

# THE ISOTOPIC GEOCHEMISTRY OF $\text{CaCO}_3$ ENCRUSTATIONS IN TAYLOR VALLEY, ANTARCTICA: IMPLICATIONS FOR THEIR ORIGIN

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Ground image of the Lake Hoare basin (Lake Hoare on far left) looking west up Taylor Valley, Antarctica.

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## **The isotopic geochemistry of CaCO<sub>3</sub> encrustations in Taylor Valley, Antarctica: Implications for their origin**

**ABSTRACT:** Calcium carbonate (CaCO<sub>3</sub>) encrustations occur in most desert soils, including polar ones, and such encrustations preserve records of geochemical, hydrological, and atmosphere processes affecting these soils. We have collected a series of CaCO<sub>3</sub> encrustations found underneath surface rocks in the soils and tills of Taylor Valley, McMurdo Dry Valleys (~78°S lat.), Antarctica. These encrustations were analyzed for <sup>87</sup>Sr/<sup>86</sup>S and δ<sup>18</sup>O and δ<sup>13</sup>C to determine what relation they have with the underlying soils, and the material in which they are in contact, and to identify the processes that control their formation. In all but one case, the isotopic data indicate that the source of Sr to these encrustations is not from the rock on which it is associated. The primary source of Sr (and by analogy Ca) is either from dust that has been deposited through aeolian processes or from the aggregate of till material within the soils. The δ<sup>13</sup>C values for Taylor Valley encrustations ranged from 5.7 to 11.0‰, and are consistent with a carbon source from atmospheric CO<sub>2</sub>. The δ<sup>18</sup>O values range from -8.1 to -11.2‰ and are heavier than expected for equilibrium calcite precipitation from Taylor Valley meteoric water. Taken together these results indicate that the CaCO<sub>3</sub> was formed by rapid evaporation of films beneath clasts that had become supersaturated with respect to CaCO<sub>3</sub>.

**KEY WORDS:** calcium carbonate, isotopic ratio, salt deposit, McMurdo Dry Valleys, Antarctica

## **Izotopska geokemija inkrustacij CaCO<sub>3</sub> v Taylorjevi dolini na Antarktiki: izsledki, ki nakazujejo njihov izvor**

**IZVLEČEK:** Inkrustacije kalcijevega karbonata (CaCO<sub>3</sub>) so značilne za večino puščavskih prsti, tudi polarnih, v njih pa so ohranjeni podatki o geokemičnih, hidroloških in atmosferskih procesih, ki so vplivali na te prsti. Zbrali smo niz inkrustacij CaCO<sub>3</sub>, odkritih pod površinskimi kamninami v prsteh in tilih v Taylorjevi dolini – eni izmed McMurdovih suhih dolin na Antarktiki (~78° j. z. š.). Analizirali smo vsebnost <sup>87</sup>Sr/<sup>86</sup>S ter δ<sup>18</sup>O in δ<sup>13</sup>C v teh inkrustacijah, da bi ugotovili, kako so povezane s spodaj ležečimi prstmi in materialom, s katerim so v stiku, ter določili procese, ki uravnavajo njihov nastanek. Razen v enem primeru izotopski podatki kažejo, da Sr v teh inkrustacijah ne izvira iz kamnine, s katero je inkrustacija povezana. Glavni viri Sr (in po analogiji tudi Ca) so bodisi prah, ki ga je nanesel veter, bodisi agregati ledeniških sedimentov (tilov) v prsteh. V inkrustacijah iz Taylorjeve doline je bilo od 5,7 do 11 ‰ δ<sup>13</sup>C, kar se ujema z vsebnostjo ogljika iz atmosferskega CO<sub>2</sub>. Vrednosti δ<sup>18</sup>O so od -8,1 do -11,2 ‰, to pa je več, kot bi pričakovali za uravnoteženo izločanje kalcita iz meteornih vod v Taylorjevi dolini. Skupni rezultati kažejo, da je CaCO<sub>3</sub> nastal s hitrim izhlapevanjem slojev pod klasti, prenasičenimi s CaCO<sub>3</sub>.

**KLJUČNE BESEDE:** kalcijev karbonat, izotopsko razmerje, nanos soli, McMurdove suhe doline, Antarktika

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# 1 Introduction

Calcium carbonate layers within soils and as encrustations on the undersides of rocks and pebbles occur in many landscape types. It has been postulated that these layers and crusts, when moisture is drawn upwards evaporates, precipitating carbonate minerals from supersaturated films. Although pedogenic carbonate has been observed and analyzed from a variety of soils from different latitudes, most of the work has been done in warm desert and semi-arid environments. Several investigations, however, have described pedogenic carbonates in polar locales where desert conditions exist. Authigenic carbonates in cold climates can take many forms and are formed by several different processes (Lacelle 2007). Pedogenic carbonates in cold environments, such as polar regions, have been defined as those that form on the inside of soil clasts (Lacelle 2007). This particular type of carbonate deposition has been observed in the Canadian High Arctic, the Antarctic Maritime and Svalbard (Bunting and Christensen 1978; Vogt and Corte 1996; Forman and Miller 1984; Courty et al. 1994). In all these various types of such carbonates, isotopic analysis has been used to elucidate the source of C and O and to discern the processes involved in the formation of these minerals (e.g., Lacelle 2007). In addition,  $^{87}\text{Sr}/^{86}\text{Sr}$  analyses have served as a useful tool to define the source of Ca in several past investigations of pedogenic carbonates (e.g., Quade, Chivas and McCulloch 1995; Capo and Chadwick 1999; Naiman, Quade and Patchett 2000; Van der Hoven and Quade 2002).

In this paper we present  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$  data from pedogenic carbonate encrustations from soils of Taylor Valley, Antarctica, one of the McMurdo Dry Valleys. Taylor Valley (TV) is a polar desert with low precipitation rates ( $\sim 3\text{ cm a}^{-1}$ ) and a mean annual temperature of approximately  $-20\text{ }^\circ\text{C}$  (Doran et al. 2002; Fountain et al. 2010). In Taylor Valley low relative humidities generate rapid sublimation of snow and produce very low soil moisture concentrations thus limiting chemical weathering and dissolution/precipitation reactions.

The objectives of this work were to assess the sources of water, carbon and calcium in the formation of calcium carbonate and to ascertain the processes that produced these minerals. In addition, we compare the formation mechanisms of these Antarctic encrustations to encrustations formed in other desert environments.

## 2 Materials and methods

### 2.1 Study area

The McMurdo Dry Valleys (MCM) ( $77\text{--}78^\circ\text{S}$ ) are the most extensive ice-free region in Antarctica (Figure 1). The valleys are a mosaic of glaciers, soils, exposed bedrock, ephemeral streams and perennially ice-covered lakes. Since 1993 Taylor Valley (TV) has been the primary operational location of the McMurdo Dry Valleys Long-Term Ecological Research (MCM-LTER) site where meteorological, glaciological, hydrological, geochemical, and ecological research has been conducted regularly (Fountain et al. 1999).

The soils and tills in TV are derived from a number of rock types within the region. These include the Precambrian to Ordovician granitoid and metamorphic basement rocks, the Devonian aged Beacon Supergroup (sandstones, shales, conglomerates), and the Ferrar Dolerite (Jurassic age). The Ferrar intrudes the Beacon and basement rocks in the form of sills and dikes in numerous locations in the McMurdo Dry Valleys. In addition, the more recent McMurdo Volcanic rocks are present both *in-situ* as erupted cones, and also as debris transported within the tills. In Taylor Valley, the volcanics range in age from 1.50 to 3.89 Ma (Wilch et al. 1993). The TV soils are composed of unconsolidated material ranging from primarily sand to boulder size, although small grain sizes exist. Relatively flat areas are often covered by desert pavement and the active layer is only  $\sim 50\text{ cm}$  in depth.

Much work has been done in determining the glacial chronology and soil/till age of the MCM region. Several eastward advances and retreats of the Taylor Glacier (from the East Antarctic Ice Sheet) deposited till in the western parts of TV and northward advances of the West Antarctic Ice Sheet has deposited tills in eastern to central TV during glacial times (Denton et al. 1989; Hall et al. 2000). The lakes in TV have fluctuated dramatically in size, with valley-wide glacial Lake Washburn existing from approximately 23,000 to 8500 years ago (Hall, Denton and Hendy 2000) to low stands at  $\sim 1\text{ kyr}$  ago (Lyons et al. 1998). There have been numerous fluctuations in lake levels between these times (Hall et al. 2010). As the lake

level rises, soils are inundated and become lake sediments, and as the lakes decrease in size, the lacustrine sediments become part of the terrestrial environment. A portion of the organic C currently observed in the soils is ancient lacustrine organic matter, or what has been termed »legacy« organic C that had been deposited during earlier aged high stands of the lakes (Burkins et al. 2000). CaCO<sub>3</sub> that forms in the lakes and in ephemeral streams today is usually associated with algal mats, and it is clear that much of the present day CaCO<sub>3</sub> observed in the soils of MCM was actually produced within a lacustrine environment when lake levels were higher. In fact, lacustrine-derived CaCO<sub>3</sub> in soils has been observed throughout the TV (Doran et al. 1999; Hendy 2000). The stable isotope composition of current lacustrine carbonate has been previously measured (Lawrence and Hendy 1989) and can be compared to pedogenic forms of carbonate in order to ascertain the origin of carbonate minerals in these soils.

## 2.2 Sample collection, preparation, and protocol

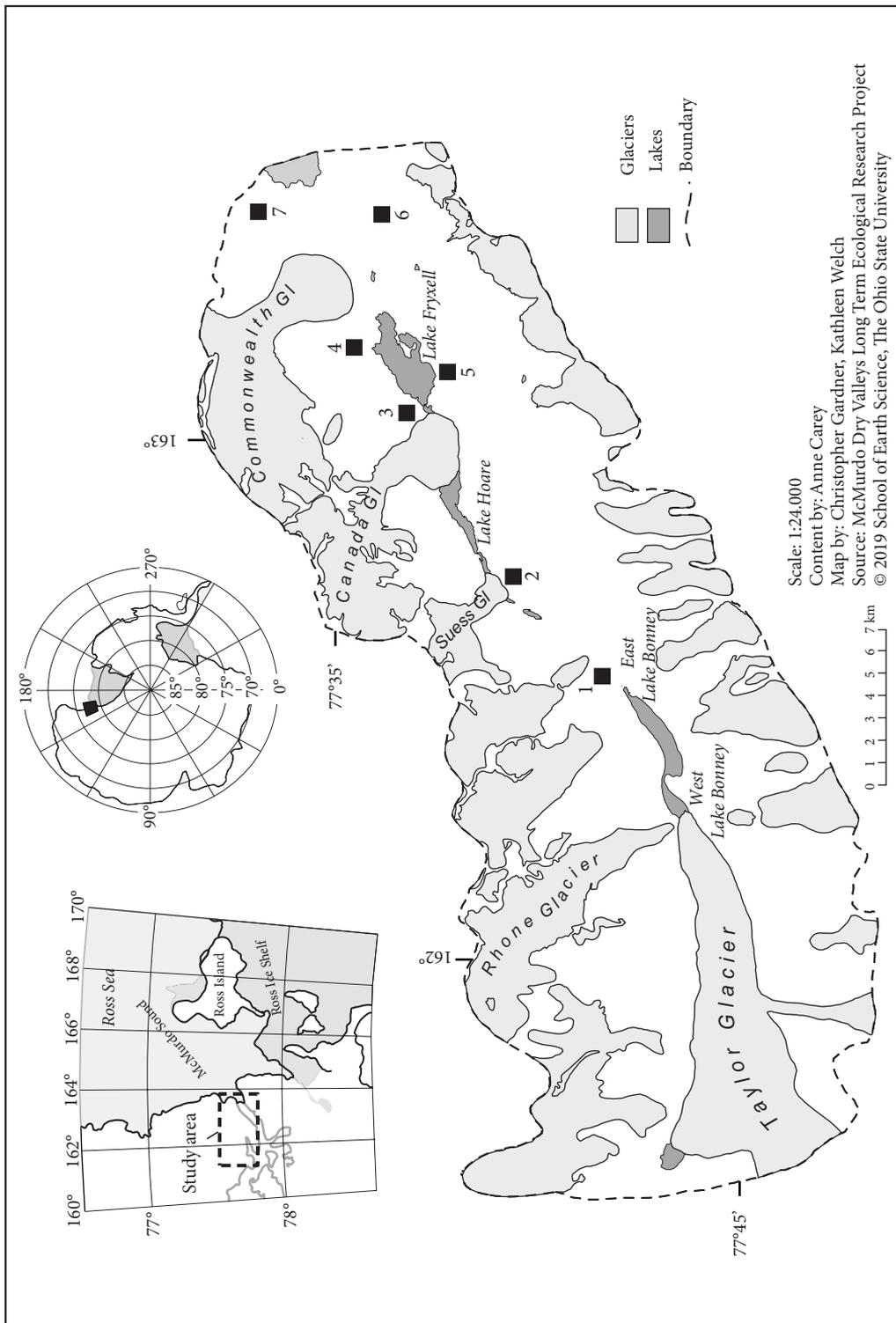
Thirteen groupings of surface »rocks« sitting at the soil surface were collected in locations throughout TV (Figure 1). Each rock was chosen for the noticeable amounts of carbonate encrustation on its underside (Figure 2).

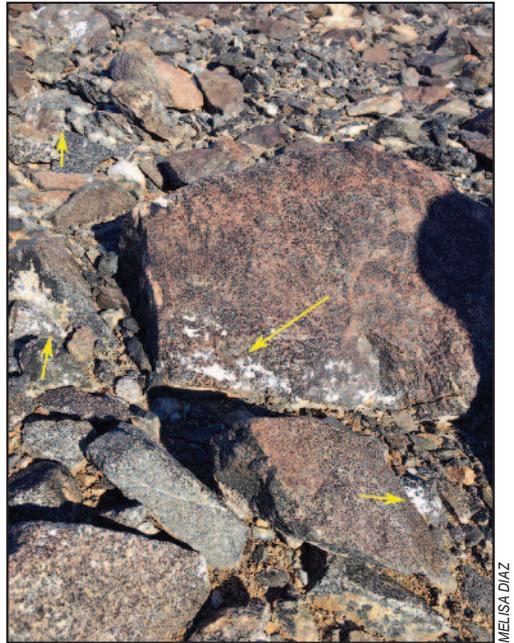
Each group of rocks was collected within a one-meter radius area and the individual specimens ranged from about 1 cm to about 6 cm in diameter. GPS coordinates were taken at each of the 13 sampling locations and local geological and surrounding landscape features were also recorded. The rocks in each group were of different lithologies, including the major bedrock types in the area: marble, basement dike, granite, gneiss (all from the basement complex), dolerite and kenyanite (McMurdo Volcanics). On return to the USA, these rocks were visually identified according to type. Rocks were kept separated throughout the sampling and analytical process. In the lab, pre-cleaned stainless steel dental tools were used to scrape off much of the encrusted calcite onto a clean piece of paper. Vinyl gloves were worn during this procedure, and each time a new rock was scraped, the dental tools and gloves were cleaned with distilled-deionized water and wiped dry between samples. About 10–100 mg of scraped material was collected and transferred into new plastic vials.

A portion of this material was analyzed for its strontium isotopic composition (<sup>87</sup>Sr/<sup>86</sup>Sr) and Sr concentration at the Radiogenic Isotopes Laboratory at The Ohio State University. Prior to dissolution, the aliquots were pre-washed using ultrapure ammonium acetate as described by Montañez et al. (1996). Roughly 10–100 mg of the carbonate scrapings were dissolved using high-purity acetic acid, and a spike of <sup>84</sup>Sr was added to analyze Sr by isotope dilution. The Sr in the samples was purified using cation exchange chromatography following procedures described by Foland and Allen (1991). The Sr isotopic measurements were made using a multi-collector MAT-261A thermal ionization mass spectrometer using dynamic multiple ion collection as described in Foland and Allen (1991). The accuracy of these measurements was determined by the analysis of reference standard, SRM987, for which the value has been determined to be 0.710242 ± 0.000010 (one sigma external reproducibility). The analytical precision of the total Sr analysis was ± 1%.

Another fraction of the carbonate from each sample was analyzed for its δ<sup>13</sup>C and δ<sup>18</sup>O compositions. Scrapings were first washed with deionized water using a vacuum filtration assembly and at least 100 µg was packaged in clear plastic vials in Columbus and sent to University of Utah, where they were analyzed as CO<sub>2</sub> on a Finnigan MAT 252 mass spectrometer following reaction with orthophosphoric acid and cryogenic purification using an automated Isocarb system (see Swart, Burns and Leder 1991). All data (including values from the literature) are reported using delta notation relative to the Pee Dee belemnite (PDB) standard for carbonates and the standard mean ocean water (SMOW) standard for waters. Analytical precision for both the δ<sup>13</sup>C and δ<sup>18</sup>O was ~0.1‰.

Figure 1: Map of Taylor Valley, McMurdo Dry Valleys, Antarctica with locations of samples. Samples included 1) NE shore of Lake Bonney, basement dike at elevation 82 m asl; 2) Defile, dolerite, gneiss, granite and marble at elevation 193 m; 3) North shore of Lake Fryxell, kenyanite at elevation 37 m; 4) NE shore of Lake Fryxell, dolerite, and granite at elevation 46 m; 5) SW shore of Lake Fryxell, basement dike and dolerite at elevation 57 m; 6) Lake Fryxell to Explorer's Cove, dolerite and granite at elevation 83 m; 7) N shore of explorer's Cove, dolerite at elevation 26 m. Not shown on this map is 8) Marble Point, basement rock at elevation 108 m located approximately 19 km north of location 7. ►





MELISA DIAZ

Figure 2: Example of rocks with carbonate encrustation at Mount Speed along the Shackleton Glacier at -84.46567, -177.1357167.

### 3 Results

$^{87}\text{Sr}/^{86}\text{Sr}$  data for CaCO<sub>3</sub> encrustations (calcite) from TV are presented in Table 1. Previously published lake and stream  $^{87}\text{Sr}/^{86}\text{Sr}$  values within each of the three lake basins are similar in their geographic distributions as the encrustation data (Lyons et al. 2002; Dowling, Lyons and Welch 2013). In general, the  $^{87}\text{Sr}/^{86}\text{Sr}$  values for all TV soils and waters increase (i.e., become more radiogenic) with increasing distance from the Ross Sea coast (Jones and Faure 1968; Lyons et al. 2002; Dowling, Lyons and Welch 2013). There also is an increase in  $^{87}\text{Sr}/^{86}\text{Sr}$  with increasing distance from the coast for all rock types except for the marble (Lyons et al. 2002). The range of  $^{87}\text{Sr}/^{86}\text{Sr}$  values for lakes and streams is on the lower end of  $^{87}\text{Sr}/^{86}\text{Sr}$  values of the various rock sources within the entire MCM regime, perhaps suggesting the relative importance of both seawater and McMurdo Volcanic sources of Sr to the lakes (Lyons et al. 2002; Dowling, Lyons and Welch 2013). The range of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for carbonate encrustations in TV is smaller and is slightly less radiogenic than the lakes and streams (Table 1). There is no relation between the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in carbonate encrustations and the rock type from which they were taken nor between the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the encrustations and elevation.

The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  data from the CaCO<sub>3</sub> encrustations and other materials in TV are presented in Table 2. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values range from -5.70 to -11.02, and -8.13 to -11.18 (PDB), respectively. In general, the  $\delta^{13}\text{C}$  values are much more enriched than the soil organic matter (Burkins et al. 2000) and the  $\delta^{18}\text{O}$  values are more enriched than the lacustrine carbonate in TV (Hendy et al. 1977; 1979).

## 4 Discussion

### 4.1 Source of Ca to the CaCO<sub>3</sub> encrustations based on Sr isotopic analysis

Naiman, Quade and Patchett (2000) and Van der Hoven and Quade (2002) have demonstrated in Arizona soil, in the desert southwest of the USA, that there are two primary sources of Ca that form pedogenic

Table 1:  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for calcite encrustations and soils in TV (\*Jones and Faure 1968).

Rock type coated with the $\text{CaCO}_3$ crust	$^{87}\text{Sr}/^{86}\text{Sr}$	Mean	Standard Deviation	Sr (ppm)
Marble Point (basement dike)	0.7081			890
Northern shore of Explorers Cove (dolerite)	0.7081			584
Between coast and Lake Fryxell		0.7083	0.00000	
Granite	0.7083			431
Basement dolerite	0.7083			827
North east of Lake Fryxell		0.7089	0.00000	
Dolerite	0.7089			504
Granite	0.7089			443
North central of Lake Fryxell (kenyite)	0.7090			202
South east of Lake Fryxell		0.7087	0.00010	
Basement dike	0.7088			268
Basement dike	0.7087			470
Dolerite	0.7086			429
Defile		0.7101	0.00148	
Gneiss	0.7109			1030
Granite	0.7109			497
Marble	0.7079			1740
Dolerite	0.7108			625
Northeast of Lake Bonney (basement dike)	0.7118			327
Soils				
Basin of Lake Bonney*	0.7136			
Near Lake Fryxell*	0.7089			
Near LaCroix Glacier*	0.7125			
Near Canada Glacier*	0.7101			

Table 2:  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  for Taylor Valley soil  $\text{CaCO}_3$  encrustations. The far-right column reflects the  $\delta^{18}\text{O}$  of water in equilibrium with the  $\delta^{18}\text{O}$  of the carbonate. Values are in ‰.

Sample no.	Pee Dee Belemnite		$\delta^{18}\text{O}$ Standard Mean Ocean Water	
	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Coplen et al. 1983	Water
12BD	7.47	-8.56	22.09	-12.3
25A*	5.70	-10.30	20.29	-14.1
25B	8.39	-8.23	22.43	-12.0
25D	9.14	-9.33	21.29	-13.1
46D	8.49	-10.82	19.76	-14.6
46G	8.18	-11.18	19.38	-15.0
59D	7.95	-8.13	22.53	-11.9
59Gn	8.42	-9.37	21.25	-13.2
59Gr	11.02	-10.37	20.22	-14.2
59M	7.24	-9.64	20.97	-13.4
69DB1	7.15	-10.50	20.09	-14.3
69G	7.33	-10.33	20.26	-14.1
75D*1	7.04	-8.54	22.11	-12.3
88B1	6.73	-10.39	20.20	-14.2
99K	7.20	-10.74	19.84	-14.6

carbonates: the local parent geologic material and aeolian dust. Much of the Ca in CaCO<sub>3</sub> in TV has been hypothesized to have originated from either the *in-situ* weathering of marble, mafic volcanic rock debris within the tills, and/or dust containing carbonates (Campbell and Claridge 1977; Keys and Williams 1981; Green, Angle and Chave 1988). The McMurdo Volcanics source of dissolved Sr is important to Lake Fryxell as it is found only in tills in the Lake Fryxell basin (Lyons et al. 2002). Measurements from the surface of nearby Canada Glacier yielded a value of 0.70991 (Dowling, Lyons and Welch 2013).

As noted above, there is little relationship between the <sup>87</sup>Sr/<sup>86</sup>Sr of the rock types and the encrustations taken from them. The <sup>87</sup>Sr/<sup>86</sup>Sr values from the CaCO<sub>3</sub> encrustations on the dike samples were less radiogenic than the dikes themselves. The CaCO<sub>3</sub> encrustations from the dolerites have much lower <sup>87</sup>Sr/<sup>86</sup>Sr values than the Ferrar Encrustations on the granites and the dolerite samples were much less radiogenic than the granites (e.g., Lyons et al. 2002). Similarly, the one <sup>87</sup>Sr/<sup>86</sup>Sr value from an encrustation on a gneiss sample was 0.7109, which is also much less radiogenic than the Olympus Granite-Gneiss, which ranges between 0.7150 and 0.7210. The authigenic carbonate from the kenytite (McMurdo Volcanics) sample had an <sup>87</sup>Sr/<sup>86</sup>Sr value more radiogenic than the McMurdo Volcanics themselves (~0.7030 to 0.7045).

Clearly Sr within the encrustations has different Sr isotopic compositions than their »carrier« rocks. These data strongly suggest that the source of Sr, and by inference Ca, is not from the direct chemical weathering of the *in-situ* parent rocks but is also at least in part from another source. There is one encrustation that did not fit this pattern – the one in association with a piece of marble from ~22 km inland (Figure 1) had an <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.7079. The only reported <sup>87</sup>Sr/<sup>86</sup>Sr value from the Asgard Marble is 0.7088, but that sample came from Wright Valley just to the northwest of Marble Point, far from our sample location (Faure, Jones and Owen 1973). Since the <sup>87</sup>Sr/<sup>86</sup>Sr value for the marble encrustation (0.7079) is only slightly less radiogenic than the Asgard Marble, it is probable that the Ca in the CaCO<sub>3</sub> encrustation was derived from the marble itself, thereby overwhelming any contribution from the aerosol.

Extensive chemical weathering occurs within the TV environment, but that weathering has only been documented in the austral summer where there is abundant liquid water in the fixed stream channels that drain glacier melt water (Nezat, Lyons and Welch 2001; Gooseff et al. 2002). Because there is no overland flow and only a few locations where subsurface melt affects the surficial soils (Levy et al. 2012), most of the soil in TV has little contact with liquid water during the year (Fountain et al. 1999). Snow provides this water, but snow is rapidly sublimated instead of going through prolonged melting and any accumulated snow remaining from the previous winter disappears by the end of the austral summer (Fountain et al. 1999).

## 4.2 Dust flux to MCM and its chemical signature

Aeolian transport significantly redistributes particulate material in the MCM and it has been suggested that the geometry of TV dictates the direction of net dust flux with transport from higher elevations to lower elevations down-valley (Lancaster 2002; Šabacká et al. 2012; MacDonell, Fitzsimons, and Moelg 2013). Mean daily wind speeds are higher up-valley to the west nearer to the Taylor Glacier and East Antarctic Ice Sheet and decrease near the coast (Fountain et al. 1999; Doran et al. 2002). This results in higher aeolian sediment flux up-valley (Lancaster 2002). Strong katabatic winds (especially in the austral winter) can transport dust from higher elevations to the lower elevations down valley (i.e., to the east). The aeolian dust flux in the MCM region has been measured ~1 m above the landscape surface and the values generally decrease from west to east as described above, ranging from 1.10 to 0.24 g m<sup>-2</sup> yr<sup>-1</sup> for Lake Bonney and Explorers Cove/New Harbor (eastern most portion of TV), respectively (Lancaster 2002). The dust fluxes in the Lakes Fryxell and Hoare basins are dominated by fine grained (<50 μm) material, while Lake Bonney basin is primarily sand size particles (>90% by weight). The general up-valley increase in particle flux and grain size may suggest that the Lake Bonney basin and the Lakes Fryxell-Hoare basin dust inputs have different chemical compositions. Recent work from collectors placed close to the ground indicates that the aeolian material being blown in TV is of local origin, different size fractions have different major element geochemistries, and the finer grained fraction has higher Ca concentrations (Deuerling et al. 2014). More recent work on aeolian samples collected at higher elevations off the ground (1 m) suggest a more homogeneous geochemistry (Diaz et al. 2018).

The geologic materials up-wind (i.e., west) of TV are primarily Ferrar Dolerite and the Beacon Supergroup rocks. The dolerite has  $^{87}\text{Sr}/^{86}\text{Sr}$  values of 0.712–0.714, while to our knowledge only the carbonates in the Beacon rocks have been analyzed, and they are very radiogenic (i.e.  $>0.725$ ) (see data and references in Lyons et al. 2002). Samples collected in aeolian collectors on Taylor Glacier in the Bonney basin (west) and in Explorers Cove (east) yielded  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.71575 and 0.70864, supporting the notion that the dust is from very local (i.e., individual basin) sources (Diaz 2017) and are generally within the range of the values for our carbonate encrustations (Table 1).

### 4.3 Local soil as a source of Sr

As noted above, the Sr isotope ratios of the encrustations are geographically similar to what has been previously reported for TV stream waters (Lyons et al. 2002; Dowling, Lyons and Welch 2013). The most recent values for the Fryxell and Hoare basins range 0.70837–0.71084 and 0.70837–0.71091, respectively, while the Bonney Basin samples are more radiogenic, ranging between 0.71255 and 0.71418 (Dowling, Lyons and Welch 2013). As previously noted, the few measurements on TV dust yield similar values. The stream values have a narrower range than the encrustations, but the geographic trends are similar. Dowling, Lyons and Welch (2013) concluded that in the Fryxell and Hoare basins the dissolution of  $\text{CaCO}_3$  must play an important role in contributing dissolved Sr and Ca to these streams, and that the primary source may be from pieces of Asgard Marble within the stream beds. They also suggested that the initial  $\text{Sr}^{2+}$  that occurs in the authigenic carbonate minerals within the soils probably originates from the weathering of a wide range of sources, including previously existing secondary carbonates and Ca-rich dust.

Much research has clearly demonstrated that calcite within crystalline rocks, even at very low abundances, is the major contributor of dissolved Ca to aquatic systems (e.g., Lyons et al. 2005; Andrews and Jacobson 2017). As a polar example, it has been shown that the dissolution of fracture-filling calcite from moraines on Baffin Island is a major source of Sr, and hence Ca, to pedogenic crusts (Lacelle, Lauriol and Clark 2007). The  $^{87}\text{Sr}/^{86}\text{Sr}$  values available for the lithologies in TV are whole rock values. Unfortunately, we are unable to evaluate whether calcite in the crystalline rocks in the soils and tills of TV is a potential source of Sr. It should be noted that calcite fillings in volcanoclastic rocks from Minna Bluff, ~150 km south of our study area, had  $^{87}\text{Sr}/^{86}\text{Sr}$  values of 0.70327 (Antibus et al. 2014), suggesting that calcite within at least the McMurdo Volcanics could be a source of Ca and Sr to these soils.

The MCM soils are primarily glacier deposited tills and lacustrine sediments and, as mentioned above, consist of materials from all the regional bedrock groupings; they are not derived from one lithology. There are differences in the amounts of various types of material (e.g. the Ross tills having abundant kenyanite) and their ages, so the soils are a heterogeneous mix of geologic materials (Foley et al. 2006). These differences in both lithology and age lead to important differences in the geochemistry of the soils from basin to basin in TV. These geographical differences superimpose important ecological and biogeochemical differences such as landscape-scale differences in N:P ratios (Barrett et al. 2007). Soils also demonstrate an increase in radiogenic Sr moving inland, with a value of 0.7089 in the Fryxell Basin, increasing to 0.7101 along the transition from the Fryxell to the Hoare Basin, 0.7125 as the eastern reaches of the Bonney Basin, to 0.7136 within the more western portions of the Bonney Basin (Jones and Faure 1968) which is reflected in both stream waters and local dusts.

The general pattern of increasing radiogenic ratios of these carbonate encrustations from east to west in TV fits with all the available stream, lake, dust and soil data. In general, the carbonate samples are slightly less radiogenic than their corresponding soils, suggesting that in the Fryxell and Hoare basins the McMurdo Volcanics may be preferentially weathered within the soils. This idea of selective weathering of the till materials is not a new one as it has been mentioned as a mechanism to explain the variation of major ion stream chemistry and the Sr isotopic compositions for the stream waters of the Fryxell Basin (Lyons et al. 2002; Dowling, Lyons and Welch 2013). In the Bonney basin, the less radiogenic (than the soil) carbonate values might reflect input from marine aerosol or more intensive weathering of the Ferrar Dolerite. The process of dissolution and reprecipitation of  $\text{CaCO}_3$  within the soil profile may play an important role in maintaining the Sr isotopic variation constrained to some overall local basin-wide value. All these data support the idea that this trend of less to more radiogenic values from east to west in TV reflects local, rather than far-afeld, input of Sr.

#### 4.4 Sources of Carbon and Oxygen to the CaCO<sub>3</sub> encrustations

The stable isotopic geochemistry of C and O in modern soil carbonate is primarily determined by the local climate. Other work has clearly demonstrated that  $\delta^{18}\text{O}$  values are well correlated with the isotopic composition of the local meteoric water and  $\delta^{13}\text{C}$  values are related to vegetation type and soil respiration rates (Cerling 1984; Lipar et al. 2017). At low biological respiration rates in the soil, the influence of atmospheric CO<sub>2</sub> on the  $\delta^{13}\text{C}$  signal is more pronounced. In cold climates several types of carbonate precipitates exist that are produced through different processes which lead to different isotopic compositions (Lacelle 2007). The evaporation and transpiration of water and sublimation of snow and ice can lead to loss of pCO<sub>2</sub> that can also greatly affect both the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  signatures of pedogenic carbonates (Marion, Introne, Van Cleve 1991; Clark and Lauriol 1992). The freezing of liquid water causes supersaturation with respect to CaCO<sub>3</sub> and the non-equilibrium conditions produced by this process can affect the stable isotopic composition of the CaCO<sub>3</sub> produced (Clark and Lauriol 1992; Courty et al. 1994; Lacelle, Lauriol and Clark 2007). Such kinetic fractionation usually leads to enrichment of the isotopes in the carbonate minerals. The difference in thermal conductivity between the larger clasts, where precipitation occurs, and the finer grained soil influences this process, as the freezing front moves more rapidly in the larger material. This type of pedogenic carbonate, formed in the active layer of high latitude soil, is common (Lacelle 2007).

The  $\delta^{13}\text{C}$  signature of soil respiratory CO<sub>2</sub> depends in part on the nature and amount of organic matter present in the soil. In modeling the  $\delta^{13}\text{C}$  values of pedogenic carbonates, Cerling (1984) used values of -13‰ and -27‰ for pure C<sub>4</sub> and pure C<sub>3</sub> plant biomass, but CO<sub>2</sub> from this organic matter source can mix with atmospheric CO<sub>2</sub> ( $\delta^{13}\text{C} = -6.5‰$ ) to produce an intermediate value of  $\delta^{13}\text{C}$  of soil CO<sub>2</sub>. Measurements of materials in the sub-Arctic boreal region of Saskatchewan, Canada show a positive correlation between  $\delta^{13}\text{C}$  values of pedogenic carbonates and organic carbon in the soils (Landi, Mermut and Anderson 2003). Even pedogenic carbonates from interior Alaskan floodplain sediments fall in the range of those of Cerling (1984), having values as depleted as -7.9‰, clearly demonstrating a biologically influenced signal (Marion Introne, Van Cleve 1991).

Soil organic matter in TV is extremely low, resulting in great part from past climate and glacial histories, and has accumulated in soils in a distinct low elevation pattern (<250m above sea level) corresponding to the spatial distribution of ancient lacustrine systems. The mean  $\delta^{13}\text{C}$  values for various organic matter sources in MCM soils range between -20.8 and -24.3‰ (Burkins, Virginia and Chamberlain 2000). Because the organic matter concentrations in soil are so low, the CO<sub>2</sub> flux from Antarctic soils is also extremely low. The CO<sub>2</sub> present in Antarctic soils may originate from atmospheric sources or via the *in-situ* respiration of organic C (Parsons et al. 2004). CO<sub>2</sub> fluxes in TV soils fluctuate throughout the day and show very low concentrations of CO<sub>2</sub> escaping from the soil. In the Lake Fryxell and Hoare basins, CO<sub>2</sub> is actually taken up by soils during rapid decreases in soil temperature (Parsons et al. 2004). Recent work in hot desert soils clearly shows that similar diel variations driven by inorganic processes play a significant role in CO<sub>2</sub> dynamics (Ma et al. 2013). It is unknown if these diel variations have influence on CaCO<sub>3</sub> dynamics within the active layer of Antarctic soils.

The  $\delta^{13}\text{C}$  values for the TV carbonate encrustations are very enriched with values ranging from +5.7 to +11.0‰ (Table 2). These values contrast greatly with the modern lacustrine carbonates in Lake Fryxell which range from +3 to -18‰ depending on water depth (Lawrence and Hendy 1989). Using a CO<sub>2</sub>-CaCO<sub>3</sub> fractionation factor of -14.4 (10<sup>3</sup>ln $\alpha$ ) at 0°C (Friedman and O'Neil 1977), the  $\delta^{13}\text{C}$  values for a TV pedogenic carbonate with a 100% atmospheric CO<sub>2</sub> source would be +7.4‰. Ten out of fifteen of the TV encrustations are within  $\pm 1‰$  of this value, suggesting that the primary source of C to these carbonates is atmospheric CO<sub>2</sub>. Only one sample is more than 1‰ greater than this value. That one sample (from a basement dike specimen from SW Lake Fryxell) may have some carbon derived from CO<sub>2</sub> respired organic matter or, perhaps, it was formed at a warmer temperature. Ancient lacustrine carbonates obtained in what are now TV soils show a more depleted, but still positive, set of  $\delta^{13}\text{C}$  values (2.4–6.8‰), suggesting a larger percentage of biologically respired CO<sub>2</sub> (Hendy et al. 1979). The lack of a biological source or influence on the C in these TV CaCO<sub>3</sub> soil encrustations is not a surprise given the low organic carbon present in the soils and the very low CO<sub>2</sub> fluxes from the soils, as noted above (Burkins et al. 2000; Parsons et al. 2004). The  $\delta^{13}\text{C}$  of the TV encrustations are very similar to what has been previously reported for pedogenic carbonates (1.5–9.0‰) in Wright Valley just north of TV (Nakai et al. 1975).

Previous work on authigenic carbonates in Antarctica reflects the influence of the  $\delta^{18}\text{O}$  of the water present. Aragonite that was deposited subglacially on gneissic bedrock in the Vestfold Hills, Antarctica ( $68^{\circ}30' \text{ S}$ ) has very depleted  $\delta^{18}\text{O}$  values ranging from  $-17.3$  to  $-14.1\text{‰}$  (Aharon 1988). Lacustrine carbonates deposited at higher lake stands in TV are also depleted with  $\delta^{18}\text{O}$  values of  $-32$  to  $-46\text{‰}$  (Hendy et al. 1977; 1979). In both cases, these  $\delta^{18}\text{O}$  values reflect the extremely depleted values associated with the local meteoric waters derived from glacier melt (Gooseff et al. 2006).

These TV encrustations have  $\delta^{18}\text{O}$  values (Table 2) more similar to the Type 3 evaporite calcite crusts for other polar regions reviewed by Lacelle (2007) than the subglacial and lacustrine-derived carbonates from the Antarctic. There is no reflection in the TV carbonates of the very depleted  $\delta^{18}\text{O}$  values for the snow/ice melt waters observed in the TV region, which range from  $-27$  to  $-40.4\text{‰}$  (Gooseff et al. 2006). Our  $\delta^{18}\text{O}$  values from the encrustations when converted to water at  $0^{\circ}\text{C}$  in equilibrium with the carbonate produce values of  $-11.9$  to  $-15.0\text{‰}$  (Table 2). Given this enrichment with respect to the TV meteoric waters, the data suggest strong evaporative loss of  $^{16}\text{O}$  prior to carbonate precipitate. Evaporation of thin films and water droplets has also been used to explain enriched  $\delta^{18}\text{O}$  in carbonate encrustations in warm deserts (Knauth, Brilli and Klonowski 2002; Quade et al. 2007). These high  $\delta^{18}\text{O}$  values in the TV encrustations are undoubtedly due to precipitation during extensive evaporation and light isotope loss.

#### 4.5 Formation of Taylor Valley pedogenic carbonate

We envision the following scenario for carbonate mineral encrustation formation in polar desert systems like the McMurdo Dry Valleys. During snowfall events small amounts of Ca are solubilized from the Ca-containing minerals and rocks (probably  $\text{CaCO}_3$ ) in the soils, and/or mineral dusts and/or desiccated marine aerosols. Given that snowfall deposition is minimal ( $\leq 3 \text{ cm a}^{-1}$ ), and relative humidity is extremely low, sublimation and evaporation rates are high. During the evaporative process calcite becomes supersaturated in the remaining water film and is precipitated with  $\text{CO}_2$  as the primary carbonate source as indicated by the  $\delta^{13}\text{C}$  values. These Taylor Valley carbonate encrustations form in an extremely arid setting and demonstrate that carbonate mineral formation in soils can occur with little to no biological processes being involved. This lack of biological process affecting  $\delta^{13}\text{C}$  compositions of  $\Sigma\text{CO}_2$  is also observed in TV streams (Lyons et al. 2013). These Antarctic carbonate encrustations form an extreme position in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  when compared to other cold environment authigenic carbonates and a rapid rate of precipitation leading to non-equilibrium conditions due to a rapid loss of  $\text{CO}_2$  as outlined in Lacelle (2007).

## 5 Conclusions

Except for the carbonate crust on a marble sample, which obtained its Sr (Ca) from weathering of the parent marble, it is hypothesized that the carbonate encrustations on all the other TV rock samples receive their Sr (and by inference their Ca) from surface soil sources including potential locally derived aeolian debris. The encrustations are less radiogenic than the soils from their respective lake basins indicating that selective dissolution of volcanic materials and/or marine aerosol may play an important role in their formation. The  $\delta^{13}\text{C}$  values of the rock encrustations indicate they are produced in place with atmospheric  $\text{CO}_2$  as the primary carbon source. Our results suggest that the  $\delta^{13}\text{C}$  signature can be used to ascertain the difference between pedogenic and lacustrine carbonate in MCM soils. The  $\delta^{18}\text{O}$  values of the  $\text{CaCO}_3$  encrustations do not directly reflect the very depleted values of the local melt water source. The  $\delta^{18}\text{O}$  values for the  $\text{CaCO}_3$  encrustations suggest extensive evaporation has led to their formation, similar to deposits from warm deserts, as well as other active layer and polar soil environments. The  $\delta^{18}\text{O}$  data indicate that evaporation/sublimation of water, perhaps in thin films, plays a major role in the production of these encrustations.

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