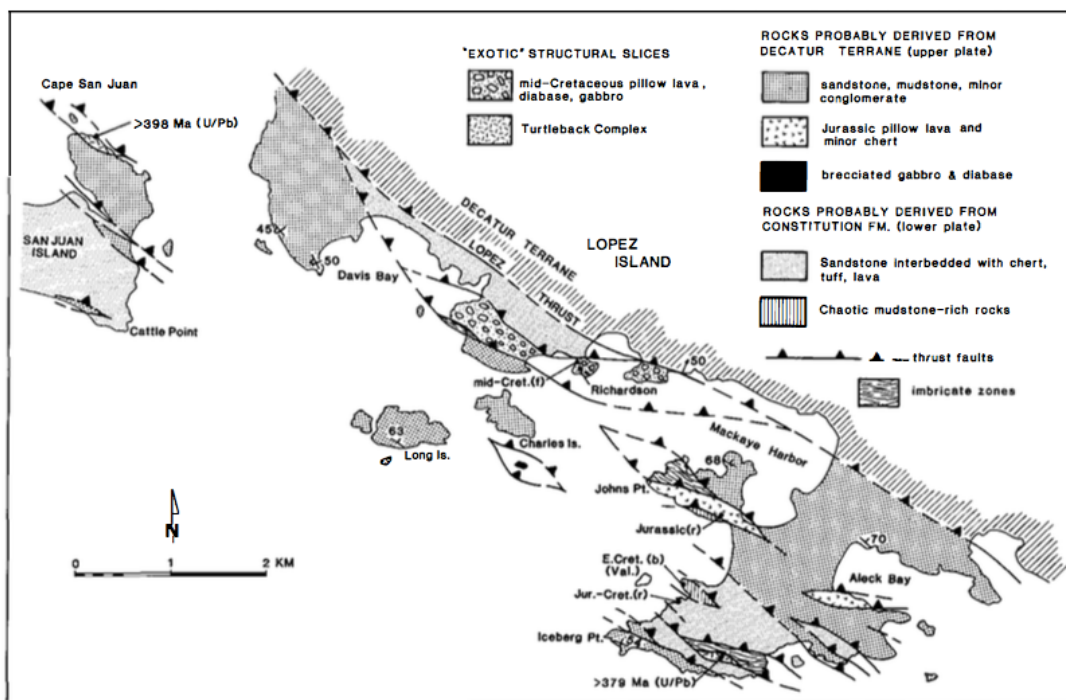


Figure 2: Map of Lopez Island. Source: Brandon et al. 1988

*Davis Head.* Davis Head, a promontory located on the southern coast of Lopez Island, exposes part of the LSC where a fault juxtaposes volcanic rocks over mudstones. The basalts contain small, angular grains of igneous and high-pressure, low-temperature metamorphic minerals such as lawsonite, prehnite, and plagioclase. An extensive system of carbonate veins in varying states of deformation cuts through the Davis Head volcanic rocks. Finite strain analysis of the region conducted by Feehan

suggests that the strain rate at Davis Head remained relatively constant over its history, suggesting that the veins were continually deformed from the time of precipitation until exhumation was complete.



*Figure 3: Aerial Photograph of Davis Head, Lopez Island*

#### IV. Characterization of Samples

*Sample Collection.* In order to further explore Feehan's results, we conducted a new analysis of Davis Head carbonate veins. Samples were collected along an approximately 50 m transect of the outcrop. After an initial visual survey to determine the location of the volcanic–mudstone contact and the overall characteristics of veining across the rocks, eighteen samples were chosen, photographed, and collected for further testing. Samples were selected to reflect the diversity of vein size and deformation.



*Figure 4: Photograph of Davis Head Outcrop*

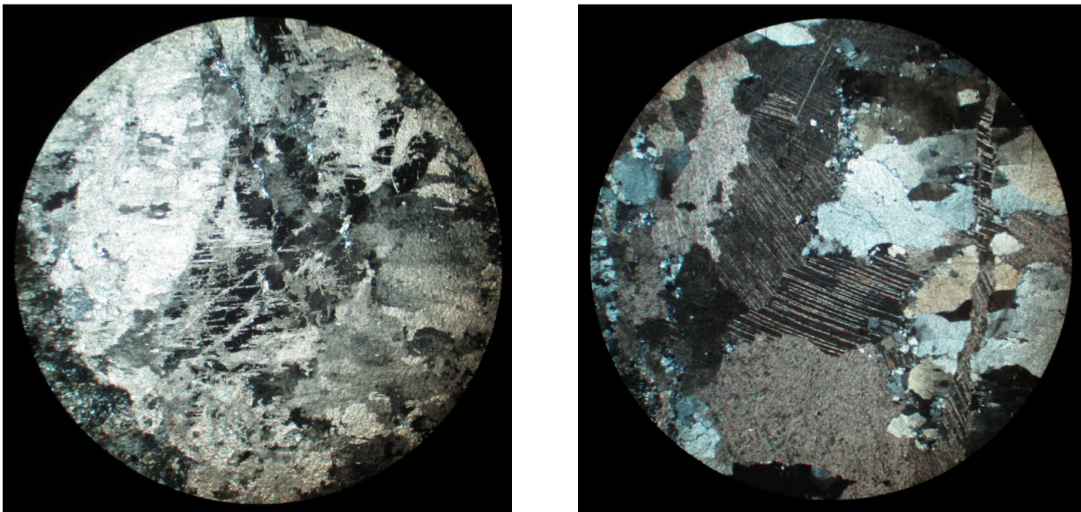
*Vein Description.* The Davis Head vein system is extremely heterogeneous both mineralogically and spatially, likely reflecting a complex formation history. Veins range in thickness from a few millimeters to several centimeters. These morphological variations follow no obvious spatial patterns. Previous work by Brandon and others (1988) argues that veins within the Lopez Structural Complex formed as a result of deformation cleavage caused by stresses within the host rocks during subduction and exhumation. While not all veins intersect the outcrop at the same angle, they general fall into two categories, supporting the relationship between vein formation and local stress patterns. The first type occurs at a high angle and intersects the outcrop nearly perpendicularly. The second type has a low dip and a non-perpendicular strike with respect to the cliff face, exposing large surfaces of the vein walls when eroded. These two vein morphologies typically occur together and exhibit crosscutting relationships. While the strong coastline weathering makes it difficult to assess the vein morphologies accurately, in general the high-angle veins are thinner and more highly deformed, while the low-angle veins are thicker and less deformed. Regardless of angle, however, most veins exhibit some degree of deformation such as folding and boudinaging, indicating that they experienced large stresses after precipitation. The degree of deformation varies greatly from one vein to the next, even in cases where veins are located very close together or have a crosscutting relationship. The diversity in orientations relative to the outcrop thus makes assessing the veins' relative ages difficult.



*Figure 5: Photographs of Samples 5 (left) and 6 (right) in situ*

*Mineral Textures.* After the eighteen samples were collected and returned to the lab, we prepared twenty thin sections. Extra thin sections were made to account for large variations within two of the collected veins. The 30- $\mu\text{m}$  thick sections were observed under plane and cross-polarized light. Although their large-scale morphologies are highly heterogeneous, the veins from Davis Head possess similar micro-scale textures. In general, veins are characterized by large crystals of aragonite, which appear light gray in plane light and exhibit wavy extinction under cross-polarization. Much smaller crystals of calcite occur along grain boundaries or within small veins cutting through aragonite crystals. The calcite minerals appear randomly oriented, and many exhibit twinning, likely as a result of high stresses during crystallization. The large difference in crystal size and the spatial relationships between the two minerals suggests that calcite has replaced aragonite in these veins. Since metamorphic aragonite forms only at high pressures, the replacement textures observed in these samples are likely the result of retrograde recrystallization during exhumation of the Lopez Structural Complex. There is no optical evidence, however, that this phase transition occurred by dissolution of

aragonite and re-precipitation of calcite. Rather, the mineral textures suggest that retrograding occurred between two solid phases. While replacement textures were observed across the whole outcrop, the degree of preservation of the primary aragonite varies between samples. Retrograding therefore appears to be a localized process within this vein system.



*Figure 6: Photomicrographs of Samples 1 (left) and 5 (right)*

*Mineral Composition.* While it is clear from thin sections that veins contain both primary aragonite and secondary calcite, the variability of retrograding across the outcrop makes the degree of replacement difficult to determine optically. Therefore, we used powder X-Ray Diffraction to quantify the proportions of minerals within each vein. Vein samples were taken from each rock using clean pliers. Each vein was then ground to a fine powder in an agate mortar and placed in a sterile, sealed vial. Powder X-Ray Diffractometers from the Yale University Geology & Geophysics and Chemistry departments were used to analyze these powders. Most spectra

contained well-defined peaks for both aragonite and calcite as well as quartz, indicating that vein-forming fluids contained a significant amount of dissolved  $\text{SiO}_2$  as well as carbonate.

In order to measure the degree of retrograding, we compared the aragonite and calcite XRD peaks using the formula described in Dickinson & McGrath, 2001, for binary mixtures of calcium carbonate:

$$X_C = X_A \frac{A_C}{A_A \times 3.5}$$

Where  $X_C$  and  $X_A$  are the mole fractions of calcite and aragonite, respectively, compared to total calcium carbonate, and  $A_C$  and  $A_A$  are the areas under the X-ray diffraction peaks associated with calcite and aragonite. We found that, as observed qualitatively in thin section, the fraction of aragonite preserved in the veins varies widely, from a high of 95.4% to a low of 0%.

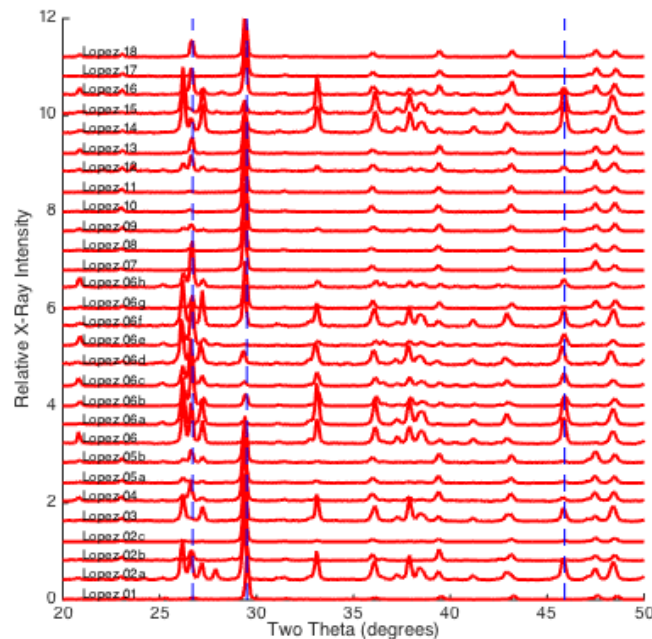


Figure 7: X-Ray Diffraction Spectra of Vein Matrices



*Fluid Inclusions.* All of the veins contain inclusions trapped within their carbonate minerals. In general, these inclusions are very small, ranging from under one micron to a few microns in diameter. Many show evidence of warping and necking, indicating that they underwent deformation after forming. The inclusions were identified using the microscope on a Raman spectrometer at 100x magnification (after Dailey 1985, Ueno et al. 2006, White 2009, Frezzotti et al. 2012). While the inclusions under one micron were too small to be described in detail using this equipment, visual observation of the larger examples revealed mobile bubbles within the inclusions, indicating a two-phase fluid. We performed a more detailed analysis of 36 visually identified inclusions and 2 vein matrix controls using the Raman spectrometer. While the Raman spectra confirmed the presence of calcite, aragonite, and quartz in all the samples, it failed to identify any fluid phases in the inclusions, even when fluid phases could be observed visually. This discrepancy is likely due to the low sensitivity of Raman spectroscopy to fluid phases such as water and methane compared to solid mineral phases. The fact that many inclusions were under 1 micron in size, smaller than the beam diameter of the instrument, may have caused the fluid signal to be drowned out by those of the surrounding minerals. Further investigation of these inclusions using other techniques, such as decrepitation, would contribute greatly to our understanding of the conditions under which these veins formed.

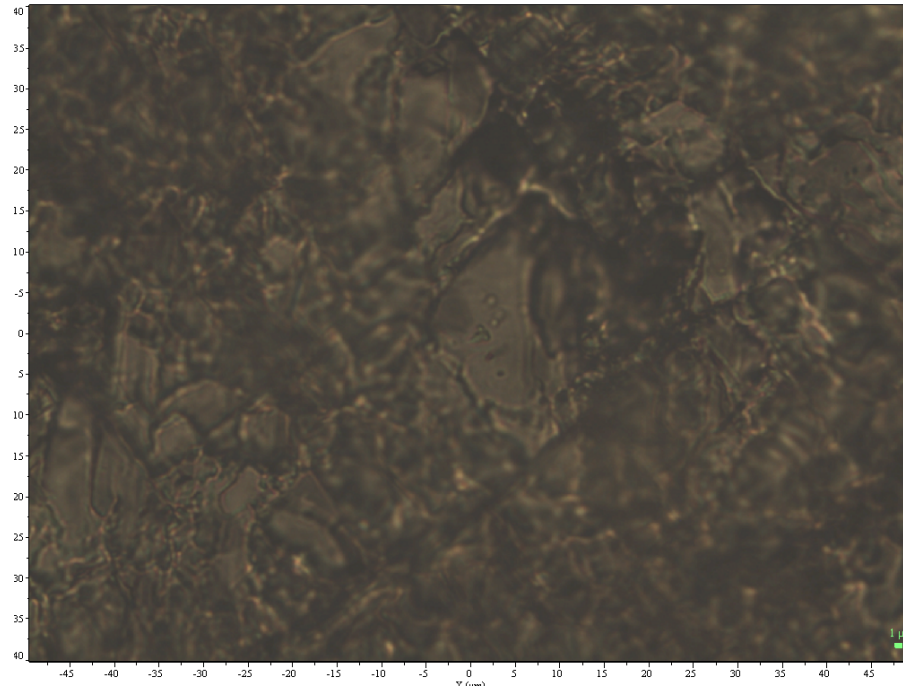


Figure 8: Micro-photograph of fluid inclusions from Sample 5

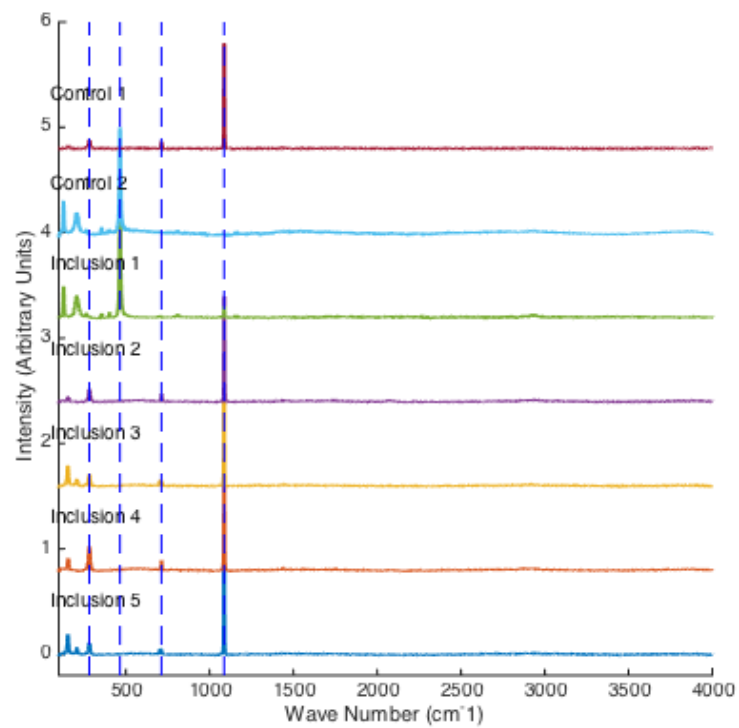


Figure 9: Raman Spectra of Vein Fluid Inclusions in Sample 5

## **V. Isotopic Analysis**

*Feehan's 1997 Study.* The first study of carbonate vein isotopic compositions at Davis Head was completed by Jeffrey Feehan in his 1997 dissertation. Feehan attempted to use stable isotopes of carbon and oxygen to trace the source of fluids circulating through the SJC accretionary wedge during structural burial and exhumation. This analysis was intended to differentiate between surface water and metamorphic fluids advecting through intergranular pore spaces in the rocks. Because these two categories of fluid would enter the wedge from opposite directions, a better understanding of the fluid's source would help explain the nature of mass transport in the thrust zone. Feehan chose to focus on carbonate veins in outcrops such as Davis Head, as well as other localities from different slices of the accretionary wedge, because of their association with thrust-related pressure solution cleavage.

Feehan selected twenty-seven samples of carbonate veins from Davis Head. The veins chosen for isotopic analysis were thin, mostly ranging in width from 1 to 2.5 mm with a maximum of 5 mm (Feehan 1997). The veins were interpreted as forming in tensile fractures because the vein angles were oriented approximately normal to the cleavage planes of the outcrop (Feehan 1997). The veins exhibited varying amounts of deformation and shortening along their long axes, ranging from highly boudinaged and buckled to undeformed. Because finite strain analysis of the Lopez Structural Complex indicated approximately constant strain rates across the outcrop, Feehan concluded that the various degrees of deformation represented different generations of veins forming within the outcrop. The Davis Head vein carbonates produced a  $\delta^{13}\text{C}$  range of -0.7 to -50.9‰ PDB and a  $\delta^{18}\text{O}$  range of -12.3

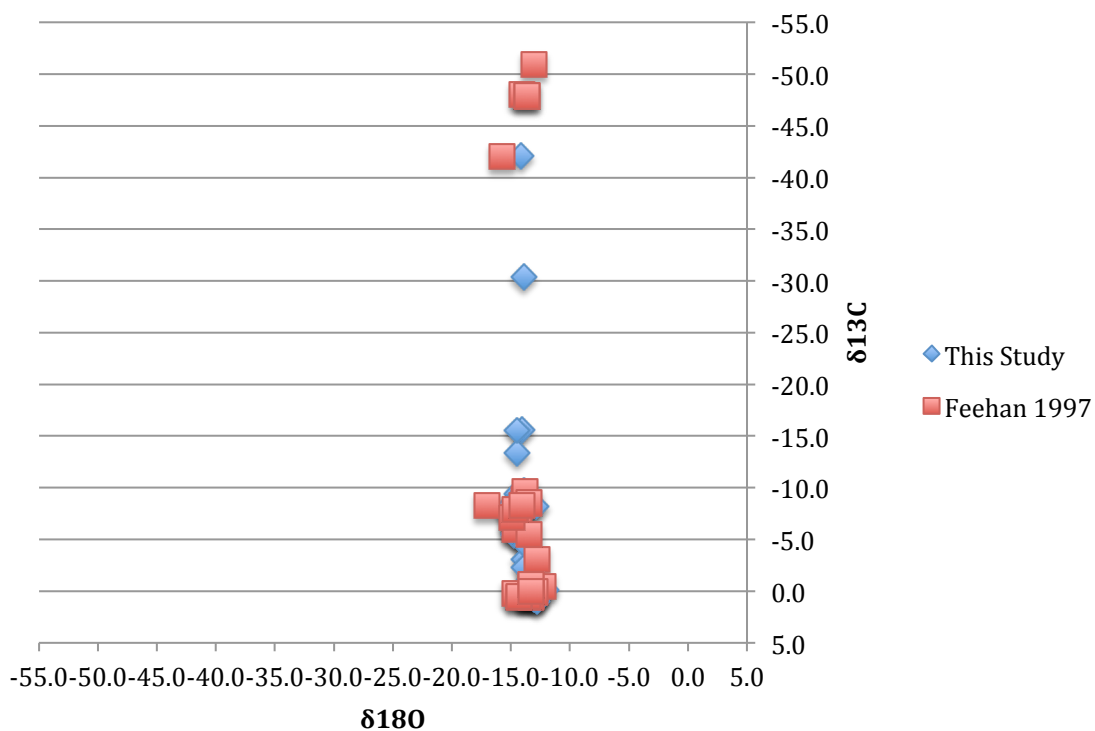
to -17.0 ‰ PDB (Feehan 1997). While Feehan found no correlation between vein deformation and carbon isotopic composition overall, the lightest carbon, between -47 and -50.9‰, occurred in moderately to strongly deformed veins.

*This Study.* The new analyses in this study focused on the outcrop where Feehan first found isotopic evidence of possible deep life. By conducting the same stable isotope tests of carbon and oxygen that Feehan performed in 1997, we attempted not only to confirm his initial results but also to provide more evidence for deep life in the LSC carbonate vein system. Unfortunately, Feehan's samples were not available for testing, so our investigation was limited to measuring newly collected veins and comparing them to the data recorded in Feehan's 1997 dissertation.

We obtained twenty-nine powdered samples of carbonate veins from the rocks collected at the outcrop. Samples were prepared in the same way as those for X-Ray diffraction testing, described above. We measured at least one vein from each of the eighteen rock samples. For samples 02, 05, and 06, we conducted more detailed investigations involving multiple data points. Samples 02 and 06 contain multiple veins with complex crosscutting relationships, while sample 05 is unusually thick. By sampling multiple points on these rocks, we hoped to better understand the degree of isotopic variation on an extremely local scale. All samples were tested at the Yale University Analytical and Stable Isotope Center (YASIC).

The results of our isotopic analysis show a remarkably large spread in  $\delta^{13}\text{C}$ , ranging from +1.0 ‰ to -42.1 ‰ VPDB. This large heterogeneity across the outcrop is not, however, reflected in the  $\delta^{18}\text{O}$  data, which range from -12.0 ‰ to -15.4 ‰ VPDB. Furthermore, the two stable isotope data sets do not correlate (i.e. veins with

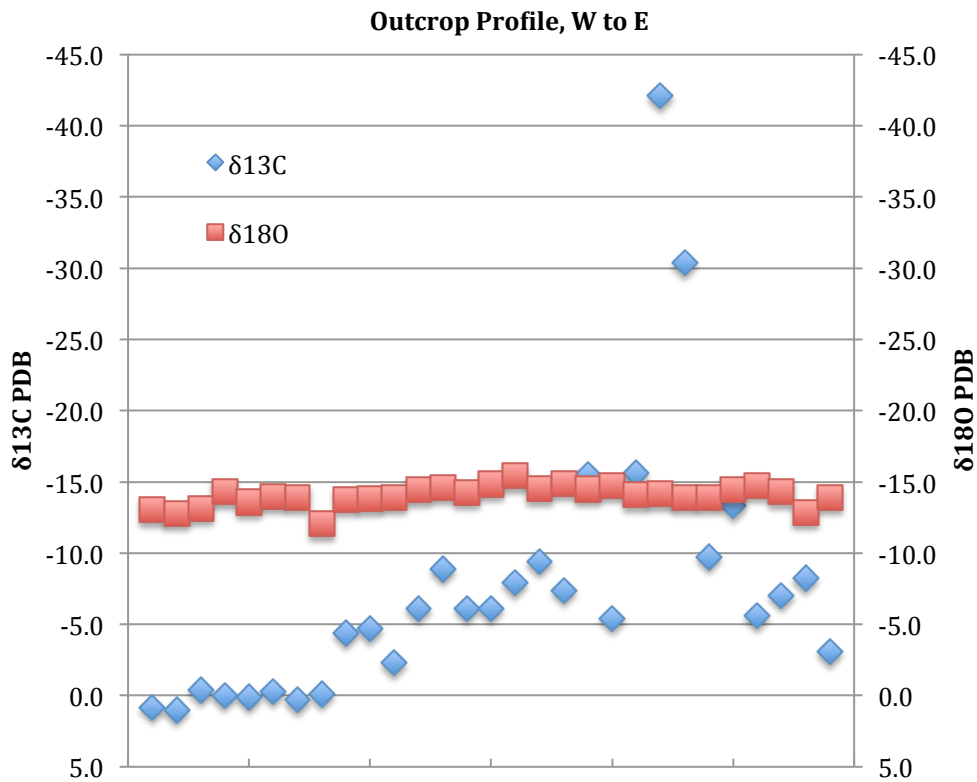
the lightest carbon isotopes do not also contain especially light oxygen). Our and Feehan's data exhibit the same pattern of large heterogeneity in  $\delta^{13}\text{C}$  but very consistent  $\delta^{18}\text{O}$  numbers across the outcrop. The lack of correlation between carbon and oxygen isotopes suggests a corresponding disconnection between the drivers of the carbon and oxygen isotope systems in the Davis Head vein system.



*Figure 10: Davis Head Stable Isotopes, 1997 & 2015*

In general, veins on the western side of the outcrop had stable carbon isotope values close to 0‰ PDB, while those on the eastern side were significantly depleted with respect to  $^{13}\text{C}$ . The lowest  $\delta^{13}\text{C}$  measurements both originated from sample 05, a several-cm thick vein situated at a low angle to the outcrop. Even within this single

vein, the amount of depletion of  $^{13}\text{C}$  varied by nearly 12‰. Surrounding this unusual sample was a ‘halo’ of other veins with relatively negative  $\delta^{13}\text{C}$  values for several meters in either direction. We observed no correlation between vein morphology and stable carbon isotope values. While more veins from this area should be collected to learn the precise extent of this light-carbon zone, the concentration of negative values around sample 05 suggests that a highly localized process allowed the precipitation of carbonates strongly depleted in  $^{13}\text{C}$ .



*Figure 11: Outcrop Transect of Stable Isotope Measurements*

The final isotopic analysis conducted in this study measured the mass of the entire carbonate anion in order to determine the temperature at which the minerals formed. Ten powdered samples from a broad range of the outcrop were analyzed

for their content of  $\text{CO}_3^{2-}$  anions with molecular weights of 47 and 48 by the clumped isotope lab at the California Institute of Technology. By comparing these values against standards, we predicted the temperatures at which these anions formed using a standard clumped isotope thermometer (e.g. Zaarur et al. 2013). Crucially for this system, the solid-solid transformation between aragonite and calcite preserved the characteristics of the carbonate isotopologues (Stolper and Eiler 2015). In this case, carbon and oxygen stable isotopes in the primary aragonite veins precipitated at depth would not be expected to reorganize themselves as the minerals retrograde to calcite. Therefore, the formation temperatures predicted by the clumped isotope analysis should reflect the temperatures of the original fluids in the vein system at depth, rather than a closure temperature imprinted on the veins by later exhumation and recrystallization. The large variability in  $\Delta_{47}$ , ranging from +4.0‰ to -26.7‰, lends credence to this assumption. If the molecular weights of the carbonate anions were in fact reset by retrograding of aragonite to calcite during tectonic uplift, one would expect that all of the clumped isotopes would reflect the pressure-temperature conditions associated with the mineralogical phase change and would thus have very similar values to one another. The fact that these clumped isotopes are, in fact, quite heterogeneous indicates real heterogeneity in hydrothermal fluid conditions at the time the veins were precipitated.

## VI. Discussion

In this discussion we consider the origin of the Davis Head aragonite veins and the evidence for a biological driver for their development. We focus first on the interpretation that veins formed by the oxidation of biogenic methane, based on the presence of light carbon in the veins, their low formation temperatures, and the short subduction timescale of the wedge. We then consider the context in which methane oxidation took place using vein formation temperatures, variations in carbon stable isotopic compositions, and stable isotopes of oxygen. Finally, we consider alternative deep carbon sources discussed in the literature. We believe that collectively, these data present strong evidence that bacteria were active at pressures exceeding half a gigapascal.

*Source of Carbonate Veins.* As reported above, we recorded  $\delta^{13}\text{C}$  values as low as -50‰ in some of the Davis Head aragonite-calcite veins. Such light isotopes of carbon are rare in similar subduction zone settings. A close analogue to the San Juan thrust system is the Franciscan formation of coastal California, a complex mélange with pervasive high-pressure, low-temperature metamorphism resulting from subduction between 150 and 70 Ma (Magaritz and Taylor 1976). A stable isotopic study of metamorphic aragonite veins hosted in Franciscan volcanic rocks measured  $\delta^{13}\text{C}$  values between 0 and -14‰, significantly heavier than the range reported here (Magaritz and Taylor 1976). While currently measurements of light carbon in metamorphic aragonite is rare, numerous researchers have invoked low  $\delta^{13}\text{C}$  in other settings to argue for the emergence of life and biological fixation of carbon in



the early Earth and extreme environments (e.g. Schopf and Klein 1992, Stakes et al. 1998, Oze et al. 2012). Specifically, a threshold of -40‰ PDB is commonly associated with the biological production and consumption of methane (Nealson and Rye 2003). While present-day methanogens produce CH<sub>4</sub> with carbon as light as -100‰ PDB, methane gas is poorly preserved in the rock record. The oxidation and mineralization of methane typically fractionates its carbon stable isotopes and results in a heavier product (Pan et al. 2006). Thus, preservation of a carbon isotopic fraction as low as -40‰ is a strong indication that lighter biogenic methane was once present in the system (Nealson and Rye 2003). The light carbon found at Davis Head therefore strongly suggests derivation from biogenic methane.

For methane gas to precipitate as aragonite minerals, its carbon must be oxidized from the -4 state in CH<sub>4</sub> to the +4 state in CO<sub>3</sub><sup>2-</sup>. While this reaction occurs readily in surface environments where oxygen is abundant (e.g. Kessler et al. 2011), the anaerobic conditions of the deep earth (Helgeson et al. 1993) require oxidation to occur by transfer of electrons. Research on environments with significant anaerobic methane oxidation, such as hydrothermal systems and petroleum fields, implicates sulfate as a primary electron receptor in this reaction (Hanson and Hanson 1996). This reaction proceeds as follows:



(Widdel and Rabus 2006)

The presence of pyrite and other sulfide minerals in close proximity to some of the Davis Head veins suggests that reduction of sulfate could have been responsible for the oxidation of methane in this system as well. Pyrite is associated

with magnetite, hematite, and possibly pyrrhotite assemblages in the wall rocks, buffering oxidation.

Sulfide reduction can either be thermochemically driven (TSR) or biogenic (BSR). TSR has been shown to be responsible for the abiotic oxidation of methane and the production of large amounts of H<sub>2</sub>S in many deep environments (e.g. Pan et al. 2006, Ding et al. 2007, Ma et al. 2008). However, this process has a high activation energy (142 kJ/mol) and thus proceeds very slowly at temperatures below ~100°C (Seewald et al. 1990, Cross et al. 2004). The mineral buffers in the Davis Head host rock would have further slowed the production of new carbon species (McCollom et al. 2007). Stratigraphic constraints on the timing of burial and exhumation of the Lopez Structural Complex, discussed above, indicate that the wedge was subducted and exhumed within a span of 16 Ma. The window of opportunity for carbonate vein production within the aragonite stability field would be significantly shorter. Thus, we believe that inorganic oxidation of methane proceeds too slowly at low temperatures to explain the large-scale methane fixation observed at Davis Head.

Due to the long time scales associated with abiotic methane fixation, we focus instead on its biogenic counterpart. In BSR, bacteria provide the activation energy to catalyze sulfate reduction, vastly increasing reaction rates to the scale of months or even days (Kessler et al. 2011). Moreover, biological methane consumption is most effective at low temperatures: below 100°C, biotic rates of sulfide oxidation are more than three orders of magnitude higher than abiotic ones (Luther et al. 2011). The rapidity of this biologically catalyzed reaction thus dominates abiotic methane

oxidation (Cross et al. 2004). The low temperature conditions at Davis Head, determined by high-pressure, low-temperature mineral assemblages and clumped isotope measurements, would have favored methanotropic catalysis of sulfate reduction over the much slower abiotic reaction. Both the temperature conditions and the stratigraphically-defined metamorphic time frame therefore point to biogenic sulfate reduction as the primary reaction driving the precipitation of carbonate veins at Davis Head.

*Environmental Context.* Jeffrey Feehan's 1997 research was guided by the concept that varying amounts of deformation in veins from the San Juans might be related to a protracted formation history. An interesting aspect of this interpretation is that it envisions that veins formed continuously over long periods of time. Feehan's fieldwork emphasized sampling with respect to deformational style, and focused only on thin veins orthogonal to cleavage formation. Despite these constraints, his results showed little to no relationship between deformation and age in the veins. In our resampling of the Davis Head outcrop, we collected a wider variety of vein morphologies and orientations. Like Feehan, we found no correlations between deformation style and any other characteristics of the veins. Therefore, we reject the hypothesis that the most deformed veins formed earliest in the sequence. We instead consider to the one clear correlation in our data, between  $\Delta_{47}$  and  $\delta^{13}\text{C}$ , to deduce formation history.

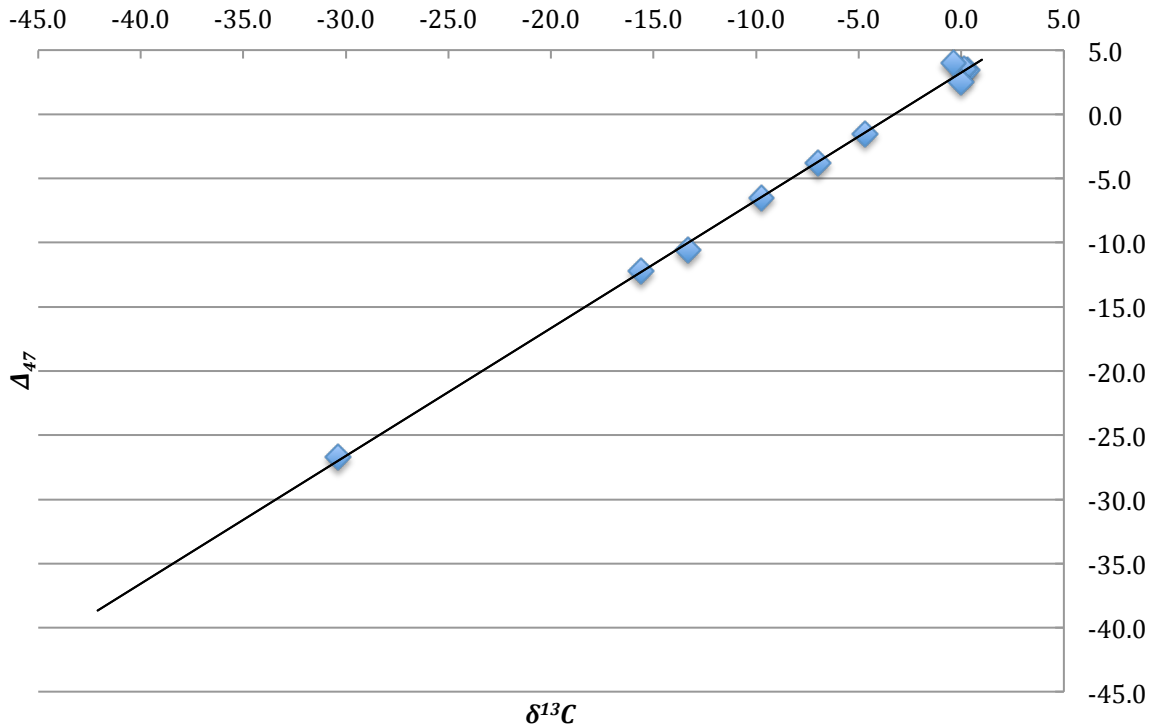


Figure 12:  $\Delta_{47}$  vs.  $\delta^{13}\text{C}$

The temperatures obtained from measurements of  $\Delta_{47}$  in the aragonite veins are highly heterogeneous, even across short distances. The lack of agreement between veins suggests that the rocks did not reach the clumped isotope resetting temperature for aragonite; thus, the data represent real formation temperatures for the vein minerals. This conclusion is supported by the lack of dissolution-precipitation textures in thin section, which indicate that clumped isotope temperatures were not reset (Stolper and Eiler 2015). The variation from surface temperatures to near peak metamorphic temperature suggests that the veins formed throughout the wedge's subduction within the aragonite stability field. While  $\Delta_{47}$  varies widely, it has a strong positive correlation with  $\delta^{13}\text{C}$ . We envision

that this strong connection between vein formation temperatures and carbon isotopic compositions reflect precipitation over an extended period of time, rather than in a single event. It is well known that isotopes fractionate more strongly in lower temperature conditions because of stronger kinetic barriers to isotope exchange. Therefore, veins formed at shallower depths can be expected to include lighter carbon, whereas those precipitated near peak metamorphic conditions contain heavier carbon. The correlation between temperature and carbon isotopic composition observed in the data thus strongly suggests that the methane was not only formed at depth, but also evolved continuously with increasing temperature during subduction. This relationship allows us to construct a history of formation in which the earliest veins to precipitate along the subduction path had the lowest formation temperatures and the lightest carbon isotopes.

While the correlation between  $\Delta_{47}$  and  $\delta^{13}\text{C}$  strongly suggests a relationship between formation temperature, vein age, and carbon fractionation, the wide range in  $\delta^{13}\text{C}$  itself points to a complex formation history. As noted above, the combined Davis Head data record a range of over 50‰ in  $\delta^{13}\text{C}$ , while  $\delta^{18}\text{O}$  varies by only 5‰. This result strongly suggests that the two isotope systems had disparate forcing mechanisms. In the case of oxygen stable isotopes, the measurements' consistency and the small water to rock ratio inferred from the low volume of veins compared to the bulk outcrop indicates that the vein-forming fluids were rock-buffered; we discuss this interpretation below. The carbon isotope system, in contrast, must have been controlled by a heterogeneous forcing mechanism. Our conclusion that biogenic sulfate reduction produced the vein carbonates implies that the

heterogeneity in carbon isotopic values reflects variable degrees of methane oxidation in the system. Because carbon fractionation is also closely tied to temperature, we imagine that isotopic values in this system were determined by temperature effects on the ability of methanotrophic bacteria to fix methane.

Oxygen isotopes in the Davis Head carbonates have exceptionally low variation in comparison to carbon isotopic values. In addition, these values are substantially offset from the carbonate and seawater isotopic standards: the average  $\delta^{18}\text{O}$  is  $-14.0\text{‰}$  PDB, and  $+16.7\text{‰}$  SMOW. The veins' enrichment in  $^{18}\text{O}$  with respect to seawater indicates that vein-forming fluids were brought into a rock-dominated isotopic equilibrium as they flowed through the San Juan thrust system. In order to determine which minerals dominated the fluid chemistry, we calculated the equilibrium oxygen isotopic values for five different possible sources of the vein-forming fluids' composition at the temperatures indicated by clumped isotope measurements (see Appendix, Table 4). We then compared these calculated values to the measured oxygen isotopic composition of the veins. The measured values most closely match the range of compositions for clay minerals,  $16\text{-}26\text{‰}$ , and were particularly similar illite-smectite assemblages at low temperatures (Savin and Epstein 1970, Sharp 2007). The full range of isotopic values for smectite is  $18\text{-}22\text{‰}$ , whereas at the low temperatures seen in these veins it is only  $17.4\text{-}19.1\text{‰}$ . Thus, the vein-forming fluid would have been buffered from isotopic changes as the rock increased in temperature during subduction (D. Rye, personal communication). On the other hand, the measured oxygen isotopes were quite different from equilibrium values for plagioclase or water in equilibrium with calcium carbonate. These

findings strongly suggest that the vein-forming fluids were in equilibrium with rocks made up of clay minerals, not volcanic or carbonate-rich rocks. The most likely candidate for this clay-rich rock is the mudstone layer that lies beneath the Davis Head volcanic slice. In this scenario, we envision that carbonate-rich fluids within the accretionary wedge originated from the mudstone layer, with which they equilibrated, and rose into the volcanic layer as tectonic pressure and temperature increased. The lack of equilibrium between the fluids and the Davis Head volcanic rocks would have created a difference in chemical potential that could have been exploited by lithotrophic bacteria at the base of the volcanic layer, where the precipitation of the aragonite veins is seen to begin.

The transition from an equilibrium environment to one with different rock and fluid chemistries may have been critical to the survival of methanotrophic bacteria at the base of the Davis Head volcanic slice. We believe that methane was produced in fluids within the mudstone layer, where organic molecules would have been plentiful. The presence of pyrite and inferred BSR reactions in the volcanic rocks indicate that the mudstone-derived source fluid also contained significant dissolved sulfate. The presence of methane and sulfate in the fluid would have been critical for the survival of anaerobic methanotrophic bacteria because their metabolism is dependent on the oxidation of  $\text{CH}_4$  and simultaneous reduction of  $\text{SO}_4^{2-}$  (Hanson and Hanson 1996). Electric potential harvested from this reaction could produce significant biological energy for the methanotrophs (Amend et al. 2003), although many anaerobic bacteria are able to produce ATP from stored quantized energy, allowing them to survive very close to equilibrium conditions

(Jackson and McInerny 2002). While the raw materials of methane oxidation would have been available in the mudstone layer, the isotopic disequilibrium between the fluids and the volcanic rocks suggests that a greater electrical potential difference may have been available as well, allowing methanotrophs to grow and fix methane.

*Alternative Carbon Sources.* While we believe that the evidence for biogenic methane fixation at depth is strong and that this methane was produced by organisms within the subducting wedge, it is useful to consider possible alternative source materials for the veins. Here, we consider two alternatives to biological methanogenesis: carbonate fixation from  $\text{CO}_2$  and abiotic methane synthesis. We discount the idea of a widespread source of subducted methane beneath the San Juan Islands because we only observe these light carbonate veins in only one location; however, further sampling is required to determine the true extent of veins formed from methane.

In the near-surface environment, carbon dioxide is a common precursor to carbonate minerals because it is abundant and already in an oxidized state. However, we believe that it was not present in quantities sufficient to precipitate veins in the San Juan thrust system. The preservation of prehnite-lawsonite assemblages, whose zeolite precursors are unstable when fluids contain  $X_{\text{CO}_2} > 0.0075$  (Thompson 1971), indicates that vein-forming fluids contained very low amounts of  $\text{CO}_2$  by the time they interacted with the Davis Head volcanic rocks. Raman analysis of fluid inclusions also failed to identify carbon dioxide in the vein-forming fluids. We therefore believe that methane, which is unreactive at low temperatures, is a better candidate for the veins' source material than  $\text{CO}_2$ .



Although the lowest values we measured at Davis Head strongly suggest that methane was biogenic, in theory the heavier methane could have formed abiotically. Abiotic synthesis of CH<sub>4</sub> from organic molecules such as CO and HCOOH, known as Fischer-Tropsch synthesis, has been demonstrated in industrial laboratory contexts. This process produces methane fractionated up to -28‰ with respect to source material (McCollom et al. 2010). However, these experiments are commonly performed at low pressures (e.g. 17 MPa) and high temperatures (e.g. 250°C), more comparable with deep-sea hydrothermal vents than with the San Juan thrust zone (McCollom et al. 2010). Fischer-Tropsch synthesis also requires the presence of native metals to serve as electron donors for the reaction. There is no evidence of native metals in the wall rocks of Davis Head or elsewhere in the LSC nappes (Brandon et al. 1988) Furthermore, Fischer-Tropsch methane synthesis does not reach carbon fractionation levels comparable to the low end member of our data. Given the differences in conditions and degrees of fractionation, the source methane for the Davis Head veins is unlikely to have a strong abiotic component.

## VII. Conclusions

While it is not possible to prove the origins of the carbonate veins at Davis Head, the environmental constraints and isotopic compositions at the outcrop produce a scenario for vein formation that we believe is credible. Our carbon stable isotope data closely matched that of Feehan's initial 1997 study and showed a range of carbon isotopic values from 0 to 50‰ PDB. This low end member corresponds to fractionation of biogenic methane known from surface conditions. The metamorphic assemblages in the volcanic wall rock and the large grains of primary aragonite visible in the veins indicate that vein emplacement occurred during regional high-pressure, low-temperature metamorphism in the San Juan thrust zone. These conditions are regionally constrained to at least 500 MPa and 100-200°C; clumped isotope formation temperatures for the aragonite veins suggest maximum temperatures were on the low end of this range, around 111°C. Many of the veins appear to have formed at significantly lower temperatures. This range of temperature conditions lies below the currently known upper temperature limit for microbial life, ~122°C; the extreme pressures evident in this region ought to stabilize these molecules, allowing life to survive at even greater temperatures (Takai et al. 2008). Their light carbon composition and the presence of CO<sub>2</sub>-sensitive assemblages indicates that the vein carbonates likely formed by oxidation of methane; the lack of dissolved oxygen in the deep earth means that this reaction likely took place in conjunction with sulfate reduction. The fact that veins formed at low temperatures means that an abiotic source of methane is unlikely, because such a process would proceed very slowly with respect to the short time frame of burial

and exhumation of the outcrop. The temperatures of vein formation correlate strongly with carbon isotope fractionation, suggesting that methane of variable weight was produced during wedge subduction. Based on this evidence, we propose that methanogens in the mudstone slice consumed buried organic molecules and produced methane of variable weight depending on temperature; this methane then rose into the pillow basalts and was fixed into carbonate anions by biogenic reduction of sulfate to H<sub>2</sub>S and ultimately to sulfide minerals. The presence of aragonite as the primary phase of carbonate mineral in the veins means that this biological process occurred at depths near 18 km. These conclusions support the concept of extremophile life existing at extreme depths within the crust.

### **VIII. Acknowledgements**

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## X. Appendix: Data Tables

Table 1: Carbonate Vein Stable Isotope & Deformation Data (Feehan 1997)

<b>Vein ID</b>	<b><math>\delta^{13}\text{C}</math> VPDB</b>	<b><math>\delta^{18}\text{O}</math> VPDB</b>	<b><math>\delta^{18}\text{O}</math> VSMOW</b>	<b>Degree of Deformation</b>
DH1	-8.3	-17.0	13.3	Weak
DH2	-7.2	-14.3	16.1	Moderate
DH5-1	-5.9	-14.7	15.7	Weak
DH8	-0.3	-13.0	17.5	Strong
DH9	-0.5	-12.3	18.2	Strong
DH10	-3.1	-12.8	17.7	Strong
DH12	0.5	-13.3	17.2	Strong
DH13	0.2	-14.7	15.7	Moderate
DH14	0.1	-13.0	17.5	Strong
DH15-1	0.6	-13.4	17.1	Moderate
DH15-2	0.5	-13.5	16.9	Moderate
DH16	0.6	-14.3	16.1	Strong
DH17	-0.6	-13.3	17.2	Moderate
DH18	0.5	-14.3	16.1	Moderate
DH19	-0.7	-13.4	17.1	Strong
DH21	-50.9	-13.1	17.4	Strong
DH22	-48	-14.0	16.4	Moderate
DH23	-42	-15.8	14.6	Moderate
DH24	-47.9	-13.6	16.8	Strong
DH25	-47.9	-13.6	16.8	Strong
DH31	-5.5	-13.4	17	Moderate
DH32	-8.9	-13.9	16.5	Weak
DH33	-9.6	-13.8	16.6	Weak
DH34	-8.5	-13.4	17	Weak
DH35	-7.1	-14.9	15.5	Moderate
DH36	-7.9	-14.7	15.7	Moderate

Table 2: Carbonate Vein Data (This Study)

<b>Sample ID</b>	<b><math>\delta^{13}\text{C}</math> VPDB</b>	<b><math>\delta^{18}\text{O}</math> VPDB</b>	<b>Aragonite/Total Carbonate</b>	<b>Degree of Deformation</b>
L01	-3.1	-13.9	0	Weak
L02A	-8.2	-12.9	0.626	Moderate
L02B	-7.0	-14.3	0.068	Moderate
L02C	-5.6	-14.7	0.095	Weak
L03	-13.3	-14.5	0.563	Moderate
L04	-9.7	-13.9	0.251	Moderate
L05	-30.4	-13.9	0.152	Weak
L05B	-42.1	-14.2	0.116	Weak
L06	-15.6	-14.1	0.94	Weak
L06A	-5.4	-14.8	0.954	Weak
L06B	-15.5	-14.5	0.763	Weak
L06C	-7.4	-14.9	0.926	Strong
L06D	-9.4	-14.5	0.848	Strong
L06E	-7.9	-15.4	0.98	Strong
L06F	-6.1	-14.8	0.651	Moderate
L06G	-6.1	-14.3	0.12	Moderate
L06H	-8.9	-14.6	0.951	Strong
L07	-6.1	-14.4	0.004	Moderate
L08	-2.3	-13.9	0.007	Moderate
L09	-4.7	-13.8	0.216	Moderate
L10	-4.4	-13.8	0	Strong
L11	-0.1	-12.0	0	Weak
L12	0.3	-13.9	0.324	Weak
L13	-0.3	-14.0	0.066	Moderate
L14	0.1	-13.6	0.859	Moderate
L15	0.0	-14.3	0.889	Weak
L16	-0.4	-13.1	0.416	Strong
L17	1.0	-12.8	0.021	Weak
L18	0.8	-13.1	0.027	Moderate



Table 3: Carbonate Vein Clumped Isotope Data (This Study)

<b>Sample ID</b>	<b><math>\Delta_{47}</math></b>	<b><math>\Delta_{48}</math></b>	<b>T (°C)</b>
L02B	-3.8	3.0	32.1
L03	-10.6	-2.6	29.2
L04	-6.5	-0.5	35.3
L05	-26.7	-0.5	-12.5
L06	-12.2	-0.5	24.4
L09	-1.5	-0.4	62.1
L12	3.4	-0.3	87.8
L14	3.5	0.9	111.5
L15	2.6	-1.9	98.6
L16	4.0	3.0	82.4

Table 4: Oxygen Isotope Equilibria

<b><math>\delta^{18}\text{O}</math> SMOW (measured)</b>	<b>T (°C)</b>	<b><math>\delta^{18}\text{O}</math> SMOW (H<sub>2</sub>O &lt;-&gt; CaCO<sub>3</sub>)</b>	<b><math>\delta^{18}\text{O}</math> SMOW (Plagioclase)</b>	<b><math>\delta^{18}\text{O}</math> SMOW (Kaolinite)</b>	<b><math>\delta^{18}\text{O}</math> SMOW (Illite)</b>	<b><math>\delta^{18}\text{O}</math> SMOW (Smectite)</b>
17.61	32	-4.24	19.62	18.68	--	19.12
17.41	32.4	-4.37	19.42	18.47	17.70	18.92
16.89	111.5	6.12	19.89	18.02	18.73	19.32
16.68	62.1	-0.04	19.15	17.79	17.68	18.62
16.58	87.8	3.26	19.35	17.71	18.06	18.80
16.58	35.3	-4.63	18.64	17.65	16.95	18.14
16.37	24.4	-7.02	18.24	17.43	16.44	17.76
16.17	98.6	4.07	19.05	17.31	17.82	18.49
15.96	29.2	-6.44	17.92	17.03	16.17	17.43



