

Article

# The Kilmar Magnesite Deposits: Evaporitic Metasediments in the Grenville Supergroup, Morin Terrane, Quebec

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Received: 10 July 2019; Accepted: 7 September 2019; Published: 14 September 2019



**Abstract:** Mesoproterozoic magnesite deposits are found associated with dolomitic marble and intercalated with metasedimentary rocks of the Grenville Supergroup in the granulite facies Morin terrane (Grenville Province, Quebec). This study examines one of the remaining ore deposits exposed on the surface (at the Dobbie mine), and presents stable isotope and mineralogical data for a marine evaporitic origin. The magnesite ore zone has  $\delta^{18}\text{O}(\text{Mag}) = 25.5 \pm 0.4\text{‰}$  (VSMOW) and  $\delta^{13}\text{C}(\text{Mag}) = 1.7 \pm 0.2\text{‰}$  (VPDB;  $n = 7$ ), while surrounding dolomitic marble has  $\delta^{18}\text{O}(\text{Dol}) = 24.2 \pm 0.6\text{‰}$  and  $\delta^{13}\text{C}(\text{Dol}) = -0.2 \pm 0.7\text{‰}$  ( $n = 11$ ). These values are at the high end of the range for other Morin terrane marbles, and this and sharp transitions in stable isotope ratios between lithologies argue for preservation of evaporitic enrichment in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ . Boron isotope ratios ( $\delta^{11}\text{B} = 15.5\text{‰}$  to  $22.7\text{‰}$ ) are also consistent with a marine evaporite origin. Identifying evaporitic protoliths in metasedimentary rocks is important for determining pre-metamorphic depositional environments, and in this case links the sedimentary setting of the Morin terrane to the Adirondack Lowlands (New York, NY, USA). The identification of the Kilmar magnesite deposits as evaporitic also has implications for the formation of sedimentary exhalative base metal deposits in the Grenville Supergroup.

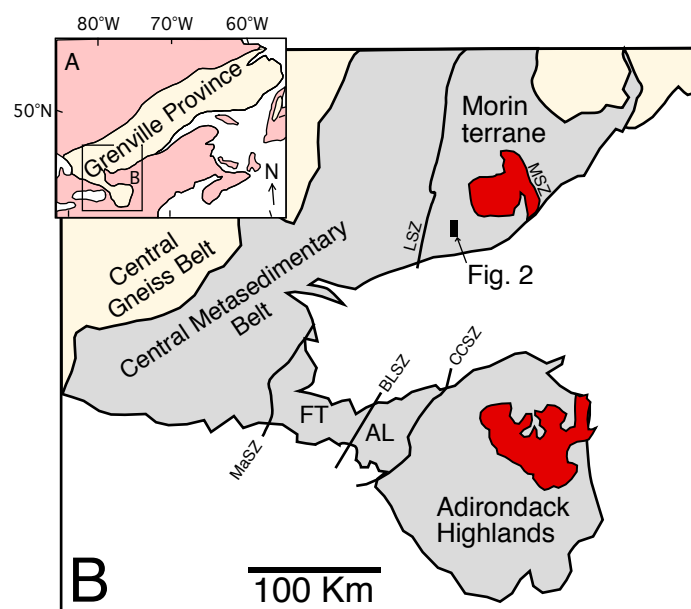
**Keywords:** Grenville Province; Grenville Supergroup; Morin terrane; magnesite; oxygen isotopes; carbon isotopes; boron isotopes

## 1. Introduction

Stratiform magnesite deposits in the Kilmar area north of the Ottawa river are hosted in Mesoproterozoic dolomitic marbles of the Grenville Supergroup in the Morin terrane (Grenville Province, QC, Canada). Magnesite was mined in the Kilmar district from five mines that span ~6 km North–South. These deposits were initially extracted by open pit methods followed by underground mining, and were active from 1913 until depletion of the ore in 1993 [1]. This study focuses on the Dobbie mine (Gamble mine in some sources), the northernmost of the Kilmar deposits, which operated as an open pit from 1918–1948 [2]. The Kilmar district has historically been interpreted to have a hydrothermal replacement origin [3,4], but these deposits have not been evaluated in the context of modern depositional models for magnesite [5]. In addition, the suggestion that the Kilmar deposits are metamorphosed evaporites has implications for paleoenvironments of the Grenville Supergroup and exploration for exhalative base metal deposits [6]. This is especially important in the context of recent metal exploration in the Canadian Grenville Province, and the discovery of zinc showings in Grenville Supergroup marbles at Kilmar and in the immediate area [7].

## 2. Geologic Setting

The Morin terrane (Figure 1) is made up of a package of granulite facies metasedimentary rocks and orthogneiss intruded by the 1.15 Ga Morin Anorthosite-Mangerite-Charnockite-Granite (AMCG) suite [8,9]. Pre-1.15 Ga rocks include the Mont-Tremblant gneiss, a suite of ca. 1.3 Ga intermediate to felsic arc rocks [10], and marble, quartzite, pelitic schist, and amphibolites of the Grenville Supergroup. The Grenville Supergroup (originally Grenville series) was first described in the nineteenth century by William Logan at its type locality near the Ottawa River, and was recognized to contain significant magnesite deposits ~10 km to the north in 1900. Based on structural relationships the Mont-Tremblant gneiss was inferred to be the basement for Grenville Supergroup rocks [11], which was confirmed by a detrital zircon study that yields a maximum depositional age of 1245 Ma and documented a significant ~1.3 Ga detrital component [12]. The extent to which rocks elsewhere assigned to the Grenville Supergroup are truly correlative or coeval has been an open question [13], but the detrital zircon population of Morin terrane quartzites and those from the Adirondack Mountains of New York and the New Jersey Highlands (USA) point to contemporaneous sedimentation in similar back-arc environments that received input from broadly similar source regions [12].

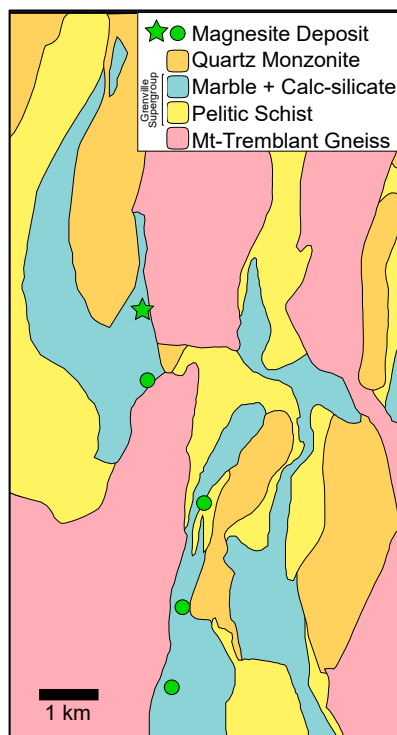


**Figure 1.** (A) Location map of the Grenville Province and (B) geology of the Allochthonous Monocyclic Belt, showing the Marcy and Morin anorthosite massifs after [12]. AL = Adirondack Lowlands, FT = Frontenac terrane, BLSZ = Black Lake shear zone, CCSZ = Carthage-Colton shear zone, LSZ = Labelle shear zone, MaSZ = Maberly shear zone, MSZ = Morin shear zone.

Grenville Supergroup metasedimentary rocks contain granulite facies mineral assemblages, and regional calcite-graphite carbon isotope thermometry yields  $755 \pm 38$  °C temperatures [14].  $^{206}\text{Pb}/^{207}\text{Pb}$  ages of titanite from marbles are mostly ca. 1120–1110 [15], suggesting that high-grade metamorphism of the Grenville Supergroup in the Morin terrane was first caused during the accretionary 1.19–1.14 Ga Shawinigan orogeny, and in places clearly is retrogressed by the contact effects of 1.15 Ga AMCG-suite plutons [16].

The geology of the Kilmar magnesite district is described by [3,4,17], who were able to base their descriptions on several of the working mines. This description is summarized from these sources. Rocks from the Kilmar magnesite ore zone are typically magnesite–dolomite–serpentine rocks, sometimes having accessory diopside and phlogopite, brucite veins, and occasional quartz, talc, titanite, pyrite, sphalerite, galena, apatite, magnetite, and graphite. Ductile deformation has produced concordant lens-like ore zones, with a maximum thickness of ~45 m. The horizons where the ore zones

are found generally strike North–South (Figure 2), and are intercalated with Grenville Supergroup marbles, diopside–quartz calc silicate rock, and garnet–sillimanite schist and gneiss. The sequence is bounded by the Mont-Tremblant gneiss and by the quartz monzonite of the Morin AMCG suite, which intrudes Grenville Supergroup rocks and the ore zone, and is associated with hydrothermal alteration. These relationships have historically been taken as indicating that the magnesite ore zone was a replacement deposit caused by igneous fluids.



**Figure 2.** Morin terrane geology in the area of the Kilmar magnesite deposits, after [7] and references therein. Star is the location of the Dobbie mine.

### 3. Materials and Methods

Samples for this study were collected from a transect of the dolomite-hosted magnesite ore body exposed in the south wall of the Dobbie mine open pit in 2005. Representative samples of the host rock, ore, and veins were collected, and were supplemented by samples from dumps. Samples were examined using polarized light and backscattered electron microscopy, and select samples were analyzed for stable isotope ratios, X-ray diffraction (XRD), and bulk rock geochemistry.

For the oxygen and carbon isotope analysis each sample was crushed, washed, hand-picked for purity, and ground and sieved to  $<70\ \mu\text{m}$ , after [18]. Powdered ore and host dolomitic marble samples were dissolved using 100% phosphoric acid in off-line reaction vessels [19]. Ca. 10 mg of dolomitic marble host-rock were dissolved for five hours at  $50\ ^\circ\text{C}$  in an 80% ethylene glycol/20% water bath. Upon removal from the constant-temperature bath, dissolution was quenched by submerging the reaction vessel in ice water before evolved  $\text{CO}_2$  was extracted, cryogenically purified, and was analyzed in dual-inlet mode using a Thermo Finnigan Delta Plus Advantage mass spectrometer at Colgate University [14]. Magnesite and dolomite replicates had average precisions of  $\pm 0.04\text{‰}$  and  $\pm 0.13\text{‰}$  for carbon and oxygen isotopes, respectively. NBS-19 analyzed in this lab during this period averaged  $\delta^{13}\text{C} = 2.04 \pm 0.02\text{‰}$  (VPDB) and  $\delta^{18}\text{O} = 28.58 \pm 0.04\text{‰}$  (VSMOW).

Ore samples contain an intimate intergrowth of dolomite and magnesite, which is impractical to separate mechanically for the isotope analysis. The dissolution method of [18] was used to sequentially analyze  $\text{CO}_2$  evolved from 60 mg of powdered dolomite + magnesite in the same reaction vessel. For the ore samples the procedure for the dolomite analysis above was used, and the aliquot of  $\text{CO}_2$

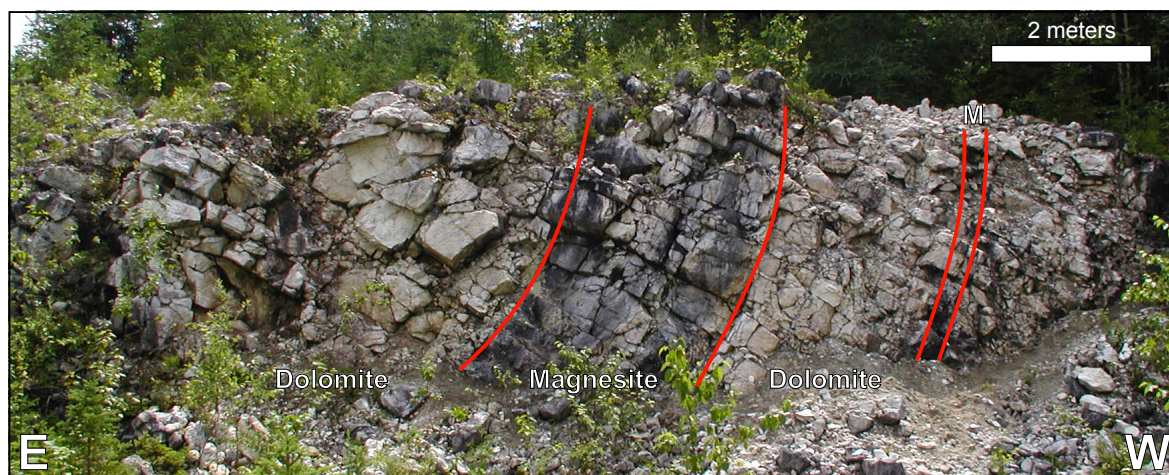
evolved after five hours was extracted and analyzed. The reaction vessels were then returned to the heating bath for 30 h of continued reaction at 50 °C. Based on the solubility of magnesite and dolomite in phosphoric acid [18], the second aliquot of CO<sub>2</sub> is a mixture of gas evolved from both minerals. This second aliquot of CO<sub>2</sub> was discarded, and the reaction vessels were returned to the heating bath for an additional 30 h. The final aliquot of CO<sub>2</sub> was extracted after quenching the reaction, and is predominately gas produced from magnesite dissolution [18]. Dolomite and magnesite oxygen isotope ratios were calculated using the phosphoric acid fractionation factors of [20].

Mineral identification was aided by using an energy dispersive X-ray spectrometer on an electron microscope. X-ray diffraction was also employed for mineral identification using a Philips PW3040 X-ray Diffractometer. Random powder mounts (<4 µm) of whole-rock powders and treated oriented clay mounts (<2 µm) were analyzed for the identification of phyllosilicates. Whole-rock geochemistry of three dolomitic marble and three magnesite ore samples were determined by ICP-MS at XRAL Laboratories/SGS Canada (Table 2). Three ore samples, one dolomitic marble, and one regional calcite marble [14] were analyzed for the boron isotope ratio by acid digestion and MC-ICP-MS using a Neptune Plus mass spectrometer at ALS Scandinavia AB (Luleå, Sweden), and are reported relative to NIST SRM 951. Two samples were duplicated and averaged  $\pm 0.25\%$ .

## 4. Results and Discussion

### 4.1. Outcrop Description and Mineralogy

The south wall of the Dobbie open pit measured ~15 m across in 2005, exposing the remaining orebody's ~2 m thickness (Figure 3). This lens of magnesite ore is mostly dark blue-gray in color, strikes north-south, and dips ~70° to the east. In addition to the main ore body, a thin layer of gray magnesite rock is present roughly 2.75 m from the west edge of the wall. The layer is ~0.25 m thick, and has a similar orientation as the ore body. The ore is surrounded by a white-green dolomitic marble, with some samples containing a high percentage of magnesite (Table 1). The contact between the ore body and surrounding rocks is slightly irregular, but distinct and sharp.



**Figure 3.** Geology of the south wall of the Dobbie open-pit mine, showing the remaining magnesite ore body in 2005.

The ore zone is made of three minerals: Dolomite, magnesite, and serpentine, which comprise >99% of the total rock (Figure 4a). Ore body samples range from ~10% to 50% magnesite (determined by image processing of the BSE images), averaging  $32 \pm 16\%$ . Dolomite ranges from 20–50% (averaging  $35 \pm 10\%$ ) and serpentine 20–40% (averaging  $33 \pm 6\%$ ). Dolomite cross-cuts magnesite in ore body samples (Figure 4a). Serpentine is not commonly cross-cut by dolomite, contains magnesite inclusions, and appears to have formed as pseudomorphs of diopside [4]. Surrounding dolomitic marbles

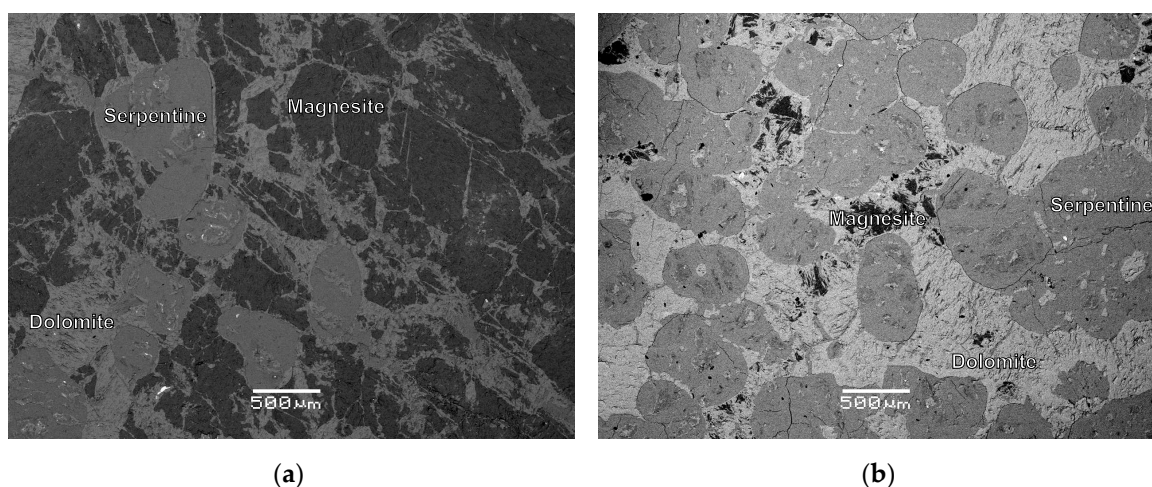


(Figure 4b) have an average composition of  $14 \pm 13\%$  magnesite,  $53 \pm 19\%$  dolomite,  $32 \pm 19\%$  serpentine, and trace amounts ( $<1\%$ ) of strontianite and celestine. In these samples some dolomite is also texturally late.

**Table 1.** Stable isotope data from the Dobbie mine, Kilmar magnesite district, Quebec.

Sample	L	$\delta^{13}\text{C}$ (Dol)‰	$\delta^{18}\text{O}$ (Dol)‰	$\delta^{13}\text{C}$ (Mag)‰	$\delta^{18}\text{O}$ (Mag)‰	$\delta^{11}\text{B}$ ‰	%Mag	%Dol	%Serp	Distance (m)
GE-1	D	0.63	24.45				33	49	13	0
GE-2	D	0.44	23.71				9	63	28	1.1
GE-3	M	1.54	25.19	1.88	24.62		25	41	34	3.0
GE-5	D	−0.90	23.91				10	55	34	4.3
GE-6	D	−1.10	24.67				10	43	47	5.2
GE-7	D	−0.11	22.83				8	91	1	5.4
GE-8	M	1.36	23.20	1.27	24.79		12	49	39	5.7
GE-9	M	1.61	26.15	1.81	25.56	15.5	40	25	35	5.9
GE-10	D/M	1.10	24.41				9	48	43	6.4
GE-11	M	1.63	25.91	1.75	25.51	15.5	41	32	27	7.0
GE-12	M	1.77	25.68	1.92	25.83	18.4	37	34	29	7.4
GE-13	M	1.83	25.58	1.82	25.42		34	35	30	7.8
GE-14	M	1.77	26.20	1.73	25.60		56	18	26	8.0
GE-15	D	0.85	24.30				6	53	41	8.1
GE-16	D	−0.57	24.44				7	70	23	8.3
GE-17	D	−0.88	24.29				Tr	33	67	8.7
GE-18	D	−0.77	24.94			22.6	4	48	48	10.3
GE-20	D	−0.17	24.34				31	27	42	11.9
GE-21	D	0.57	23.89				35	23	42	12.4

Note: L = lithology, D = white dolomitic marble, M = gray magnesite ore, Tr = trace. Marble sample 96MR29 [14] has  $\delta^{11}\text{B} = 6.13\text{‰}$ .



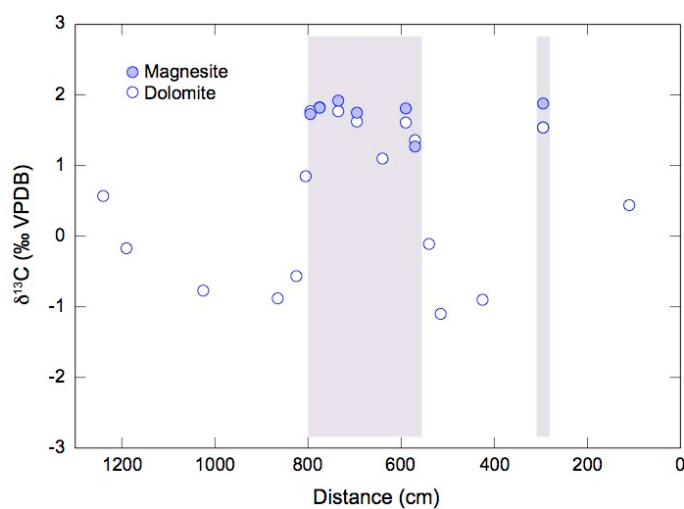
**Figure 4.** Backscattered electron images: (a) Magnesite ore; (b) dolomitic marble.

Six samples were analyzed by XRD to confirm mineral identifications. Magnesite and dolomite were detected in the ore samples, as was a  $7.3 \text{ \AA}$  phyllosilicate that texturally is likely to be antigorite serpentine. Cm-scale, post-tectonic fibrous veins were also confirmed to be brucite. A distinctive mica-rich sample was collected from the mine dump, and is similar to rocks described by [17] as typically found near the contacts with intrusive quartz monzonite. The XRD of this sample identified phlogopite and serpentine mixed with small amounts of illite, likely a mica weathering product. This sample also contains calcite and a  $15.7 \text{ \AA}$  phase seen in glycolated XRD mounts that may be the mixed layer phyllosilicate corrensite.

#### 4.2. Oxygen and Carbon Isotope Ratios of Magnesite and Dolomite

Oxygen and carbon isotope ratios are distinct between magnesite ore and host dolomitic marble (Table 1). Dolomitic marble wall rocks to the deposit have  $\delta^{18}\text{O} = 24.2 \pm 0.6\text{‰}$  (VSMOW) and  $\delta^{13}\text{C} = -0.2 \pm 0.7\text{‰}$  (VPDB,  $n = 11$ ). The magnesite ore zone has magnesite  $\delta^{18}\text{O} = 25.5 \pm 0.4\text{‰}$  and  $\delta^{13}\text{C} = 1.7 \pm 0.2\text{‰}$  ( $n = 7$ ). A magnesite-rich layer separated from the main ore lens (GE-3) has  $\delta^{18}\text{O} = 24.6\text{‰}$  and  $\delta^{13}\text{C} = 1.9\text{‰}$ . A dolomite-rich layer from within the orebody (GE-10) has  $\delta^{18}\text{O} = 24.4\text{‰}$  and  $\delta^{13}\text{C} = 1.1\text{‰}$ . Dolomite from magnesite ore samples is more variable in composition ( $\delta^{18}\text{O} = 25.3 \pm 1.0\text{‰}$ ,  $\delta^{13}\text{C} = 1.6 \pm 0.2\text{‰}$ ,  $n = 8$ ). As a first-order interpretation, these carbon and oxygen isotope ratios are in the typical range for marine carbonate rocks and their metamorphic equivalents, and are distinct from igneous isotope ratios.

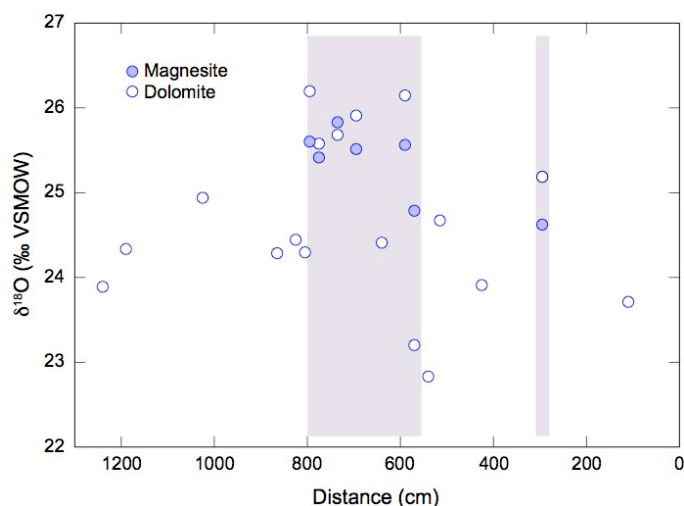
The differences in oxygen and carbon isotope ratios between the magnesite ore and dolomitic marble host rock argue for preservation of pre-metamorphic heterogeneities in isotope ratios (Figures 5 and 6). This is especially true for carbon isotopes, where a  $\sim 1.5\text{‰}$  difference between the ore and dolomitic marble host rock has been preserved through granulite facies metamorphism. The difference in the oxygen isotope ratio has considerably more scatter. The cross-layer metamorphic fluid flow would tend to homogenize the oxygen and carbon isotope ratios of different layers [21], which is not observed here. The only evidence for isotopic exchange between the host dolomitic marble and magnesite ore is at the edges of the orebody and in the isolated magnesite ore stringer, where  $\delta^{18}\text{O}(\text{Mag})$  is slightly lower than the average for other magnesite ore samples. For this reason, we take  $\delta^{18}\text{O}(\text{Mag}) = 25.6 \pm 0.2\text{‰}$  from the four samples in the center of the ore to be indicative of pre-metamorphic isotope ratios and to reflect magnesite formation. Note that the  $\delta^{13}\text{C}$  of all magnesite samples (including the ore stringer) is consistently high, suggesting the preservation of protolith  $\delta^{13}\text{C}$  values through metamorphism. This kind of protolith-derived layer-to-layer variability is commonly preserved in granulite facies rocks, and is an indication of negligible cross-layer fluid flow during metamorphism [21].



**Figure 5.** Transect of carbon isotope ratios of magnesite and dolomite across the south wall of the Dobbie mine. Gray shows location of magnesite ore.

It is difficult to assess isotope equilibrium between magnesite and secondary dolomite in the ore rocks because fractionations between dolomite and magnesite are small and not well constrained. The carbon isotope fractionation between magnesite and dolomite in the ores is positive and small ( $\Delta^{13}\text{C}(\text{Mag-Dol}) = 0.10 \pm 0.15\text{‰}$ ), which is consistent with a high-temperature equilibrium. However, carbon isotope fractionation of magnesite and dolomite are too similar to be an effective thermometer at these temperatures [22]. Oxygen isotope fractionations are more variable ( $\Delta^{18}\text{O}(\text{Mag-Dol}) = -0.08 \pm 0.78\text{‰}$ ) which is a strong function of magnesite:dolomite ratio

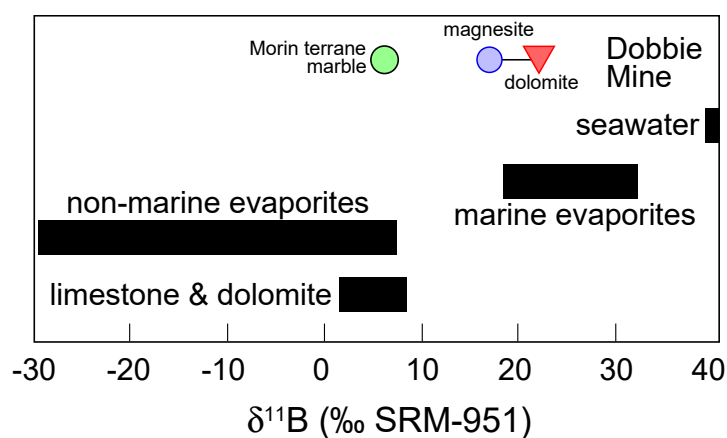
in the rocks, mainly because of the variability in  $\delta^{18}\text{O}(\text{Dol})$ . Excluding the samples, which were more likely to equilibrate with the dolomitic marble host-rock (from the edges of the orebody and the magnesite stringer),  $\Delta^{18}\text{O}(\text{Mag-Dol}) = 0.25 \pm 0.32\text{‰}$ , consistent with granulite facies equilibrium [22]. The high-temperature isotopic equilibrium with magnesite indicates that this texturally-secondary dolomite is likely locally-derived, and precipitated under low water/rock ratios.



**Figure 6.** Transect of oxygen isotope ratios of magnesite and dolomite across the south wall of the Dobbie mine. Gray shows the location of magnesite ore.

#### 4.3. Boron Isotope Ratios

Boron isotope ratios of Kilmar samples range from  $\delta^{11}\text{B} = 15.5\text{--}22.7\text{‰}$ , and average  $\delta^{11}\text{B} = 18.03 \pm 3.42\text{‰}$  ( $n = 4$ ). For comparison, a representative calcite marble from the southern Morin terrane (from outside of the ore zone) has  $\delta^{11}\text{B} = 6.13\text{‰}$ . Boron isotopes correlate well with oxygen isotopes in magnesite from ore zone rocks ( $r^2 = 0.98$ ). Boron isotope analyses of Precambrian carbonate rocks are sparse in the literature, and the ancient evolution of seawater  $\delta^{11}\text{B}$  is relatively poorly constrained [23], making interpretation of these data somewhat preliminary. Boron isotopes of modern seawater and evaporitic marine sediments typically have high  $\delta^{11}\text{B}$  values, similar to the results from magnesite ore, while most metamorphic rocks, continental crust, and non-marine evaporites have lower values (Figure 7).



**Figure 7.** Boron isotope ratios of samples from the Dobbie mine and a comparison sample of Morin terrane marble. Representative boron isotope compositions from [24].

Boron isotopes from large Proterozoic evaporitic magnesite deposits in China have  $\delta^{11}\text{B} = 16$  to 18‰ [25], which is very similar to the results here and also consistent with a marine origin for the Kilmar magnesite deposits.

#### 4.4. Major and Trace Elements

Major and trace element compositions of dolomitic marble and magnesite ore zone rocks are reflective of the mineralogy of these rocks (Table 2); CaO ranges from 9–25 wt%, reflecting the dolomite content, and  $\text{SiO}_2$  ranges from 2–20 wt%, reflecting the serpentine content. Most trace elements have low concentrations, with  $\Sigma(\text{REE}) = 11\text{--}25$  ppm for the dolomitic marble and 3.6–5.1 ppm for the magnesite ore samples (Figure 8), which is near detection limits. The exception to this is Sr, which is 1100–2920 ppm for the dolomitic marble and 510–810 ppm for the magnesite ore samples, and correlates well ( $r^2 = 0.92$ ) with the CaO content. This indicates that the dolomite content is controlling Sr in these rocks. The dolomite content seems to control the REE composition in both lithologies. When the silica-rich sample GE18 is excluded,  $\Sigma(\text{REE})$  also has a strong correlation with CaO ( $r^2 = 0.92$ ).

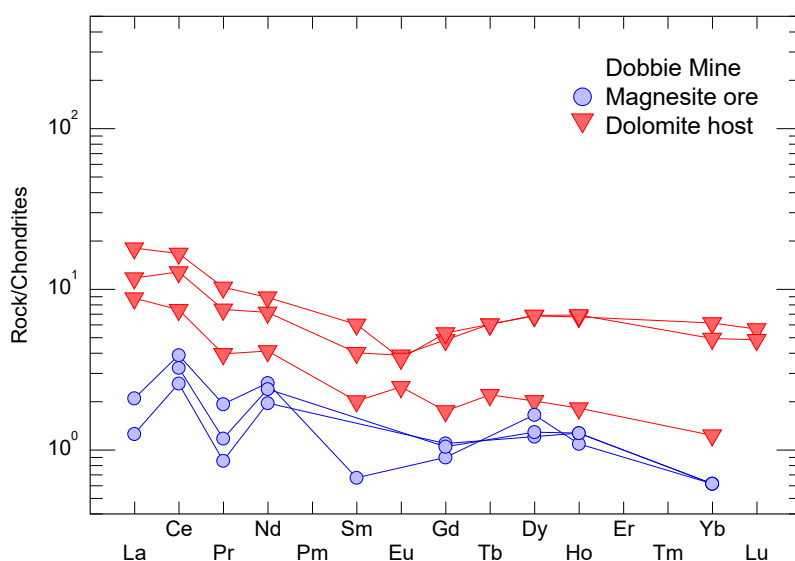
**Table 2.** Major and trace elements from the Dobbie mine, Kilmar magnesite district, Quebec.

Sample	L	SiO <sub>2</sub> wt%	Al <sub>2</sub> O <sub>3</sub> wt%	Fe <sub>2</sub> O <sub>3</sub> wt%	MnO wt%	CaO wt%	V ppm	Ni ppm	Zn ppm	Rb ppm	Sr ppm	Y ppm	Zr ppm
GE-2	D	6.12	0.03	0.16	0.05	25.00	10	<5	71	<0.2	2920	12.5	2.8
GE-7	D	16.20	0.05	0.47	0.05	18.50	10	7	253	0.4	2040	6.8	0.7
GE-9	M	2.13	0.05	0.54	0.08	15.00	10	5	68	<0.2	810	4.5	<0.5
GE-11	M	2.64	0.05	0.52	0.08	9.38	23	6	77	0.3	510	4.2	<0.5
GE-12	M	4.55	0.10	0.36	0.06	10.10	13	<5	90	0.2	640	4.1	<0.5
GE-18	D	20.40	0.04	0.37	0.09	15.20	19	<5	278	0.2	1100	14.2	3.1

Sample	L	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Dy ppm	Ho ppm	Er ppm	Yb ppm	Lu ppm
GE-2	D	2.8	7.9	0.7	3.3	0.6	0.22	0.97	1.69	0.37	1.24	1	0.14
GE-7	D	2.1	4.6	0.37	1.9	0.3	0.14	0.35	0.50	0.1	0.34	0.2	<0.05
GE-9	M	0.5	2.4	0.18	1.2	0.1	<0.05	0.18	0.41	0.06	0.27	0.1	<0.05
GE-11	M	0.3	1.6	0.08	0.9	<0.1	<0.05	0.22	0.30	0.07	0.17	0.1	<0.05
GE-12	M	<0.1	2.0	0.11	1.1	<0.1	<0.05	0.21	0.32	0.07	0.20	0.1	<0.05
GE-18	D	4.3	10.3	0.96	4.1	0.9	0.21	1.07	1.70	0.38	1.11	0.8	0.12

Note: L = lithology, D = dolomitic marble, M = magnesite ore.



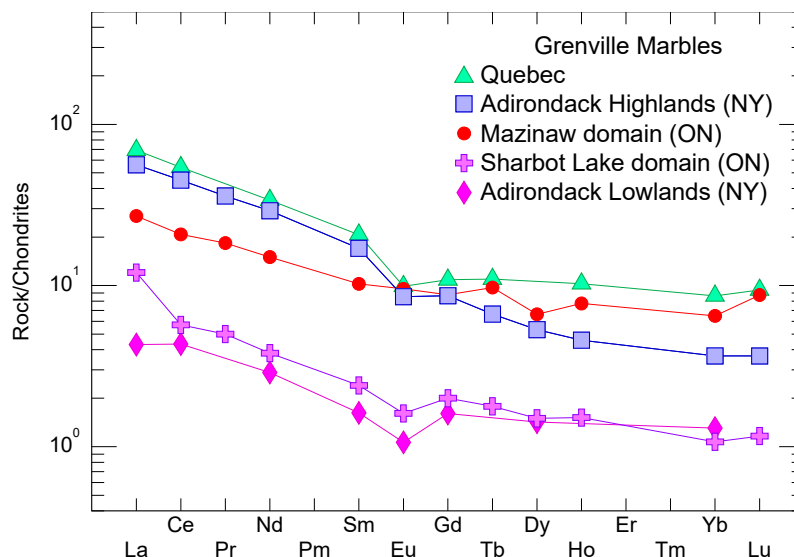
**Figure 8.** Rare Earth Element composition of the magnesite ore and dolomitic marble from the Dobbie mine, normalized to chondrite [26].



In some magnesite deposits, REE signatures have been interpreted as being strongly controlled by the REE of detrital clays in protolith rocks [27]. Alumina contents of the dolomitic marble and magnesite ore are very low (0.03 to 0.10%), and do not correlate with REE compositions; thus clays are not likely to represent an important REE contribution in the Kilmar deposits, even given the overall low REE abundances of these rocks. For example, if the  $\text{Al}_2\text{O}_3$  contents of the Kilmar rocks are taken to represent a clastic contribution similar to the North American Shale Composite (NASC), then the detrital clay component could account for <1 ppm of the total REE budget in the dolomitic marble and magnesite ore protoliths.

Rare Earth and trace element compositions of the Kilmar magnesite ores are comparable to other magnesite deposits. Iron and Mn contents are relatively low compared to other deposits, especially those attributed to metasomatism [5]. Rare Earth Element compositions are in the range for sparry (sedimentary) magnesite deposits, and lack the negative Ce anomalies reported for some [5]. It is unclear if the positive Ce anomalies in magnesite are geochemically meaningful or are an analytical effect of being close to instrumental detection limits.

Rare Earth element compositions of Kilmar host dolomitic marbles are similar to other Grenville marbles for which data are available (Figure 9). In general, Grenville marbles are LREE-enriched ( $(\text{La}/\text{Sm})_n \approx 2\text{--}5$ ), HREE depleted ( $(\text{Sm}/\text{Yb})_n \approx 1\text{--}4$ ), and have REE contents that range from ca. 1–200x chondritic values for LREE and 0.4–30x for HREE [28–31]. The Kilmar dolomitic marbles fall at the lower end of the range in terms of LREE enrichment. Some Grenville marbles show the negative cerium anomalies expected for primary chemical precipitates from seawater, most notably low-Al calcite marbles and some dolomitic marbles from the Sharbot Lake and Mazinaw domains of Ontario [28,31]. Negative cerium anomalies are small or lacking from Adirondack marbles [29,30], and is not present in the Southern Quebec composite marble of [32] ( $n = 7$  samples), or the Kilmar dolomitic marbles. This could be attributable to alteration after primary deposition. In terms of REE, the Kilmar dolomitic marbles are most similar to dolomitic marbles from the Adirondack Lowlands [29].



**Figure 9.** Average Rare Earth Element composition of Grenville marbles, normalized to chondrite [26]. See text for sources of data.

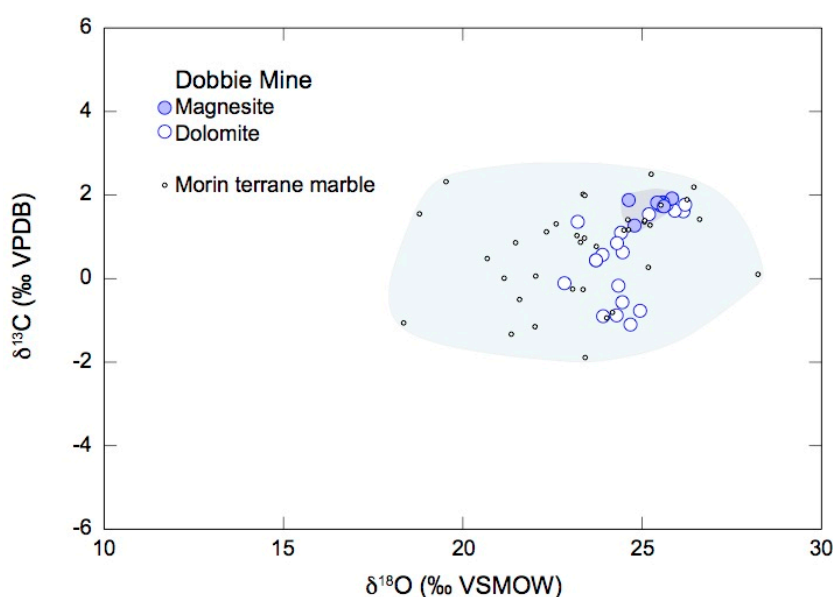
## 5. Discussion

### 5.1. Comparison to Grenville Marbles in Nearby Terranes

Oxygen and carbon isotopes in Grenville marbles are reflective of depositional conditions and later metamorphic effects. It has long been recognized that Grenville marbles have isotope ratios similar to marine limestones [33], which suggests that depositional isotope ratios have been broadly preserved

in carbonate with minor effects of calcite-graphite exchange, metamorphic devolatilization reactions, and the contact effects of plutonic rocks. Although interpretation of oxygen isotopes of Grenville marbles is complicated by the water-rock interaction history, carbon isotopes are more robust and often show differences from terrane-to-terrane. For example, in the New Jersey Highlands carbon isotope ratios of unmineralized samples of the Franklin marble are very restricted ( $\delta^{13}\text{C} = 0.3 \pm 0.7\text{‰}$ ,  $n = 46$ ), which is interpreted as reflecting a common depositional setting for these rocks [34]. However, oxygen isotope ratios in those rocks range from  $\delta^{18}\text{O} = 16.8\text{‰}$  to  $24.5\text{‰}$ , reflecting pre-metamorphic seafloor hydrothermal systems [34]. Similar isotopic provinciality and the preservation of sedimentary isotope ratios is seen in the Elzevir terrane of Ontario:  $\delta^{13}\text{C}$  values of marbles are  $\sim 3\text{‰}$  higher than contemporaneous Grenville marbles in nearby terranes, consistent with restricted basin deposition [35].

Oxygen and carbon isotope ratios of Kilmar host dolomitic marbles are statistically indistinguishable from other marbles from the Morin terrane ( $\delta^{18}\text{O} = 23.3 \pm 0.4\text{‰}$ ,  $\delta^{13}\text{C} = 0.7 \pm 1.2\text{‰}$ ,  $n = 37$ , [14]), and with  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  near the maximum values for Morin terrane marbles (Figure 10). The Morin terrane and geologically similar Adirondack Highlands + Lowlands all have large ranges in  $\delta^{13}\text{C}$  [36], and carbon isotopes from these three terranes are statistically indistinguishable by *t*-test. However, carbon isotopes of Grenville marbles in the Elzevir terrane, Frontenac terrane, and Parry Sound domain of Ontario, the Central Metasedimentary Belt of Quebec, and the Franklin marble of New Jersey are statistically distinct from those in the Morin terrane [34,35,37–39].



**Figure 10.** Oxygen and carbon isotopes of samples from the Dobbie mine and regional Morin terrane marbles [14].

The relatively high  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of the Kilmar magnesite rocks have several possible explanations. Evaporative environments are typically enriched in  $^{18}\text{O}$  by evaporation and  $^{13}\text{C}$  by  $\text{CO}_2$  degassing and other processes [40,41]. It is also important to note that some fundamental processes that result in isotope shifts during metamorphism are likely to be of minor importance in these rocks. Metamorphic devolatilization reactions during metamorphism can lower  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , but does not result in high isotope ratios [14]. Magnesite-dolomite isotope fractionations in these rocks are small because of their similar crystal structures and high temperatures, so exchange between these minerals will not appreciably shift either isotope ratio. Graphite was not observed in the analyzed samples, so carbonate-graphite exchange could not have lowered carbonate  $\delta^{13}\text{C}$  values.

## 5.2. Magnesite Ore Deposit Models

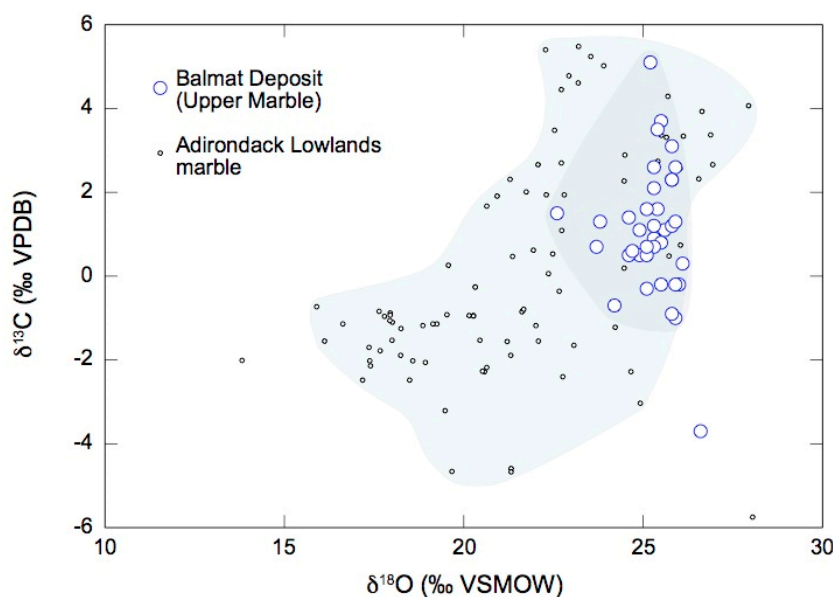
There are two primary environments that produce large magnesite bodies. The first is cryptocrystalline magnesite associated with alteration of ultramafic rocks. Cryptocrystalline magnesite is often either found as veins within ultramafic bodies or as concretions in nearby sediments [42]. Carbon isotope ratios of cryptocrystalline magnesite are distinctly low ( $\delta^{13}\text{C} \approx -10\text{‰}$ ), indicating a component of oxidized organic carbon in magnesite-depositing fluids [43]. Ultramafic rocks are rare in the Morin terrane [8], and are not associated with the Kilmar deposits [4]. The geology and carbon isotopes of the Kilmar deposits effectively exclude the class of cryptocrystalline magnesite deposits as possible protoliths.

The second major mode of magnesite genesis are sparry deposits hosted in metasediments. As a class, sparry deposits probably represents several modes of magnesite formation and later modification. Some deposits are thought to have syngenetic protoliths, being formed during evaporation or diagenetic replacement in a sedimentary environment [44–46]. These deposits typically have oxygen and carbon isotope ratios similar to marine carbonates. The lower oxygen isotope ratios of some magnesite deposits ( $<10\text{--}15\text{‰}$ ) often correlates with higher metamorphic grade of orogenic host rocks, suggesting high-temperature fluid interaction [43]. In some magnesite deposits hydrothermal alteration by meteoric water may have lowered oxygen isotope ratios (e.g., [47]), an effect which is not uncommon in marine evaporitic dolomites [48], but is not observed at Kilmar. The magnesite and dolomitic marble host rock from the Dobbie mine are more consistent with a marine or marine diagenetic origin than a later metasomatic genesis. The stratiform geometry of the magnesite, its interbedded nature with the host dolomitic marble, and layer-to-layer variability in (marine) stable isotope ratios all suggest a sedimentary origin.

## 5.3. Regional Implications for Depositional Settings of Ores in Grenville Marbles

Recent models for sedimentary exhalative zinc sulfide deposits hosted in carbonates typically involve a shallow water carbonate platform depositional environment and emphasize association with evaporitic sediments [6,49]. Several geologic features have been taken to suggest evaporitic environments for high-grade marble protoliths, in the context of Zn mineralization, including anhydrite layers, stratiform magnesite or brucite, dolomite-rich marbles, and tourmaline-rich layers e.g., [6,50–52]. The most clear example of this association is the world-class Balmat Zn mining district in the Adirondack Lowlands, where massive sphalerite is found associated with thick anhydrite layers in a meta-evaporate sequence [50]. Anhydrite is also recognized at the exhalative Cadieux sphalerite deposit in the Central Metasedimentary Belt of Quebec, which is hosted by a similar dolomitic marble sequence as the Balmat ore deposits [52]. The regional geologic context of Balmat and Cadieux are somewhat different, which may be reflected in different fluid compositions: The Cadieux deposit is associated with metavolcanic rocks and has sulfides with an average  $\delta^{34}\text{S}$  of  $-2.3\text{‰}$  CDT [53], consistent with igneous sulfur, while the Balmat ore deposits are not associated with metavolcanic rocks and have sulfides with sedimentary  $\delta^{34}\text{S}$  values = 13 to 16‰ [54].

The Kilmar magnesite deposits and the carbonate hosts to the Balmat ore deposits have similar oxygen and carbon isotope ratios, which may prove to be a useful characteristic for evaluating evaporitic protoliths. The Balmat ore deposits have relatively high  $\delta^{18}\text{O}$  values when compared to other marbles in the Adirondack Lowlands, similar to the relationship between the Kilmar magnesite deposits and marbles of the Morin terrane (Figures 10 and 11). High  $\delta^{18}\text{O}$  values (23–27‰) are also seen in the Salerno Lake and Thirty Island Lake deposits of the Ontario Grenville Province, which are sedimentary exhalative zinc deposits that may belong to the same class as Balmat [55]. In contrast, Grenville Supergroup exhalative zinc deposits associated with volcanic rocks have a larger span of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  that trend to lower values, suggesting mixing with igneous fluids [55,56], consistent with the evidence from sulfur isotopes [53].



**Figure 11.** Oxygen and carbon isotopes of samples from the evaporitic Balmat zinc deposits [50] and the Adirondack Lowlands [36].

**Author Contributions:** Conceptualization and writing, W.H.P.; methodology, W.H.P. and G.R.E.; investigation, G.R.E.

**Funding:** This research was funded by a Carter-Wallace research fellowship to W.P. and a Linsley/McLelland summer assistantship to G.E. from Colgate University. Acquisition of the mass spectrometer at Colgate University was supported by the US National Science Foundation (EAR-0216179). Publication supported by the Malcolm '54 and Sylvia Boyce Fund for Geology Research at Colgate University.

**Acknowledgments:** We thank Serge Perreault (Quebec Department of Natural Resources) for arranging access to the Dobbie Mine and encouragement in this study. G.E. thanks Richard April and Di Keller for assistance with the XRD analysis and encouragement during a class project on some of these samples. An anonymous referee is thanked for their thorough review.

**Conflicts of Interest:** The authors declare no conflict of interest.

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