

The Carbonation of Serpentinites in the Orange-Milford Belt, Connecticut, USA

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## Abstract

The Orange-Milford belt of Connecticut contains carbonated serpentinites, or listvenites, that are characterized by a rich, olive-green color and cross-cutting yellow veins. They occur within the Maltby Lakes Metavolcanics (Ordovician). Previous research on their mineralogy suggests that the rocks were initially ultramafic in origin and had subsequently undergone hydration and carbonation in a pre-metamorphic event (Karsh, 1998). Currently, research is lacking on how the Orange-Milford serpentinites were carbonated, although there are several distinct possibilities: fluid rock interaction on the seafloor or during tectonic emplacement, or following emplacement and exhumation (Karsh, 1998). In this project, I examine the pre-metamorphic environment of the protolith and conduct an in-depth case study of carbon sequestration in ultramafic rocks through petrological analysis of thin sections prepared by J.J. Ague and stable isotope analysis of  $^{13}\text{C}$  and  $^{18}\text{O}$  along a profile extending across the carbonated serpentinites and associated metavolcanic rocks.

Petrological study of the mineral assemblages in specimens across the profile found little trace of carbonate in the metavolcanic section, suggesting that it was not carbonated in conjunction with the yellow and gray-green serpentinite sections. Furthermore, the extensive presence of magnetite potentially limits the temperature of serpentinization to  $>200^\circ\text{C}$ , although additional analysis is required for further constraints. Stable carbon and oxygen isotope ratios suggest that carbonation occurred at temperatures between  $150\text{-}200^\circ\text{C}$  via seawater circulation.  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$ , plotted against each other, fit a temperature-isotope curve corresponding to a hydrothermal fluid with isotopic values of  $\delta^{18}\text{O} = 0\text{‰}$  and  $\delta^{13}\text{C} = -4\text{‰}$  to  $-6\text{‰}$ , which is consistent with conditions at 459.5 Ma wherein  $\delta^{13}\text{C}$  dipped to its lowest values during the Ordovician, coupled with modifications from organic carbon and hydrothermal inputs. This coincides with metamorphism during Taconic orogeny, rather than immediately before Acadian orogeny as is initially hypothesized by Karsh (1998).

## Introduction

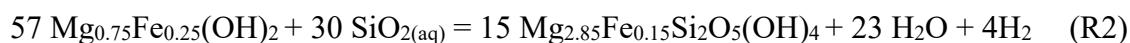
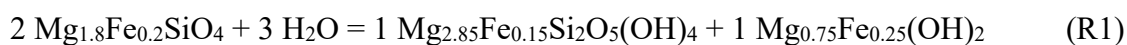
Mantle peridotites may undergo carbonation and hydration, or serpentinization, at low temperatures. Listvenites, or altered ultramafic rocks, frequently develop serpentine-carbonate-magnesite assemblages (Halls & Zhao, 1995). In-situ carbonation occurs when CO<sub>2</sub>-rich fluids interact with subsurface rock formations to create carbonate minerals. First, hydrothermal fluids leach calcium from ultramafic rocks, as evinced by alkaline Ca(OH)<sub>2</sub>-rich fluids surrounding partially-serpentinized oceanic peridotites (Bonatti *et al.*, 1980). Olivine and pyroxene hydrolysis releases OH<sup>-</sup> and, in conjunction with increased concentrations of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>, creates favorable conditions for carbonate deposition (Bonatti *et al.*, 1980).

Various examples of metamorphosed peridotites are found worldwide. For example, in their analysis of listvenites in the Samail Ophiolite of Oman, Falk & Keleman (2015) determined that the rocks likely formed between 96-78 Ma from pyroxene-depleted peridotites. Carbonate clumped isotope thermometry indicated that the samples formed between 80-130°C, which would have been reached between depths of 10-50 km along a subduction zone geotherm (Falk & Keleman, 2015). Furthermore, radiogenic analysis of the listvenites found elevated <sup>87</sup>Sr/<sup>86</sup>Sr levels relative to Quaternary carbonates in the ophiolite, suggesting that Sr-enriched carbonate sediments may have been incorporated into the listvenites, and that “the fluid mediating Sr [and] CO<sub>2</sub> ... transfer could have been derived from sediment-equilibrated seawater [or] from devolatilization of hydrous minerals in sediments” released at subduction zone pressures (Falk & Keleman, 2015).

In addition to characterizing the temperature of formation for listvenites, stable isotope analysis can be used to understand the fluid source involved in the carbonation process. Piccoli *et al.* (2016) analyzed carbon and oxygen isotopes in calcite from eclogite-facies marbles from Alpine Corsica. Their presence along metasomatized fluid channels suggested that the marbles also underwent hydrothermal alteration. δ<sup>13</sup>C<sub>VPDB</sub> values were similar to those of marine carbonates near subduction zones, while δ<sup>18</sup>O<sub>VSMOW</sub> values were similar to “fluids equilibrated with silicates in mafic or ultramafic rocks”; therefore, the authors concluded that the samples were likely formed through “interaction with aqueous fluids bringing isotopic signatures of both dissolved carbonates and mafic/ultramafic reservoirs” (Piccoli *et al.*, 2016).

Listvenite mineralogy is reflective of protolith and environmental conditions during formation. During serpentinization, for instance, interactions between seawater and Fe<sup>2+</sup> in

olivine generates  $\text{Fe}^{3+}$ , required for serpentinite and magnetite formation. Low-temperature (<200°C) serpentinization produces Fe-rich brucite and low levels of magnetite; conversely, moderate-temperature (200-300°C) serpentinization produces Fe-poor brucite and high levels of magnetite, while virtually all high-temperature (>300°C) serpentinization experiments produced significant magnetite (Klein *et al.*, 2014). Bach *et al.* (2006) hypothesize that magnetite is formed through the breakdown of brucite, peaking during 60-70% serpentinization of peridotite and constrained by levels of  $\text{SiO}_{2(\text{aq})}$  present in the interacting fluid:



Thus, temperature is likely a constraint on magnetite replacement of brucite, as higher temperatures may be reached during advanced stages of serpentinization.

Listvenites formed via fluid-rock seafloor interactions most frequently occur due to precipitation from low-temperature (<130°C) fluids as they circulate through the upper crust, or during mixing between seawater and hydrothermal fluids (Grozeva *et al.*, 2017). In these environments,  $\text{CO}_2$  is primarily derived from dissolved molecules in seawater, but can also be sourced from “degassing of magmatic fluids, decomposition of organic-rich sediments, and leaching of inclusions and basaltic glass” (Grozeva *et al.*, 2017). In their isotopic analysis of aragonitic listvenites, likely formed due to high seawater concentrations of  $\text{Mg}^{2+}$  relative to  $\text{Ca}^{2+}$ , Bonatti *et al.* (1980) found significantly elevated  $\delta^{18}\text{O}$  values (+34.16-35.70) typical of bottom water temperatures (0-4°C), suggesting that little tectonic activity occurred during seawater alteration of the serpentinized peridotites.

Seawater circulation may also deposit carbonates during tectonic emplacement. At mid-ocean ridges, for instance, ultramafic rock is created or exhumed, then altered. Oxygen and carbon analysis of carbonate veins in serpentinized dunites and harzburgites revealed similar aragonite  $\delta^{18}\text{O}$  values as Bonatti *et al.* (1980) and carbonate values between +8.4-18.3‰, with relatively heavier  $\delta^{13}\text{C}$  values (+7.2-8.7‰) implying “enrichment of  $^{13}\text{C}$  through partial reduction of seawater carbonate to  $^{12}\text{C}$ -rich methane” during thermogenic methanogenesis at temperatures above 350°C; however, the lower temperatures suggested by  $\delta^{18}\text{O}$  values indicate conductive cooling as the hydrothermal fluids slowly ascended through a detachment fault exposing the mantle peridotites and precipitated carbonate (Bach *et al.*, 2011).

The carbonation mechanism differs slightly at a subduction zone as fluids are released from the subducting plate at depths >30-50 km and alter ultramafic rocks in the overriding plate (Cutts *et al.*, 2021). In particular, deep-sea trenches and the “leading edge of the mantle wedges” above subduction zones are notable carbon sinks (Keleman *et al.*, 2018). The aforementioned Samail Ophiolite contains listvenites generated through decarbonation of underlying sediments, which increased CO<sub>2</sub> concentrations in surrounding fluids (Keleman *et al.*, 2018; Piccoli *et al.*, 2016). Furthermore, rock volume and mass increased during rapid serpentinization and carbonation, generating fractures in the brittle material that likely promoted fluid circulation levels (Keleman *et al.*, 2018). Stable isotope analysis of carbonate veins and hybrid carbonate-bearing serpentinites of the Ligurian West Alps by Scambelluri *et al.* (2016) obtained low  $\delta^{13}\text{C}$  values (-2.6-0.7‰ and -0.4-1.6‰, respectively) and  $\delta^{18}\text{O}$  values (+12-22‰ and +12.7-14.9‰), indicating peridotite dehydration and subsequent carbonation at 550°C, pertaining to 2-2.5 GPa pressures along the subduction gradient.

First discovered in 1811 by Yale professor Benjamin Silliman, carbonated serpentinites in the Orange-Milford belt of Southern Connecticut are characterized by their rich, olive-green color and cross-cutting yellow veins. The Orange-Milford listvenites were formerly quarried for ornamental use by the Verd-Antique Company. Marble from the location was highly prized for containing “spots of precious serpentine, of a deep olive green, admitting of a high polish,” and was therefore used as dimension stone in prominent buildings, including the White House and the Smithsonian Institute (Karsh, 1998). Previous research on their mineralogy suggests that the rocks were initially ultramafic in origin and had subsequently undergone hydration and carbonation in a pre-metamorphic event before deformation and metamorphism during Acadian orogeny (Karsh, 1998). Currently, it remains to be determined how the Orange-Milford serpentinites were carbonated, although several distinct situations may have resulted in such changes to the protolith: fluid rock interaction on the seafloor or during tectonic emplacement, or subsequent to tectonic emplacement and exhumation (Karsh, 1998). In this project, I seek to examine the pre-metamorphic environment of the protolith and conduct an in-depth case study of carbon sequestration in ultramafic rocks.

The purpose of this project is to define the environment in which the Orange-Milford carbonated serpentinites were formed. Rock samples were extracted from an outcrop located at 286°59.73' and 41°15.75' mapped by Ague (1997, unpublished). Research primarily involved

analyzing stable oxygen and carbon isotopes in the samples via mass spectrometry to understand the “origin and sequence of fluids involved in the fluid-rock interaction episodes” (Karsh, 1998). The rocks provide a natural analog for the study of mineral-based carbon sequestration relevant for remediation of atmospheric carbon dioxide in serpentinites. Although this rock type could be a large reservoir for anthropogenic CO<sub>2</sub>, appreciable gaps in knowledge persist as serpentinites have received less attention in sequestration research than the more commonly studied peridotites.

### **Methodology**

Specimens of the Orange-Milford serpentinites, currently residing in the Yale petrology collection, were taken from profiles across lithologic contacts between metavolcanics and carbonated serpentinites. Thin sections of selected samples across the profile, prepared by Ague (1997, unpublished), and their petrological features were observed on a Leica petrographic microscope at a range of magnifications. The samples were prepared for <sup>13</sup>C and <sup>18</sup>O analysis at the Yale Analytical and Stable Isotope Center (YASIC) as follows. First, samples were selected from the specimens based on their location in discrete sites likely to contain distinct and detectable levels of carbonates. Second, powdered rock material from the standards and each sample from each location were drilled using a Dremel<sup>®</sup> MultiPro<sup>®</sup>; and third, 100μg of each were weighed into vials. Three standards were used: Carrara marble (PX), Yule Marble (YM), and Merck calcium carbonate CAS 471-4-1 (MERC). Lastly, each sample and three sets of each standard were run through a Kiel IV Carbonate Device to measure their  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{VPDB}}$  levels in the method derived from French (2016).

### **Study Area**

The Orange-Milford serpentinites are located in the Maltby Lakes Metavolcanics of south-central Connecticut (Karsh, 1998). As shown in Figure 1, the location is bounded on the west by the East Derby Shear Zone, characterized by fine-grained phyllites and phyllonites in greenschist and amphibolite facies, and on the east by the Triassic sandstones and igneous rocks of the Hartford Basin (Deasy, 2015; Wathen, 2020). According to Karsh (1998), thermobarometric analysis of the Wepawaug schist indicate greenschist-facies metamorphic conditions of 400-500°C and 7 kbars for serpentinite metamorphism. Greenschist-facies phyllites and schists – derived from sedimentary and volcanic protoliths – dominate the geology of the

Orange-Milford belt; the carbonated serpentinites hosted by the metavolcanics dip approximately 35-45°NW (Karsh, 1998).

A profile of the study area mapped by Ague (1997, unpublished), seen in Figure 2, includes a 4.0 m diopside zone extending northwest from the metavolcanic-metaultramafic contact at 0.0 m; prominent minerals include diopside, spinel, chlorite, and forsterite (Karsh, 1998). Yellow carbonated serpentinites are found between 4-8 m, and gray-green serpentinites are found between 8-23.5 m (Karsh, 1998). Samples for this study were extracted from the metavolcanics, the diopside zone, and both serpentinite zones. A metavolcanic layer dips at 40°NW between 12.2-13.6 m, and predominantly contains chlorite, albite, epidote, and actinolite. The cross-section spans NW-SE with a bearing of approximately 120° – perpendicular to the strike of layering depicted on the geologic map.

## **Results**

### *Mineral Identification*

A brief overview of minerals within each thin section can be found in Table 1. Samples I 1.65 m, Ia 2 m, Ib 2m, and I 3.8 m pertain to the diopside zone. Samples I 4.3 m and IIa 42 m were extracted from the yellow carbonated serpentinite section of the profile, while samples I 18.6 m, I 21.2 m, II 21.5 m, II 29.3 m, and IIb 42 m were extracted from the gray-green carbonated serpentinite section that comprises the majority of the profile.

Diopside zone: Sample I 1.65 m was characterized by irregularly arranged crystals of varying habits, including blocky and bladed. Serpentine was arranged evenly throughout, though diopside constituted the majority of the thin section. Isometric crystals, likely garnet, were sparsely scattered. Sample Ia 2 m showed crystals of similar size and shape as sample I 1.65 m, though a prominent serpentine band separated two diopside-dominated sections. Disperse garnets were also present, in addition to opaque inclusions of spinel, likely magnetite. Larger, linear magnetite crystals were found among majority-serpentine crystals in sample Ib 2 m. Sample I 3.8 m, similarly, displayed linear bands of magnetites within a serpentine matrix, in addition to scattered diopsides.

Yellow carbonated serpentinite: Sample I 4.3 m included irregularly arranged crystals of blocky habit with opaque magnetite banding occurring at irregular directions and intervals. Small concentrations of serpentine were sparsely scattered throughout, occasionally in a layered fashion. Garnets were scattered throughout a chlorite-dominated matrix. Sample IIa 42 m

contained rounder, irregularly arranged calcite crystals, occasionally exhibiting deformational twinning. Serpentine crystals were deformed into curvilinear shapes. Opaque magnetite of varying sizes was also present.

*Gray-green carbonated serpentinite:* Sample I 18.6 m contained irregularly arranged crystals. Serpentine crystals were distributed prominently throughout. Significant amounts of chlorite and magnetite were also found. Sample I 21.2 m exhibited a similar assemblage, and also included calcite and garnet crystals. Sample I 21.5 m was characterized by a serpentine matrix with acicular crystals of varying sizes. Calcite crystals exhibiting deformational twinning were arranged perpendicular to the linearly arranged matrix, which also included irregularly arranged magnetites. Sample II 29.3 included serpentine and linearly-deformed magnetite arranged throughout a chlorite matrix. Serpentine found in sample IIb 42 m is constrained to one lateral half of the thin section, and is comprised of irregularly arranged platy crystals. Blocky, intergrown calcite crystals, some demonstrating deformational twinning, dominate the other half.

#### *Stable Isotope Analysis*

Locations on each sample from which powdered rock material was extracted are depicted in Figure 3. Carbonate  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  levels from the diopside zone, yellow carbonated serpentinite, and gray-green carbonated serpentinite samples are recorded in Table 2 and plotted against distance along the profile in Figures 4 and 5. Apart from sample -17.2 m, no sample from the metavolcanic zone contained significant levels of carbonate, suggesting that carbonation did not occur along the profile preceding the diopside zone. Similarly, multiple samples from the diopside zone and serpentinites also contained negligible levels of carbonate, though this may be attributed to relatively higher levels of serpentine and magnetite in the selected areas.

$\delta^{13}\text{C}_{\text{VPDB}}$  values of each sample ranged between -6.53 to -4.18‰. Samples appeared to become lighter in  $\delta^{13}\text{C}_{\text{VPDB}}$  further along the profile. For example, sample 2.0 m had a  $\delta^{13}\text{C}_{\text{VPDB}}$  composition of -4.69‰, compared to -6.51‰ for sample 21.2 m. One exception was for sample -17.2 m from the metavolcanic zone, which had a  $\delta^{13}\text{C}_{\text{VPDB}}$  value of -6.51‰.

$\delta^{18}\text{O}_{\text{VSMOW}}$  compositions ranged between +10.39-14.55‰ for samples along the positive range of profile. All, except for sample 7.7 m II and 10.9 m II, ranged between +10.39-11.96‰ with little variation between distances. The two outliers had  $\delta^{18}\text{O}_{\text{VSMOW}}$  values of 13.99‰ and 14.55‰, respectively; sample -17.2 m had a relatively low  $\delta^{18}\text{O}_{\text{VSMOW}}$  value of 8.79‰. These



samples were likely carbonated at hydrothermal veins in a separate, later process from the overall carbonation of the serpentinite regions, thusly causing the different isotopic signatures.

## Discussion

### *Mineral Composition*

The temperature of serpentinization governs resultant mineral formation and fluid and gas chemistries (Klein *et al.*, 2013). At higher temperatures, Fe-rich brucite reacts with  $\text{SiO}_{2(\text{aq})}$  to generate serpentine and magnetite. Magnetite is effectively only created through serpentinization, as unaltered peridotites have weak magnetic signatures, and their carbonation does not create magnetite, which rather inhibits carbonation due to the formation of a protective hematite layer (Oufi & Cannat, 2002; Alexander *et al.*, 2007). Extensive magnetite and little brucite were found in samples from the diopside zone, yellow carbonated serpentinite, and gray-green carbonated serpentinite regions, indicating that significant amounts of brucite had broken down into magnetite under higher-temperature conditions. Thus, the mineral assemblage of the Orange-Milford listvenites suggests serpentinization across the profile occurred at temperatures  $>200^\circ\text{C}$ . Examples of listvenites exhibiting similar assemblages of magnetite, serpentine, and chlorite include Upper Proterozoic ophiolites from Northern Africa that were serpentinized during Barrovian-type tectonic emplacement (Halls & Zhao, 1995; Buisson & Leblanc, 1987).

### *Stable isotope ratios*

$\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  were plotted against each other and compared to a temperature-mineral composition curve derived from the fractionation factors  $\Delta_{\text{Calcite-CO}_2}$  of Bottinga (1968) and  $\Delta_{\text{Calcite-H}_2\text{O}}$  of Friedman & O'Neil (1977) in the manner of Masters *et al.* (2000), as shown in Figure 5. The samples follow a positive trend on the plot when fit with a hydrothermal fluid with an isotopic composition of  $\delta^{18}\text{O} = 0\text{‰}$  and  $\delta^{13}\text{C} = -4\text{‰}$ . The oxygen isotope value is representative of seawater, though the prominence of dissolved bicarbonate in seawater typically results in heavier carbon isotope values; however, discrepancies may be attributable to organic carbon sources on the seafloor or  $\text{CO}_2$  inputs from hydrothermal vents (Master *et al.*, 2000). Furthermore, the Early to Middle Ordovician, during which the Orange-Milford listvenites were hypothesized to be carbonated, was characterized by light  $\delta^{13}\text{C}$  values that reached approximately  $-4\text{‰}$  at 459.5 Ma – coinciding with Taconic orogeny in New England (Saltzman & Thomas, 2012). As such, the model suggests that the serpentinized peridotites were carbonated

through circulation of modified seawater at temperatures between 150-200°C, which is consistent with the range suggested by the presence of magnetite in the mineral assemblage.

Two samples at 7.7 m and 10.9 m exhibited relatively higher  $\delta^{18}\text{O}$  values of 13.996‰ and 14.554‰, respectively. These samples were located in veins, and thus these differences in  $\delta^{18}\text{O}$  may reflect the infiltration of metamorphic fluids from surrounding rock following overall carbonation of the serpentinites; for instance, Palin (1992) found similar  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in the neighboring Wepawaug Schist, suggesting that the fluids by which the Wepawaug metacarbonates were metamorphosed may have also penetrated portions of the Orange-Milford listvenites.

### *Carbon Sequestration in Serpentinites*

Here, we have shown that carbonation of seafloor serpentinites may occur at low- to moderate-temperature settings through seawater circulation. In recent years, listvenites have been regarded for their role in the carbon cycle as a potential *in situ* sink for  $\text{CO}_2$ . Global reserves of accessible serpentinitized peridotites could potentially mineralize over 10000 Gt C, or all carbon stored in worldwide coal reserves (Power *et al.*, 2013). Various methods of anthropogenic sequestration with listvenites have been proposed: introducing  $\text{CO}_2$  to serpentinite mine tailings in conjunction with sulfuric colonies of *Acidithiobacillus* spp., an acidophile bacteria capable of dissolving serpentinite and increasing the rate of carbonate precipitation; injecting  $\text{CO}_2$ -rich fluid into hydraulically fractured serpentinites; and sequestering  $\text{CO}_2$  in porous, serpentinite-hosted saline reservoirs (Power *et al.*, 2013). However, development of new technologies exploiting the reactive capabilities of listvenites must be preceded by further understanding of serpentinitization and the rates and levels of the rocks' carbonation in natural situations.

### **Conclusion**

The methods described here were designed to explore the environment of serpentinitization and carbonation of listvenites presently found in the Orange-Milford belt. Petrological study of the mineral assemblages in specimens across the profile found little trace of carbonate in the metavolcanic section, suggesting that it was not carbonated in conjunction with the yellow and gray-green serpentinite sections. Furthermore, the extensive presence of magnetite potentially limits the temperature of serpentinitization to  $>200^\circ\text{C}$ .

Stable carbon and oxygen isotope ratios suggest that carbonation occurred at temperatures between 150-200°C via seawater circulation.  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$ , plotted against each other, fit a temperature-mineral curve corresponding to a hydrothermal fluid with isotopic values of  $\delta^{18}\text{O} = 0\text{‰}$  and  $\delta^{13}\text{C} = -4\text{‰}$  to  $-6\text{‰}$ , which is consistent with conditions at 459.5 Ma wherein  $\delta^{13}\text{C}$  dipped to its lowest values during the Ordovician and following modification by organic carbon and hydrothermal inputs. This coincides with metamorphism during Taconic orogeny, rather than immediately before Acadian orogeny as initially hypothesized by Karsh (1998).

### **Further Steps**

Future research on the Orange-Milford listvenites may discuss the following topics:

- 1) Quantifying the level of  $\text{CO}_2$  within the rocks, and potentially determining the time scale of carbonation for greater understanding of natural carbon sequestration in serpentinites,
- 2) Constraining the temperature of serpentinization through X-ray diffraction analysis of serpentine polymorphs and Raman spectroscopy, electron microprobe analysis, and scanning electron microscopy of magnetite, and
- 3) Further analysis of how the metavolcanic section became metamorphosed.

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## Figures

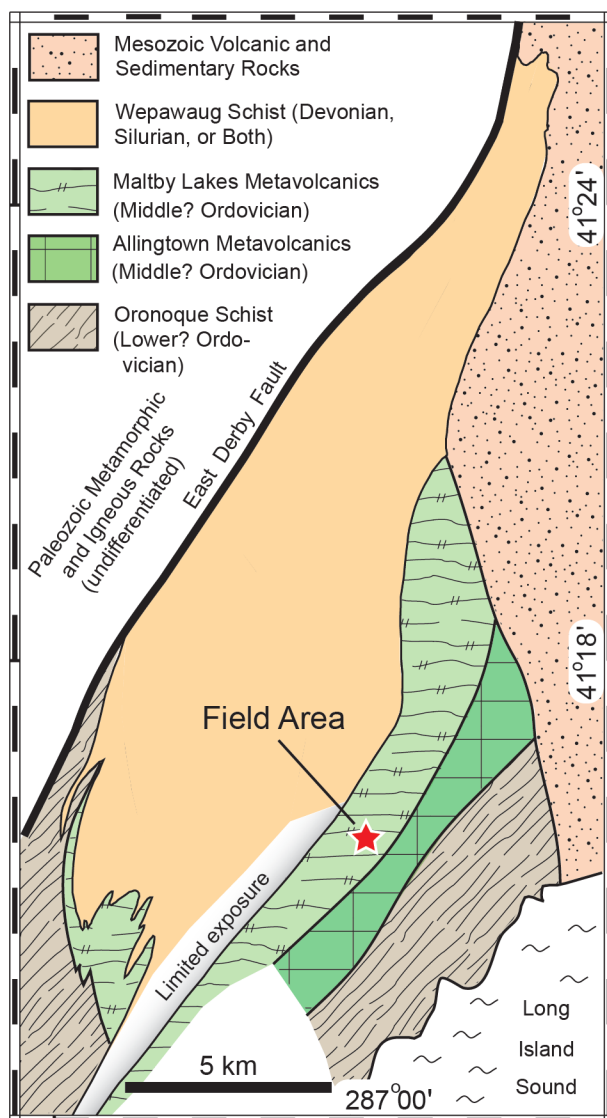


Figure 1. Geologic map of the Orange-Milford belt (Ague, 1994; Fritts, 1962a, 1962b, 1963, 1965a, 1965b; Rodgers, 1985). Modified after Philpotts & Ague (2022).

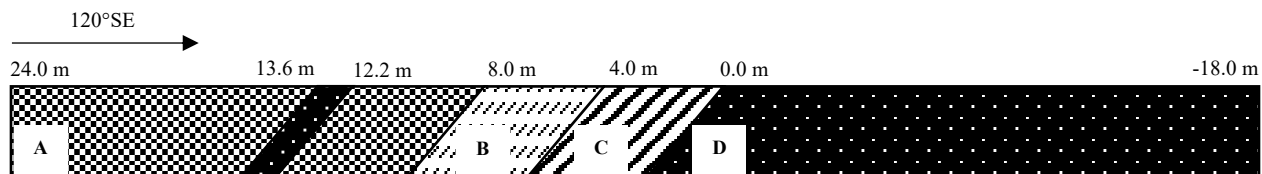


Figure 2. Profile of the Orange-Milford serpentinite outcrop from which samples were primarily extracted. A) Gray-green carbonated serpentinite, dominated by calcite, serpentinite, spinel, chlorite, diopside, and garnet; a metavolcanic layer is found between 13.6-12.2 m B) Yellow carbonated serpentinite, dominated by calcite, serpentinite, spinel, and chlorite. C) Diopside zone, dominated by diopside, spinel, and chlorite D) Metavolcanic zone, dominated by chlorite, quartz, albite, epidote, and actinolite. Modified after Karsh (1998).

<b>Sample ID</b>	<b>Observations</b>
I 1.65 m	Irregularly arranged blocky and blady crystals. Dominated by diopside; other minerals include serpentine and garnet.
Ia 2 m	Two distinct sections of irregular diopside crystals separated by a serpentine and calcite band. Diopside sections include smaller crystals of garnet and spinel (magnetite).
Ib 2 m	Irregularly arranged blady crystals. Dominated by serpentine with linear arrangements of magnetite.
I 3.8 m	Irregularly arranged blady crystals. Dominated by serpentine with linear arrangements of scattered magnetite and diopside crystals.
I 4.3 m	Irregularly arranged blocky crystals. Dominated by diopside. Opaque banding occurs at irregular directions and intervals. Scattered serpentine crystals, though some are arranged in linear concentrations. Sparsely scattered magnetite crystals.
I 18.6 m	Irregularly arranged blady crystals. Dominated by fibrous serpentine crystals and chlorite. Scattered magnetite crystals.
I 21.2 m	Irregularly arranged crystals. Dominated by blady serpentine crystals and calcite. Scattered magnetite and garnet crystals
II 21.5 m	Linearly arranged crystals. Dominated by fibrous serpentine crystals. Scattered twinned diopside crystals and unevenly distributed magnetite.
II 29.3 m	Linearly arranged acicular crystals. Dominated by serpentine. Scattered linearly deformed magnetite.
IIa 42 m	Irregularly arranged acicular crystals. Dominated by serpentine and a fine chlorite matrix. Scattered linearly deformed magnetite.
IIb 42 m	Bands of linearly arranged blocky crystals with asymmetrically arranged acicular crystals. Dominated by calcite, with some crystals exhibiting deformational twinning, and serpentine. Scattered magnetite.

*Table 1.* Mineralogical observations of thin sections prepared by J. J. Ague from the sampled profile in the Orange-Milford Belt.



Figure 3. Specimens of Orange-Milford listvenites from which powdered rock samples were drilled. A) 2.0 m B) 4.3 m C) 7.7 m I D) 7.7 m II E) 8.1 m I and II F) 8.6 m



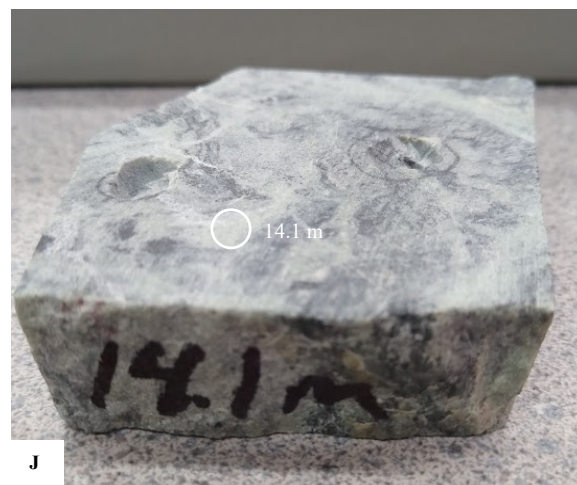
G



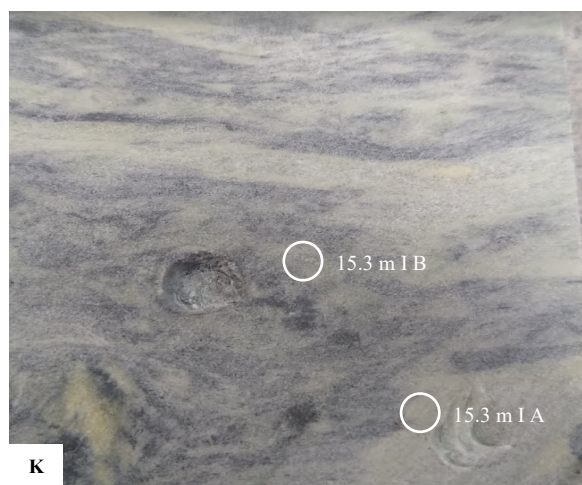
H



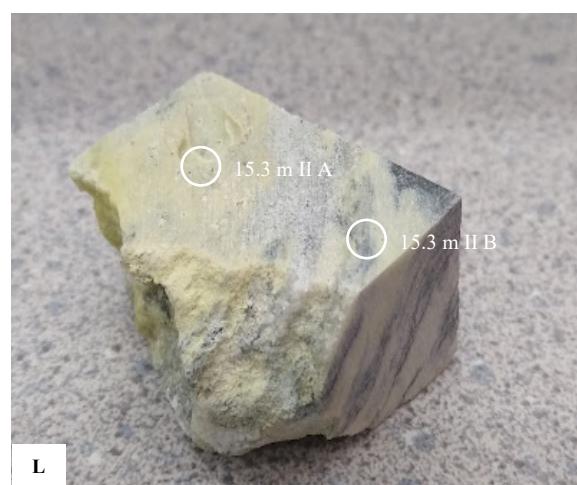
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Figure 3 (cont.). Specimens of Orange-Milford listvenites from which powdered rock samples were drilled. G) 10.9 m I H) 10.9 m II I) 13.6 m A and B J) 14.1 m K) 15.3 m I A and I B L) 15.3 m II A and II B



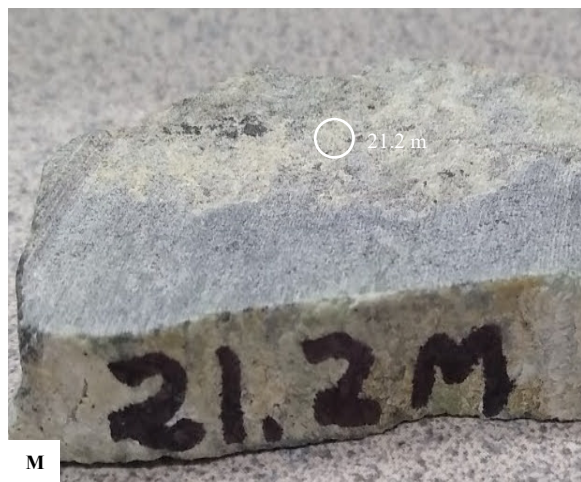


Figure 3 (cont.). Specimens of Orange-Milford listvenites from which powdered rock samples were drilled. M) 21.2 m  
N) -17.2 m

<b>Sample ID</b>	<b><math>\delta^{13}\text{C}_{\text{VPDB}}</math></b>	<b><math>\delta^{13}\text{C}_{\text{VPDB}}</math> SD</b>	<b><math>\delta^{18}\text{O}_{\text{VSMOW}}</math></b>	<b><math>\delta^{18}\text{O}_{\text{VSMOW}}</math> SD</b>
-17.2 m	-6.510	0.051	8.794	0.139
2 m	-4.686	0.039	10.500	0.129
4.3 m	-4.591	0.060	10.901	0.167
7.7 m I	-4.177	0.022	11.025	0.067
7.7 m II	-4.496	0.039	13.996	0.101
8.1 m A	-4.356	0.079	11.008	0.107
8.1 m B	-4.410	0.078	11.965	0.109
8.6 m	-4.538	0.048	11.154	0.083
10.9 m I	-4.771	0.061	11.193	0.053
10.9 m II	-6.533	0.058	14.554	0.114
13.6 m A	-4.375	0.018	11.862	0.131
13.6 m B	-4.502	0.044	10.493	0.059
14.1 m	-5.556	0.026	10.647	0.056
15.3 m I A	-5.539	0.039	10.753	0.031
15.3 m I B	-5.607	0.025	10.386	0.077
15.3 m II A	-5.610	0.032	10.529	0.094
15.3 m II B	-5.647	0.022	10.760	0.080
21.2 m	-6.511	0.029	10.886	0.087

*Table 2.*  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  values (with standard deviations) for samples along the profile.

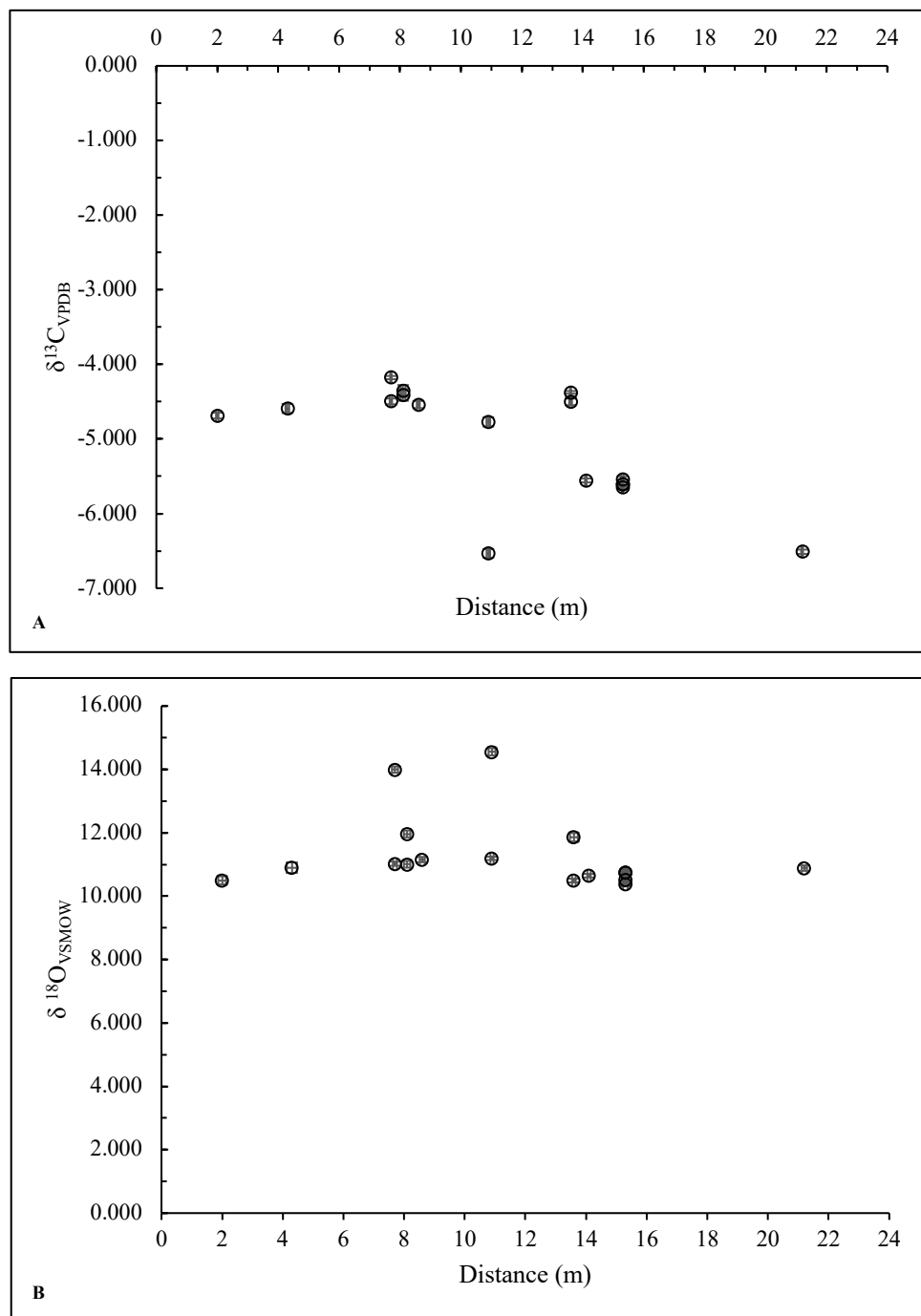


Figure 4. A)  $\delta^{13}\text{C}_{\text{VPDB}}$  and B)  $\delta^{18}\text{O}_{\text{VSMOW}}$  values of carbonate in the Orange-Milford listvenites in the diopside zone and serpentinite regions, plotted against distance from the metavolcanic-metaultramafic contact (0.0 m).

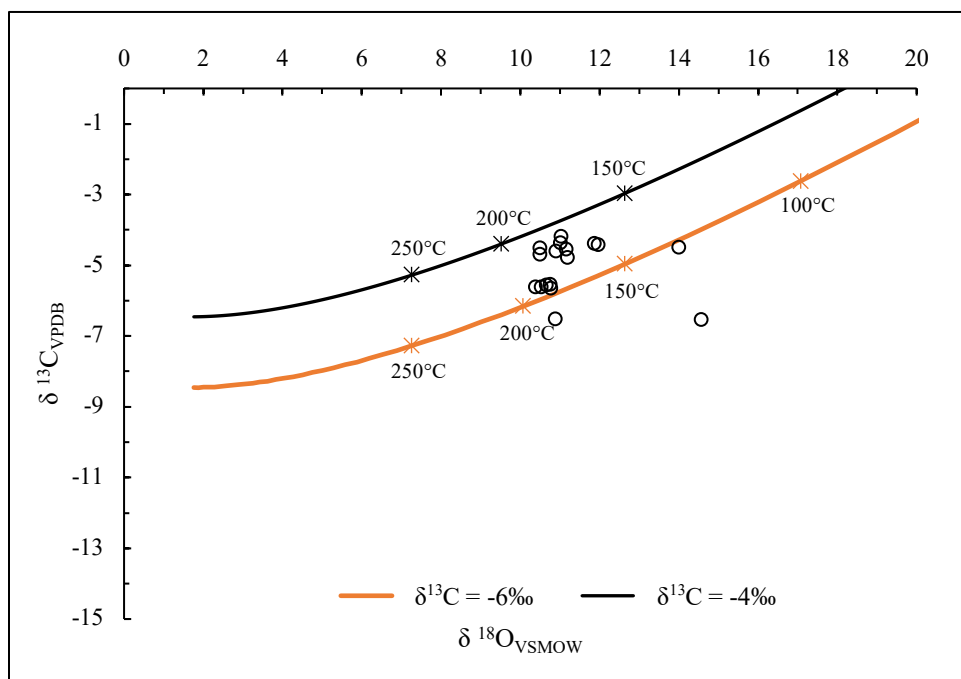


Figure 6.  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  plot of the Orange-Milford listvenites located in the diopside zone and serpentinite regions. Data were fit with a model for carbonate precipitation from a  $\text{CO}_2$  or  $\text{H}_2\text{CO}_{3(\text{aq})}$ -bearing fluid of constant composition ( $\delta^{18}\text{O} = 0\text{‰}$ ,  $\delta^{13}\text{C} = -4\text{‰}$  and  $-6\text{‰}$ ) and plotted against a temperature-mineral composition curve calculated from  $\Delta_{\text{Calcite-CO}_2}$  of Bottinga (1968) and  $\Delta_{\text{Calcite-H}_2\text{O}}$  of Friedman & O'Neil (1977) (Masters *et al.*, 2000).

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