

Article

A Silicocarbonatitic Melt and Spinel-Bearing Dunite of Crustal Origin at the Parker Phlogopite Mine, Notre-Dame-du-Laus, Quebec, Canada

Robert F. Martin^{1,*} and Dirk Schumann²

- ¹ Department of Earth and Planetary Science, McGill University, 3450 University Street, Montreal, QC H3A 0E8, Canada
- ² Fibics Incorporated, 1431 Merivale Road, Ottawa, ON K2E 0B9, Canada; dschumann@fibics.com
- * Correspondence: robert.martin@mcgill.ca

Received: 30 August 2019; Accepted: 3 October 2019; Published: 6 October 2019



Abstract: The Parker phlogopite mine, located near Notre-Dame-du-Laus, Quebec, 74 km north of Ottawa, is well known among mineral collectors for its centimetric euhedral crystals of black spinel. Among the dozens of phlogopite mines active in the early 1900s in the Mont-Laurier–Bancroft corridor in the Central Metasedimentary Belt of the Grenville Province, the Parker mine is exceptional because of the association of forsterite + spinel with phlogopite. Euhedral crystals of these minerals are found "frozen" in a carbonate matrix. The carbonate dike and segregations are associated with spinel-rich dunite that contains accessory diopside, phlogopite, and pargasite, as well as ilmenite and apatite. The interstitial melt crystallized to calcite + dolomite. Hematite appeared as flakes in the melt owing to net loss of hydrogen, and the spinel underwent oxidation-induced exsolution. Our spinel crystal entrapped a domain of carbonate during growth. It also entrapped globules of boundary-layer melt that crystallized to a carbonate + sulfate + phosphate + silicate + oxide assemblage. Such globules, where present in the cumulate, are more pristine than in the coarse crystal of spinel, i.e., less affected by a hydrothermal overprint. We contend that the carbonate melt ultimately formed by the hydrous melting of marble, as supported by oxygen-isotope data on all major minerals. Melting occurred 1140 million years ago, at a time of tectonic relaxation following the Shawinigan compressive stresses.

Keywords: spinel; forsterite; phlogopite; silicocarbonatite dike; dunite; polymineralic globules; late oxidation; Parker mine; Notre-Dame-du-Laus; Quebec; Canada

1. Introduction

In the early 1900s, apatite and phlogopite were recovered from dozens of small mines in the Mont-Laurier–Bancroft corridor in the Western Quebec/Eastern Ontario portion of the Grenville Province [1,2]. These minerals are found in a calcite matrix, and an association with ultrabasic rocks, pyroxenite or dunite, is prominent in most of these. Among all these deposits, the Parker mica mine, located near Notre-Dame-du-Laus, Quebec ($46^{\circ}05.5'$ N, $75^{\circ}39.7'$ W), is among the rare ones which display strikingly euhedral crystals of black spinel associated with dunite. The isolated crystals of spinel are found in a matrix of white to pinkish calcite, along with euhedral forsterite, phlogopite, and apatite [3]. Van Velthuizen [4] described the olivine morphologically and compositionally. The Parker mine occurs in what he called "a green rock complex" exposed in an area dominated by marble (his Figure 2). We have characterized one sample of green rock in detail. It consists mostly of an accumulation of magnesian olivine (~65 vol. %) and spinel crystals. In spite of high values of Mg# (100Mg/(Mg + Fe²⁺ + Mn)), close to 90, the forsterite is devoid of Ni and Cr. The presence of an ultrabasic rock in association with apatite and phlogopite mineralization is enigmatic, and its origin has been debated in the past.



In this article, we discuss the geological setting and document the age of the Parker phlogopite mine in the Central Metasedimentary Belt (CMB) of the Grenville Province. We describe the dunite texturally and mineralogically on the basis of large-area image mosaics and 92 maps of key areas in two polished thin sections. We have identified the constituent minerals with the help of their energy-dispersion spectra. We were able to reconstruct the order of primary crystallization and the appearance of secondary minerals as the dunite cooled. Then we focused on a euhedral crystal of spinel enclosed in calcite. We scrutinized the large-area image mosaics and 60 maps of selected areas in the spinel crystal, and were able to recognize early-formed largely anhydrous minerals, and others that represent lower-temperature minerals formed in a hydrous environment. Our observations led to a reconstruction of what transpired at the Parker mine in the late Mesoproterozoic in this portion of the Grenville Province.

2. Background Information

The Parker Mine is located 74 km north of Ottawa, Canada (Figure 1). It was exploited intermittently for phlogopite in the period 1910–1913; the venture never was profitable. The pit was bulldozed over prior to 1963 because of safety concerns. It was only in 1984 that the site was partly uncovered and "rediscovered" by a team from the Canadian Museum of Nature led by Louis Moyd (1916–2006), well versed in the exploration of similar "vein-dikes". Jerry Van Velthuizen (1951–2001), a member of the team, summarized key findings [4]; no follow-up work has been published since. Belley et al. [5] described an occurrence of dark blue spinel in association with forsterite, phlogopite, and aspidolite 1.3 km to the northeast, at the Des Cèdres dam on the Lièvre River.



Figure 1. The geological setting and location of the Parker Mine with reference to Ottawa (Ontario), Montreal, the Yates prospect near Otter Lake, and Mont Tremblant (Quebec). After Wynne-Edwards [6]; GFTZ: Grenville Front Tectonic Zone, CMB: Central Metasedimentary Belt, PM: Parker Mine.

Mineral collectors know the Parker mine well for its centimetric octahedra of spinel "frozen" in a calcite matrix. The qualifier "frozen" is appropriate, as the idiomorphic crystals formed in the calcite matrix and not in cavities, as one might infer on the basis of the perfection of the idiomorphic crystals (Figure 2a). In our collection of isolated spinel crystals from the Parker Mine, we found one that has prominent inclusions of calcite (Figure 2b). It has been sliced for this investigation of the relationship between the spinel crystal and the trapped carbonate. Several smaller crystals of spinel and centimetric crystals of partially serpentinized forsterite also are found in the calcite matrix (Figure 2b).



Figure 2. Large crystals of spinel from the Parker mine. (a). This strikingly idiomorphic crystal 1.3 cm across displays both octahedral and dodecahedral faces, as do the smaller crystals of spinel. Photo: Christian Autotte, Club de Minéralogie de Montréal. (b). Large spinel crystal enclosed in a calcite matrix. Note the presence of calcite inclusions in the spinel crystal. Several smaller crystals of spinel and centimetric crystals of partially serpentinized forsterite also are found in the calcite matrix. Width of the specimen: 10 cm. Photo: Russell Proulx.

3. The Geological Setting

The Mont-Laurier terrane of the Central Metasedimentary Belt (CMB, Figure 1) consists of vast areas of marble, quartzite, and gneiss, whose heterogeneous lateral rheology has ensured an impressive record of pre-Grenvillian and Grenvillian tectonic events [7]. Marble, calcitic or dolomitic predominates in a northeast-southwest belt to the west of the Gatineau River; it is intercalated with quartzite horizons and pelitic or quartzofeldspathic gneiss. Quartzite predominates in the eastern part of the Mont-Laurier terrane, east of the Gatineau River; the Parker Mine lies in the Quartzite domain (Figure 1). These sedimentary units were deposited in a basin prior to 1.3 Ga, then were deformed and metamorphosed to the granulite facies. In the gneissic rocks of the Quartzite domain, zircon and monazite U–Pb ages of metamorphism range from 1212 ± 16 Ma to 1183 ± 9 Ma, with a poorly defined later pulse at around 1153 Ma (Table 9 in reference [7]). The regionally developed temperature attained 950 °C, at least in the northern portion of Corriveau's map-area. The U-Pb radiometric ages recorded by titanite in the marble of the Quartzite domain fall in the interval 1160-1110 Ma (Table 9 in reference [7]). In the Otter Lake area (Figure 1), the U–Pb dates determined on zircon and monazite in the leucosome of gneissic rocks are in the range 1180–1140 Ma [8]. The major episode of anatexis of quartzofeldspathic rocks and the metamorphism of marble thus began during the early Shawinigan stage of compressive events (Figure 7 in reference [9]).

4. Analytical Methods

4.1. Samples

We have investigated in detail two petrographic thin sections of dunite and of one large spinel crystal (Figure 2b). The spinel crystal was cut in half and embedded in EPO CURE epoxy in mounts 25 mm in diameter and polished for subsequent light-microscopy imaging, SEM imaging, and energy-dispersive spectroscopy (EDS) analyses.

4.2. Light microscopy

Large-area transmitted-light microscopy image mosaics were acquired from the two petrographic thin sections (Parker Mine 5 and 6) using a Zeiss AXIO Zoom.V16 light microscope (Carl Zeiss Microscopy GmbH, Göttingen, Germany) (Figure 3 and Figure S1). The mosaics were acquired with the software "ZEN Pro" using the Plan Apo Z 0.5/0.125 objective (FWD 114 mm) at a resolution of 811 nm/pixel with plane-polarized (PPL) and cross-polarized transmitted light (XPL). Reflected-light microscopy image mosaics were acquired from the two polished epoxy mounts of the spinel crystal (Parker Mine 10a, 10b) using the same light microscope with reflected light (RL) from a LED light ring mounted on the microscope objective.



Figure 3. Large-area transmitted-light microscopy mosaic of the dunite, thin section "Parker Mine 6". The upper part of the light-microscopy image mosaic shows a schematic overlay of the back-scattered electron (BSE) signal of the SEM image mosaic. The spinel crystals have a greenish color in plane-polarized light.

4.3. SEM–EDS Analyses

Large-area SEM image mosaics of both the thin sections and the spinel crystal epoxy mounts were acquired with the ZEISS Atlas 5 software (Version 5.2.3, Carl Zeiss Microscopy GmbH, Oberkochen, Germany) by using a ZEISS EVO MA 15 tungsten filament scanning electron microscope (SEM, Carl Zeiss Microscopy GmbH, Oberkochen, Germany) at Fibics Incorporated (Ottawa, Canada). The large-area light microscopy mosaics were imported into the respective Atlas 5 correlative workspace projects, aligned with the sample in the microscope, and the large-area SEM image mosaics were acquired with an accelerating voltage of 20 kV using the back-scattered electron (BSE) detector, a working distance of 11.0 mm, a 2.3 nA beam current (120 μ m aperture), a 3 μ s dwell time, and a resolution of 200 nm/pixel. The resulting large-area image mosaics of the two thin sections comprise 2824 (Parker Mine 5) and 3078 (Parker Mine 6) images, with each image tile consisting of 3072 × 3072 pixels (614.3 × 614.3 μ m), and a total pixel count of 10.1 and 8.9 gigapixels.

Once the large-area image mosaics were acquired, stitched, and image-corrected, the entire Atlas 5 datasets were exported to an autonomous series of files called the Browser-Based Viewer (BBV), which allows anyone on a PC with a web browser to examine the complete dataset at full resolution in a manner similar to that known from the application "Google EarthTM". The computer mouse is used to zoom in and out as well as to navigate through the large-area image mosaic. The Browser-Based Viewer datasets can be viewed by following the links below:

Parker Mine 5 (petrographic thin section): http://petapixelproject.com/mosaics/PM/PM5/PM5BSDPPLXPL/ index.html

Parker Mine 6 (petrographic thin section): http://petapixelproject.com/mosaics/PM/PM6/PM6BSDPPLXPL/ index.html

Parker Mine 10a (large spinel crystal): http://petapixelproject.com/mosaics/PM/PM10a/PM10aBSDRL/ index.html

Parker Mine 10b (large spinel crystal): http://petapixelproject.com/mosaics/PM/PM10b/PM10bBSDRL/ index.html

Energy-dispersive spectroscopic (EDS) analyses were also carried out on the Zeiss EVO MA 15 tungsten-filament SEM equipped with two Bruker XFlash 6/30 EDS detectors (Bruker Nano GmbH, Berlin, Germany) controlled using the Esprit 1.9 software (Bruker Nano GmbH, Berlin, Germany) An accelerating voltage of 20 kV and a probe current of 2.3 nA were used for the acquisition of EDS element-distribution maps and point analyses. The element maps and point analyses acquired were exported from the Bruker Esprit 1.9 software, arranged into figure plates using the software CoreIDRAW X9 (Version 21.3.0.755, Corel Corporation, Ottawa, ON, Canada), exported as PDF or JPG files, and linked with their respective location of acquisition in the Atlas 5 BBV datasets (see Atlas 5 BBV links). The analytical results can be viewed by clicking with the mouse in the green rectangular regions that mark the locations in which the analyses were performed. After clicking, a new browser window will open, and the PDF or the JPG file can be viewed and downloaded.

4.4. Ar/Ar Dating

The age of the phlogopite was established by the Ar/Ar method at the Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario (Douglas Archibald, analyst). The mineral and flux monitors (standards) were wrapped in aluminum foil. The resulting disks were stacked vertically into a container 11.5 cm long and 2.0 cm in diameter, and then irradiated with fast neutrons at the McMaster Nuclear Reactor in Hamilton, Ontario, for 40 h at 120 MWH.

The measured argon-isotope peak heights were extrapolated to zero-time, normalized to the ⁴⁰Ar/³⁶Ar atmospheric ratio (295.5) using measured values of atmospheric argon, and corrected for neutron-induced ⁴⁰Ar from potassium, ³⁹Ar and ³⁶Ar from calcium, and ³⁶Ar from chlorine [10].

Dates and errors were calculated using formulae given by Dalrymple et al. [11], and the constants recommended by Steiger and Jäger [12]. The isotopic data acquired can be consulted in two Excel spreadsheets in the Supplementary Materials (Tables S1 and S2).

Most of the stable isotope data were acquired by Julia Cox of the Department of Geology, University of Georgia in Athens using the laser-fluorination method. Values shown with an asterisk were acquired by Joaquin Perona, of the Departament de Cristallografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona. Values shown by a dagger were acquired courtesy of Stephen Crowley, University of Liverpool. All used the laser-fluorination method. The carbonate samples (approximately 5 mg) were reacted under vacuum in 100% phosphoric acid at 50 °C. The CO₂ is extracted on a conventional vacuum line and analyzed on a Finnigan MAT 252 mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Laboratory standards are prepared and analyzed with each batch of samples. These standards were calibrated to reference materials NBS-19 and NBS-18. The two-sigma error in δ^{13} C associated with the extraction of carbon and analysis is 0.04‰. The optimum two-sigma error associated with δ^{18} O values is about 0.2‰. The isotopic analysis of oxygen in the silicates was done using a method modified from that of [13]. The samples (0.5–2 mg, depending on availability) were reacted under vacuum with BrF₅ while heated with a variable power CO₂ laser (Synrad, 10,510–10,650 nm wavelength, 75 W maximum power). The O_2 generated was converted to CO_2 with heated graphite, and the CO_2 was analyzed with a Finnigan MAT 252 mass spectrometer at the University of Georgia. Samples were analyzed with the UWG-2 garnet standard [13]. Sample results were adjusted according to the daily average of standard results and reported relative to Standard Mean Ocean Water, Vienna convention (VSMOW).

5. Composition of the Phlogopite and Age of Mineralization

The dark amber phlogopite crystals attain 15 cm across, and occur in the matrix of white or pale pink calcite emplaced as dikes [14]. The mica was not considered "a very good splitter", which may partly explain why the Parker mine never was a successful venture. The unzoned phlogopite crystals nucleated in the carbonate matrix, along with idiomorphic forsterite and spinel. Each of these three minerals contains inclusions of the other two and of calcite. Their growth must have been coeval. Compositions of phlogopite are listed below. The phlogopite departs from its end-member composition mostly in its F content; a representative composition is

 $(K_{1.815}Na_{0.185})_{\Sigma 2} (Mg_{5.177}Fe^{2+}_{0.353}VIAl_{0.309}Ti_{0.100}Na_{0.042}Ba_{0.026}Ca_{0.002}Mn_{0.002})_{\Sigma 6.011} (^{IV}Al_{2.500}Si_{5.500})_{\Sigma 8} \\ O_{20} (OH_{3.224}F_{0.764}Cl_{0.012})_{\Sigma 4}.$

The Mg# is 93.6; the phlogopite is devoid of Ni and Cr (as are the forsterite and spinel).

Two representative crystals of phlogopite were dated using the 40 Ar/ 39 Ar isotopic system. The spectra acquired show well-defined plateaus. Crystal D-648 yielded a plateau age of 1142 ± 3 Ma. The spectrum is provided as Figure S2. A second crystal (D-469) yielded 1135 ± 4 Ma as a plateau age. The ages overlap at the one-sigma level.

6. The Minerals Encountered in the Spinel-Rich Dunite

Our representative specimen of Van Velthuizen's "green rock complex" consists of fine-grained dunite, i.e., a forsterite-dominant olivine-rich rock locally containing close to 40 vol. % of spinel (Tables 1–3, Figures 3 and 4). The olivine-group mineral is forsterite of composition Fo₉₀. Although an apatite-group mineral is present, the olivine is poor in phosphate. Lizardite has a higher Mg# value than the olivine (Table 1). The greenish spinel commonly shows incipient development of exsolution-induced domains of magnetite. The Mg# value is close to 81.7 (Table 2). The Mg# value of diopside, magnesio-hastingsite, and phlogopite is greater than that of the olivine (Tables 1 and 3), which indicates that they crystallized from the melt before the olivine. Textural data are presented below that confirm this finding in the case of phlogopite. Ilmenite, an apatite-group mineral, and dolomite are minor primary constituents. Secondary minerals have also been identified in our examination of 92 key areas in the thin sections, as documented below. Calcite and dolomite are

distributed interstitially. We consider this ultrabasic assemblage a cumulate, formed by the rapid gravitational settling of dense minerals (ρ of forsterite 3.3, spinel 3.6 g/cm³, respectively) in a carbonate growth-medium. There is evidence that the crystal mush in the dunitic cumulate has recrystallized to form an aggregate of polygonal grains that share common boundaries and define 120° triple junctions. As in all cumulates, this recrystallization involved solution in and redeposition from the interstitial low-density, low-viscosity liquid before it was buoyantly squeezed out [15]. It is common for spinel crystals growing in a melt to link into chains [16]. Conjoined crystals of spinel in Figures 3 and 4 seem to have settled in this way into the mush. The dunite contains heterogeneously distributed spinel grains, some areas being almost devoid of spinel. Note the common presence of spinel in forsterite grains. The converse also is found, though less commonly (Figures 4 and 5).

	1	2	3	4	5	6
п	core, 4	rim, 2	5	2	3	8
SiO ₂ wt. %	40.96	40.72	40.78	40.84	40.78	39.53
Al_2O_3						0.25
FeO	8.67	9.62	9.12	8.83	9.19	2.63
MnO	0.34	0.27	0.31	0.29	0.20	0.06
MgO	50.09	49.57	49.41	49.82	49.88	40.02
CaO	0.01	0.03	b.d.l.	0.04	0.03	
P_2O_5	0.01	0.01				
Cl						0.30
O≡Cl						-0.07
Total	100.08	100.22	99.66	99.82	100.07	82.72
Mg#	90.8	89.9	90.3	90.2	90.4	96.4

Table 1. Composition of forsterite and lizardite, Parker phlogopite mine, Notre-Dame-du-Laus, Québec.

	Spl	Spl	Spl	Spl	Spl	Mgt
n	5	core, 2	rim, 4	core, 7	rim, 5	3
Al ₂ O ₃ wt. %	65.53	65.60	65.03	65.66	65.94	0.24
FeO*	11.60	12.00	12.43	11.47	11.21	91.47
MnO	0.18	0.16	0.15	0.16	0.16	0.03
MgO	21.87	22.05	21.68	21.89	22.02	0.36
Total	99.18	99.81	99.29	99.18	98.33	92.10
Al apfu	1.936	1.927	1.924	1.934	1.942	0.011
Fe ³⁺	0.064	0.073	0.076	0.061	0.058	1.989
Fe ²⁺	0.179	0.177	0.185	0.179	0.177	0.978
Mn	0.004	0.003	0.003	0.003	0.003	0.001
Mg	0.817	0.819	0.812	0.818	0.820	0.021
Mg#	81.7	81.9	81.2	81.8	82.0	2.1
O.R.	26.3	29.2	29.1	25.4	24.7	67.0

Table 2. Composition of spinel and magnetite, Parker phlogopite mine, Notre-Dame-du-Laus, Québec.

The compositions were acquired with an electron microprobe (see Table 1). Conditions: column 1:15 kV, 20 mA, 10 μ m beam, ZAF method of correction; columns 2–3: 20 kV, 20 mA, 50 μ m × 50 μ m rastered beam; column 4–6: 20 kV, 20 mA, 2 μ m beam. Standards: hematite (Fe), diopside (Ca), kyanite (Si), spinel (Mg, Al), TiO₂ (Ti), NiO (Ni), vanadinite (V), and chromite (Cr). Sought but not found: Si, Ti, Ni, V, and Cr. Mg# is defined as 100Mg/(Fe²⁺ + Mn + Mg); *n*: number of analyses made. O.R. is the oxidation ratio: 100Fe³⁺/(Fe²⁺ + Fe³⁺). Column 1: Parker 2, homogeneous spinel (Spl); 2: Parker 4, Spl + exsolved magnetite (Mgt) domains near the core; 3: Parker 4, homogeneous domain near the rim; 4: Parker 2, Spl coexisting with exsolved Mgt domains near the core; 5: Parker 2, homogeneous Spl near the rim. 6: Parker 2 + 4, "primary" inclusions of Mgt in Spl. FeO*: total iron expressed as FeO.

The analytical data were acquired with a JEOL-8900L electron microprobe (JEOL USA, Inc., Peabody, MA, USA) at McGill University, operated at 20 kV, 50 nA, with a beam 5 μm in diameter

(columns 1, 2), at 15 kV, 20 nA, 10 μm (columns 3, 4), and 20 kV, 20 nA, 5 μm (column 6). The following standards were used: forsterite (Si, Mg, Fe), spessartine (Mn), orthoclase or pyrope (Al), chromite (Cr), NiO (Ni), diopside (Ca), vanadinite (Cl), and fluorapatite (P). The ZAF method of correction was employed. Sought in the forsterite but not found: Al, Cr, and Ni. Mg# is defined as 100Mg/(Fe + Mn + Mg); *n*: number of analyses made. Columns 1–4: forsterite, this work; 5: forsterite [4], 6: lizardite, this work. Lizardite was identified by X-ray diffraction [4].

	Parker-2	Parker-3	Parker-2	Parker-3
	Phl	Phl	Di	Mht
n	1	6	2	3
SiO ₂ wt. %	38.28	38.47	53.41	41.13
Al_2O_3	17.00	16.67	1.21	14.68
TiO ₂	1.15	0.93	0.09	0.50
FeO (total)	2.75	2.95	2.11	5.33
Fe_2O_3 (calc.)				(4.60)
FeO (calc.)				(1.19)
MnO	0.03	0.02	0.06	0.06
MgO	24.44	24.29	17.48	17.70
CaO	0.07	0.01	25.43	12.86
Na ₂ O	0.42	0.82	0.06	2.85
K ₂ O	10.39	9.95	b.d.l.	0.90
BaO	0.54	0.44	b.d.l.	b.d.l.
F	1.42	1.69	b.d.l.	1.28
Cl	b.d.l.	0.05	b.d.l.	0.15
(H ₂ O)	3.54	3.38		1.42
Subtotal	100.03	99.67		99.32
–(F,Cl)≡O	0.60	0.72		0.57
Total	99.43	98.95	99.85	98.75
Si <i>apfu</i>	5.454	5.502	1.945	5.961
^{IV} Al	2.546	2.498	0.052	2.039
VIAl	0.308	0.312		0.468
Ti	0.123	0.100	0.002	0.056
Fe ³⁺			0.058	0.501
Fe ²⁺	0.328	0.353		0.145
Mn	0.004	0.002	0.002	0.007
Mg	5.190	5.178	0.949	3.824
Ca	0.011	0.002	0.992	1.997
Na	0.116	0.227	0.004	0.801
Κ	1.888	1.815		0.166
(OH)	3.360	3.223		1.376
F	0.640	0.764		0.587
Cl		0.012		0.037
0	20	20	6	23
Mg#	94.0	93.6	99.8	96.2

Table 3. Composition of phlogopite, magnesio-hastingsite, and diopside, Parker phlogopite mine,Notre-Dame-du-Laus, Québec.

The level of Sr and Ni is below the detection limit (b.d.l.). The phlogopite (Phl) is fluorine-bearing. The amphibole is calcic, with B (Ca + Na) = 2.00, B Na = 0.003, A (Na + K) = 0.964, all in atoms per formula unit (*apfu*), calculated on the basis of 24 atoms of O + OH + F + Cl. It consists of magnesio-hastingsite (Mht) very close to the field of pargasite. The clinopyroxene is virtually end-member diopside (Di), with a small amount of iron in the ferric state.

The minerals in the selected high-resolution areas have been identified on the basis of their energy-dispersive spectrum (EDS). Forsterite and spinel are both present in each of the six areas illustrated (Figure 4a–f), but proportions are quite variable. Each area contains one or two carbonate minerals in interstices, again in quite variable proportions. Calcite and dolomite share a boundary

in Figure 4a; both crystallized from a single (Ca,Mg) carbonate melt. The calcite invariably contains a small amount of Mg, but in the area labeled Mg-rich calcite in Figure 4a, the Mg peak in the EDS spectrum is noticeably enhanced (Figure S4). In this suite, it is clear that not all the dolomite crystallized directly from a melt. In Figure 4d,e, for example, dolomite developed by the replacement of calcite, presumably by reaction of the melt with adjacent forsterite and perhaps also spinel. In Figure 4b, the carbonate melt crystallized magnesite and dolomite, which share a boundary. This is one of two occurrences of magnesite that we encountered. The lack of a uniform interstitial carbonate assemblage is symptomatic of a poorly blended melt phase.



Figure 4. False-color energy-dispersive spectroscopy (EDS) element-distribution maps superimposed on the back-scattered electron images showing the texture of dunite in the two thin sections from the Parker mine. EDS point analyses 1 to 10 are shown in Figure S4. Symbols: Cal: Calcite; Di: Diopside; Dol: Dolomite; Fo: Forsterite; Hem: Hematite; Liz: Lizardite; Mht: Magnesio-hastingsite; Mgs: Magnesite; Phl: Phlogopite; Spl: Spinel.

Among the minor "primary" constituents encountered in the dunite are phlogopite, diopside, and a magnesio-hastingsitic amphibole (Table 3). Phlogopite nucleated early in the carbonate melt, as it is entrapped in forsterite (Figure 4e) and spinel (Figure 5f). It was encountered in 28 of the 92 thin-section areas investigated. Diopside invariably forms a ribbon-like interface between forsterite and interstitial carbonate (Figure 4a,d,e and Figure 5b). Note that diopside does not occur at all forsterite–carbonate interfaces. We see evidence of such a reaction in 17 of the 92 areas investigated.

Even more rarely encountered, only in nine cases of the 92, is a magnesio-hastingsitic amphibole. In Figure 4f, a relatively large crystal of this amphibole is judged to have formed relatively late, as it poikilitically encloses forsterite, spinel, calcite with a dolomitized border, and dolomite. Apparently homogeneous ilmenite occurs interstitially, associated with pyrite (Figure 5a).



Figure 5. False-color EDS element-distribution maps of interstitial minerals and micro-inclusions in the spinel crystals of the dunite. (**a**) Pyrite occurs together with hematite and ilmenite at an interface between dolomite and forsterite. (**b**,**c**) Allanite-(Ce) and diopside are decorating a portion of a forsterite grain. (**d**) Ilmenite crystal at the interface between forsterite and dolomite. (**e**,**f**) Spinel crystals with hematite, dolomite, calcite, phlogopite, forsterite, and diopside inclusions. Symbols not yet defined: Aln-(Ce): Allanite-(Ce); Cch: Clinochlore; Ilm: Ilmenite. EDS point analyses 11 to 14 are shown in Figures S4 and S5.

Also present in the dunitic cumulate are hematite and a serpentine-group mineral inferred to be lizardite (present in 42 and 28 areas of the 92 investigated, respectively). As is clear in Figures 4 and 5, these secondary minerals are volumetrically rather minor. Interstitial ilmenite is visibly exsolved in Figure 5d. Allanite-(Ce) locally decorates forsterite-carbonate grain boundaries, along with lizardite, hematite, and clinochlore (Figure 5a–c). They were probably coeval, and filled contraction-induced cracks. A speck of celestine is found in secondary dolomite (Figure 5d).

High-magnification images reveal the presence of polymineralic globules in spinel and forsterite (Figure 5c,e,f and Figure 6). The minerals seem to have grown in situ in these globules after trapping in the host mineral prior to gravitational settling. In Figure 6a, the shape of the apatite and calcite conforms to the globule boundary; the two minerals share a border, which suggests that they grew

together, possibly from a single droplet of melt. We believe that hematite nucleated in the carbonate melt at that stage and became attached to the globule. A second globule in Figure 6a seems to consist only of apatite + hematite, but recall that this is a slice through a three-dimensional object.



Figure 6. False-color EDS element-distribution maps of polymineralic micro-inclusions found in the spinel and forsterite crystals in the dunite. (**a**) Globular inclusion containing calcite, hematite and apatite. (**b**) Inclusion containing diopside, dolomite, calcite, and hematite. (**c**) Inclusion of magnesite decorated with hematite crystallites. (**d**) Inclusion containing forsterite, ilmenite, magnesio-hastingsite, and phlogopite. (**e**) Inclusion with phlogopite, calcite, dolomite, hematite, ilmenite, and apatite. (**f**) polymineralic inclusion in forsterite containing spinel, hematite, dolomite, and phlogopite. EDS point analysis 15 is shown in Figure S5.

Hematite flakes also appear stuck on the polymineralic globules trapped in spinel in Figure 6b,c,e. We contend that the flakes of hematite, up to 20 μ m across, appeared at the same time as the dusting of magnetite specks in the spinel. These specks are attributed to oxidation-induced exsolution of the spinel solid-solution. These iron oxide specks form "halos" around the globules (see also Atlas 5 BBV datasets).

The polymineralic inclusion in Figure 6b consists of calcite, dolomite, diopside, and flakes of hematite. The first three minerals could have formed from a droplet of silicocarbonatitic magma. Figure 6e also contains calcite and dolomite, along with apatite, phlogopite, ilmenite, and a flake of hematite. The association is recurrent, and again could have crystallized in situ from a droplet of melt. Figure 6d shows a cluster of forsterite, ilmenite, magnesio-hastingsite, and phlogopite entrapped in

spinel. Forsterite thus was present in the carbonate melt as the spinel was growing. Figure 6f shows a granule of spinel on which dolomite and phlogopite have nucleated, along with a flake of hematite, before being entrapped in forsterite.

7. The Minerals Encountered in the Carbonate Dikes and Segregations

The specimen of marble that we chose to investigate is representative; it was specifically chosen because the centimetric euhedral crystal of spinel trapped visible inclusions of calcite. It has a much coarser grain-size (Figure 2b, Figure 7a, and Figure S3, see also Atlas 5 BBV datasets) than the greenish dunite rock. Oxidation-induced exsolution lamellae of magnetite and specks of hematite or magnetite are found in the spinel (Figure 7b,c). The specks form "halos" around the polymineralic inclusions (Figure 7c). Idiomorphic crystals of forsterite [4] and phlogopite greater than 10 cm across are present in the carbonate dikes.



Figure 7. Atlas 5 large-area SEM image mosaic (BSE signal) of one half of the large single crystal of spinel (Parker Mine 10a). (**a**) Atlas 5 large-area SEM image mosaic of the entire half of the spinel crystal. (**b**,**c**) High-resolution SEM (BSE) images of oxidation-induced exsolution lamellae of magnetite and specks of hematite (?) forming "halos" around the micro-inclusions.

13 of 21

The outer boundary of the investigated crystals of spinel contains remnants of the calcite matrix from which it grew (Figure 8a,b). Smaller crystals of spinel can also be observed in this calcite (Figure 8a). A large inclusion of calcite can be found in the center of the crystal (Figure 8c and Figure S3). Close to the outer perimeter of the spinel crystal that has escaped oxidation-induced exsolution of magnetite, monomineralic calcite inclusions do occur; some form groups in a string-like arrangement (Figure 8d). Although these might be construed to be aligned individual rhombs trapped during growth, we prefer to interpret these as melt inclusions filling negative crystal cavities in the spinel. We are influenced by the presence of conformable films of calcite below the main string, perhaps indicative of tensional gashes.



Figure 8. False-color EDS element-distribution maps of the spinel crystal. (**a**,**b**) Calcite and dolomite mineralization at the periphery of the spinel crystal. (**c**) Large calcite inclusion in the center of the spinel crystal (Figure S3). (**d**) Unusual string-like arrangement of calcite inclusions close to the periphery of the spinel crystal.

We studied 60 polymineralic inclusions trapped by the spinel crystal, and identified the minerals present on the basis of their energy-dispersive spectra. Compared to the assemblages encountered in the cumulates, we note that diopside and forsterite are absent among the minerals trapped in the spinel. The early-formed minerals (Figure 9) consist of ilmenite, phlogopite, an apatite-group mineral, anhydrite, calcite and dolomite.

The inclusions in Figure 9 are relatively pristine. Other than the hematite flakes, the minerals seem to have crystallized from a single melt within the confines of the globule's volume, which in some cases has a morphology controlled by the spinel host (Figure 9a,d). One gets the impression that the hematite nucleated independently in the melt, and continued to grow once trapped in the spinel by late dissolution of specks of hematite within radius of 10 µm from the included clusters. Figure 9b,d contain a silicocarbonate assemblage: calcite–dolomite–anhydrite–phlogopite–ilmenite and calcite–dolomite–anhydrite–phlogopite–apatite. Figure 9a is devoid of a silicate. Recall that these images illustrate random cuts in three-dimensional objects; we are thus not sampling the minerals in their correct volumetric proportions.



Figure 9. False-color EDS element-distribution maps of polymineralic micro-inclusions found in the two polished halves of the large single crystal of spinel. EDS point analyses 16 to 24 are shown in Figure S5. Symbols not yet defined: Anh: Anhydrite; Brt: Baryte; Chm: Chamosite; Qtz: Quartz.

In Figure 9c, a plate of phlogopite seems to have acted as a substrate on which ilmenite, quartz, gibbsite (or corundum), and then hematite nucleated. Both the quartz and gibbsite (or corundum) seem to have been partially etched, as there is empty space around them. The presence of quartz in a system containing forsterite is a clear indication of metastability. Hematite and ilmenite crystals growing on a crystal face of spinel seem to have acted as the site at which droplets of carbonate melt can attach. Figure 9e shows an inclusion in which calcite and dolomite crystallized in a globular shape, whereas the subhedral hematite and ilmenite crystals fill the other half of the inclusion. Calcite containing a subhedral inclusion of apatite and a domain of dolomite (Figure 9f) also has been etched, and now contains areas of clinochlore and chamosite deposited from the ambient fluid medium.

Many polymineralic inclusions show the effects of a hydrothermal overprint (Figure 10); in some instances, not much of the primary minerals is left. In Figure 10a, the apatite seems to have survived well, but the calcite has been partly dissolved. Clinochlore, chamosite, and gibbsite (or another polymorph of Al(OH)₃) are prominent. In Figure 10b, the calcite and phlogopite crystals seem to have been attacked. Phlogopite is coated by hematite in Figure 10b. Apatite has survived in the triangular inclusion in Figure 10d (presumably tetrahedral in three dimensions), but the calcite has been attacked, and the empty space has been filled with a mixture of clinochlore and chamosite.



Figure 10. False-color EDS element-distribution maps of polymineralic micro-inclusions found in the two polished halves of the large single crystal of spinel that show an extensive development of secondary minerals.

Late fractures cut the spinel; Figure 11a,b show the minerals that line the fractures, deposited from the ambient fluid phase. Calcite is prominent, as is a mixture of clinochlore and chamosite. On the scale of the hand specimen (Figure 2b), the fluid phase is in contact with forsterite, calcite and spinel. Figure 11b shows well how the spinel is dissolved along the cracks. The Al supplied to the fluid phase accounts for the precipitation of chlorite-group minerals instead of a serpentine.



Figure 11. False-color EDS element-distribution maps of minerals deposited along fractures in the large single crystal of spinel. (**a**,**b**) The fracture is filled with clinochlore, chamosite, calcite, hematite, and gibbsite (or one of the other polymorphs of Al(OH)₃).

8. Stable Isotope Data

According to our preliminary data, the oxygen isotope composition (δ^{18} O) of forsterite, spinel, phlogopite, and calcite is in the range 15–17‰ (Table 4, SMOW standard). Such values clearly are crustal. Values of the coexisting forsterite and spinel are far removed from the value expected for an upper-mantle-derived assemblage, in the range 5.5 to 5.9‰ [17]. On the other hand, the values found in calcite approach values encountered in calcite of regionally developed marble in the area. At the Yates prospect near Otter Lake, Quebec (Figure 1), Kretz [18] found δ^{18} O values of calcite in the range 17 to 28‰, and a lower value (14.5‰) where the marble is metasomatized. Peck et al. [19] also documented a range in δ^{18} O in calcite of 17 to 28‰ at Mont Tremblant (Figure 1), with the lower values characteristic of rocks more strongly affected by decarbonation reactions.

Table 4. Isotopic composition of forsterite, spinel, phlogopite, and calcite in the Parker mine suite.

	Fo	Spl	Phl	Pink Cal	White Cal
δ ¹⁸ Ο, ‰	15.3	14.9	15.1	17.0 17.0 * 17.1 [†]	16.3
δ ¹³ C, ‰				0.62 0.78 * 0.83 ⁺	0.6

Symbols used: Fo; forsterite, Spl; spinel, Phl; phlogopite, Cal; calcite. The two-sigma error in δ^{13} C associated with the extraction of carbon and analysis is 0.04‰. The optimum two-sigma error associated with δ^{18} O values is about 0.2‰. The isotopic values are quoted with reference to the VSMOW (oxygen) and VPDB (carbon) standards. * Joaquin Perona, analyst; † Stephen Crowley, analyst; unlabeled values: Julia E. Cox, analyst.

Carbon with a δ^{13} C value of -5% is proposed as the isotopic composition signature of the mantle [20]. However, a ±3‰ range of values is commonly encountered. Values of δ^{13} C in inorganic limestone are expected to be close to +2‰, whereas in limestone containing organic carbon, δ^{13} C is expected to be as low as -25%, all with reference to the PDB standard. The calcite matrix to the forsterite, spinel and phlogopite at the Parker mine, with a δ^{13} C value in the range 0.6–0.8‰, is close to what is expected in limestone. The range of δ^{13} C values in calcite in marble at the Yates prospect, is -2 to 6‰ (0.23‰ where the marble is modified by metasomatism, according to Kretz [18]), whereas at Mont Tremblant, it is -1.9 to 2.5‰ [19].

9. Discussion

In the context of Grenville studies in Quebec, Ontario, and New York, the Parker phlogopite mine is the site of a classic "vein-dike" association [21,22]. Plates of phlogopite up to 15 cm across were extracted from the calcite-cored dikes. As stated earlier, the Parker mine is distinct from the norm in being associated with forsterite rather than diopside, such that the peridotite component of the vein-dike association is dunite rather than clinopyroxenite. In addition, the locality is well known for aesthetic black spinel crystals enclosed in the calcite matrix (Figure 2a).

There are very few options when it comes to explaining the formation of dunite. We know of three scenarios. On the seafloor, dunite may form simply by infiltration of heated seawater in harzburgite, as enstatite is very efficiently converted to forsterite by incongruent dissolution [23]. A second possibility in the oceanic crust is the localized reaction expected along the interface between an ascending basaltic magma and a harzburgitic wallrock (e.g., [24]).

The third alternative, which must be the case here, involves the gravitational settling of olivine crystals, as seen in stratiform layered complexes. In our case, the same process applies, but the olivine crystals grew not in a silicate magma, but in a crustally derived carbonate magma. We have documented what seems to be the first example of a dunitic cumulate formed from a crustally derived carbonatite. Viewed in this light, the absence of chromium and nickel makes sense.

We consider the statement that the carbonatitic melt has a crustal derivation to be firmly established on the basis of our preliminary oxygen-isotope values on calcite, forsterite, spinel, and phlogopite (Table 4. Values of δ^{18} O are far from the "magmatic box" [17]. Values of +15–17‰ with respect to the SMOW standard are intermediate between values of up to 28‰ encountered regionally in the white marble of the Otter Lake and Mont Tremblant areas, to the west and east of our study area, respectively, and the value expected for an upper-mantle-derived assemblage, in the range 5.5 to 5.9‰ [17]. Were mantle-derived fluids perhaps involved as a mechanism of heat transfer to promote the fusion of marble and to shift the δ^{18} O values of all four minerals to such an intermediate range? We plan to acquire more δ^{18} O data at this location and at other sites of "vein-dike" activity in the Grenville Province to address this question. If there was an involvement of mantle-derived fluids at the Parker mine, it is not evident in an enrichment of nickel, chromium, rare-earth elements or high field-strength elements.

The δ^{18} O values of forsterite, spinel and phlogopite at the Parker mine are quite similar, which implies a high temperature of equilibration among these minerals. Application of the forsterite–calcite geothermometer [25] indicates an equilibrium temperature of the order of 1100 °C if one assumes equilibrium between forsterite and the enclosing calcite. Note that calcite is a reactive mineral; its δ^{18} O values (Table 4) could have been modified during late fluid-circulation events, such that an attempt at geothermometry would be compromised. On the other hand, there can be no doubt that the assemblage formed at a high temperature. A subsolidus modification of the oxygen-isotope signature of centimetric crystals of spinel, forsterite and phlogopite is not considered possible.

Were the regionally developed temperatures sufficient to get calcite to melt in the presence of a mixed CO_2 -H₂O gas phase? At a pressure of one kilobar, the temperature of the calcite + portlandite + liquid + vapor assemblage is 675 °C [26], and signs of melting of calcite have been noted at 650 °C [27]. Regionally developed temperatures to the north, in the Bondy gneiss complex, attained 950 °C at a pressure close to 10 kbar during the Shawinigan stage of deformation. Corriveau (Table 9 in reference [7]) quoted an estimated temperature of equilibration of 650 °C in four samples of marble and one calc-silicate rock from the Quartzite domain, and an age of metamorphism measured on titanite (U–Pb) ranging from 1165 to 1110 Ma. We conclude that regionally developed temperatures in the area were sufficient to melt marble.

In terms of the evolution of the Grenville collision zone [9], subduction and compressive stresses were actively developed during the Shawinigan episode over the interval 1200–1160 Ma. We concur with McLelland et al. [9,28] that the emplacement of the AMCG suites, for example the Morin anorthosite east of Mont Tremblant at 1150 Ma, marks a time of distension in the Earth's crust. The Parker mine crustal silicocarbonatite and associated dunite were emplaced at 1140 Ma. Any fluids rising into the crust at 1140 Ma may have had a link with the progressively sinking subducted plate or the rising asthenopheric mantle. There is no sign of pervasive deformation in the rocks at the Parker mine, nor is there at other sites of "vein-dike" activity to our knowledge. The relatively young ages of marble quoted by Corriveau, in the lower part of the 1160–1110 Ma interval (Table 9 in reference [7]), may well have been taken at sites like the Parker mine where the marble experienced an additional thermal pulse at a time of tectonic relaxation and orogenic collapse.

The dunite seems to have formed quickly. The distribution of the two dense minerals is rather chaotic; the volume proportion of spinel, the denser mineral, is highly variable (Figures 3 and 4). The ambient interstitial low-density carbonatitic melt into which these minerals sank has largely been squeezed upward to form the carbonatitic segregations and the phlogopite-bearing dikes. The rising melt was enriched in dissolved H_2O because of the massive crystallization of forsterite and spinel, which are devoid of hydroxyl. This dissolved H_2O was necessarily liberated upon crystallization of the melt. This explains the hydrothermal overprint that seriously affected the micro-inclusions trapped in the spinel (Figure 10). The dunitic cumulate cooled in a relatively anhydrous environment, to judge from the limited extent of serpentinization (Figure 6a,f).

18 of 21

Inclusions of spinel in forsterite and vice versa (Figures 4 and 6) point to their virtually simultaneous nucleation in the hydrous silicocarbonatitic magma. The necessary production of a gas phase during crystallization [26,27] provides the explanation of such rapid crystallization; the low-viscosity melt degassed quickly, and hydrogen [29] diffused out of the system. The net loss of hydrogen caused the melt to become intrinsically oxygenated, and to crystallize hematite. The spinel solid-solution also exsolved magnetite as the system cooled. The absence of sodium-dominant minerals suggests that sodium also may have left the system via the escaping gas phase.

The development of polymineralic inclusions (Figure 6), in which several minerals seem to have crystallized together within the confines of a tiny enclosure, suggests an origin by incorporation of aliquots of a boundary-layer melt developed as the host mineral grew, much as we found in the fluorapatite prisms at the Yates prospect, Quebec [30]. Such a melt contained all constituents rejected by the rapidly growing host, either forsterite or spinel. This enrichment explains how the melt inclusion crystallized to an intergrown assemblage of a sulfate (anhydrite), a phosphate (apatite), a silicate (quartz, phlogopite), along with the carbonates (Figure 6). The carbonate component consists of calcite (dominant) and dolomite, but in some instances, magnesite is present (e.g., Figure 6c, Atlas 5 BBV datasets). This may indicate that in the time available, the melt had not become well blended.

There are also subtle indications of disequilibrium in the system. For example, quartz (or another polymorph of SiO₂) is present in micro-inclusions in spinel although forsterite crystals are present close by. Quartz seems to coexist with corundum (?) or gibbsite (Figure 9c). In granulite-grade rocks, the coexistence of quartz and corundum is considered a sign of metastability [31,32]. Finally, ribbons of diopside are developed along only selected interfaces of forsterite with the interstitial (Ca, Mg) carbonate melt (Figure 4a,d,e and Figure 5b). This reaction is probably relevant to the conversion of lherzolite to wehrlite in the mantle; a primary dolomitic melt is expected to react with lherzolite as it migrates upward, causing the carbonatite to become enriched in Ca as Mg is consumed through the metasomatic "wehrlitization" of the conduit [33,34]. Why the reaction is not developed along all forsterite–(Ca, Mg) carbonate interfaces in the dunite is likely a reflection of the rapid crystallization of the assemblage upon loss of the gas phase. Presumably the reaction could only occur where the carbonate was still molten.

10. Summary and Conclusions

We describe an unusual case of a "vein-dike" association in which the peridotite member of the association is dunite rather than pyroxenite. The phlogopite-bearing carbonate dikes and accompanying dunite were emplaced 1140 million years ago, after the Shawinigan episode of subduction and deformation had come to an end. The crust was in a state of distension. In the area near Notre-Dame-du-Laus, there was perhaps a localized thermal pulse that raised the temperature significantly over that achieved during the Shawinigan orogenic event. Transfer of a fluid phase is the most efficient mechanism of heat transfer. We believe that marble melted in response to such an influx of fluid that had equilibrated with a silica-poor deep source. The prevalence of forsterite and spinel indicates that the activity of silica in that melt was quite low, and insufficient for enstatite to crystallize.

The dunite is a cumulate, largely of forsterite and spinel, but also with diopside, magnesio-hastingsite, phlogopite, ilmenite and apatite. Vestiges of the interstitial carbonate remain. The main minerals have values of δ^{18} O in the range 15–17‰, which means that they formed from a crustally derived melt. What we have is a dunite with a metasedimentary antecedent, possibly a first! The melt was initially hydrous, and became more enriched in H₂O owing to the crystallization of the anhydrous minerals. The fluxed carbonate magma was rapidly emplaced above the cumulate and developed strikingly euhedral centimetric crystals of spinel, forsterite, and phlogopite prior to freezing. Degassing of the system led to a preferential loss of hydrogen; the magma did crystallize hematite, and the spinel underwent oxidation-induced exsolution of magnetite.

More studies of this type in similar Grenvillian occurrences are necessary to test fully the validity of our petrogenetic scheme. Did melting of marble occur only at point sources, or is the scale of marble melting regional? What seems clear is that the emplacement of "vein-dikes" occurred at different times in different places. The noncommittal term "vein-dike" was favored by Moyd [21] because of his hesitation to conclude that marble did melt in the Ontario portion of the Grenville Province. It is fair to say that most metamorphic petrologists still are not aware that marble can melt. Interestingly, the first claim that it does melt where the conditions are right was made by Ortega-Gutierrez [35] on Grenvillian rocks exposed in the province of Oaxaca, Mexico. Such dikes of crustally derived carbonatite seem to be rather common in the Grenville Province.

At the Yates prospect, near Otter Lake, Quebec, the melting of marble occurred close to one billion years ago, at the terminal stage of the Grenville collisional orogeny [30]. It was in the Bancroft area, Ontario [36], and particularly in explorations with Ray McDougall at the Bear Lake diggings, that the first author started to wonder about the possibility of crustally derived carbonatites. They can be expected in any collision zone. Excellent examples do exist in the major Early Paleozoic collision that occurred late in the pan-African orogeny [37,38], although most still view them as skarns, just as in the Grenville Province. In each of these environments, there were likely many episodes of collision between continental plates. We visualize a period of quiescence and distension after each one, at which stage localized melting can be expected in the thickened crust.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/9/10/613/s1, Figure S1: Large-area transmitted-light microscopy mosaic of the dunite thin section "Parker Mine 5"; Figure S2: Argon/argon age spectrum; Figure S3: Atlas 5 large-area SEM image mosaic of the large spinel crystal (Parker Mine 10b); Figure S4: EDS point analyses 1 to 12.; Figure S5: EDS point analyses 13 to 24.; Table S1: Excel spreadsheet of the acquired isotopic data from phlogopite crystal D-648.; Table S2: Excel spreadsheet of the acquired isotopic data from phlogopite crystal D-649.

Author Contributions: Conceptualization, R.F.M. and D.S.; Formal analysis, D.S.; Investigation, R.F.M. and D.S.; Methodology, R.F.M. and D.S.; Resources, D.S.; Validation, R.F.M. and D.S.; Visualization, D.S.; Writing–original draft, R.F.M.; Writing–review & editing, R.F.M. and D.S.

Funding: This research received no external funding.

Acknowledgments: We thank Mrinal Tiwari and Jeremy Wilson of Fibics Inc. for their help with the processing of the Atlas 5 datasets. We are grateful to the constructive comments and suggestions for improvement of the two well-qualified referees.

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

References

- 1. Spence, H.S. *Phosphate in Canada;* Report; Canada Department of Mines, Mines Branch: Ottawa, ON, Canada, 1920; p. 396.
- 2. Spence, H.S. Mica; Report; Canada Department of Mines, Mines Branch: Ottawa, ON, Canada, 1930; p. 701.
- 3. Sabina, A.P. Rocks and minerals for the collector: Buckingham, Mont-Laurier, Grenville, Quebec; Hawkesbury, Ottawa, Ontario; Geological Survey of Canada: Ottawa, ON, Canada, 1986; Volume 33.
- 4. Van Velthuizen, J. The Parker mine, Notre Dame du Laus, Quebec. *Mineral. Rec.* 1993, 24, 369–373.
- 5. Belley, P.M.; O'Neil, J.; Hattori, K. Spinel and aspidolite from the Des Cèdres Dam occurrence, Notre-Dame-du-Laus, Québec, Canada. *Rocks Miner.* **2016**, *91*, 448–452. [CrossRef]
- Wynne-Edwards, H.R. The Grenville Province. In *Variation in Tectonic Styles in Canada*; Price, R., Douglas, R., Eds.; Special Paper; The Geological Association of Canada: St. John's, NL, Canada, 1972; pp. 263–335.
- Corriveau, L. Architecture de la Ceinture Métasédimentaire Centrale au Québec, Province de Grenville: Un Exemple de l'Analyse de Terrains de Métamorphisme Élevé; Commission Géologique du Canada: Ottawa, ON, Canada, 2013; p. 586.
- Schneider, D.A.; Cope, N.; Holm, D.K. Thermochronology of the Mont Laurier terrane, southern Canadian Grenville Province, and its bearing on defining orogenic architecture. *Precambrian Res.* 2013, 226, 43–58. [CrossRef]
- 9. McLelland, J.M.; Selleck, B.W.; Bickford, M.E. Tectonic evolution of the Adirondack Mountains and Grenville Orogen inliers within the USA. *Geosci. Can.* **2013**, *40*, 318–352. [CrossRef]
- Roddick, J.C. High precision intercalibration of ⁴⁰Ar/³⁹Ar standards. *Geochim. Cosmochim. Acta* 1983, 47, 887–898. [CrossRef]

- 11. Dalrymple, G.B.; Alexander, E.C., Jr.; Lanphere, M.A.; Kraker, G.P. Irradiation of samples for ⁴⁰Ar/³⁹Ar dating using the Geological Survey TRIGA reactor. *US Geol. Surv. Prof. Pap.* **1981**, *1176*, 1–55.
- 12. Steiger, R.H.; Jäger, E. Subcommission on geochronology: Convention on the use of decay constants in geoand cosmochronology. *Earth Planet. Sci. Lett.* **1977**, *36*, 359–362. [CrossRef]
- Valley, J.W.; Kitchen, N.; Kohn, M.J.; Niendorf, C.R.; Spicuzza, M.J. UWG–2, a garnet standard for oxygen isotope ratios: Strategies for high precision and accuracy with laser heating. *Geochim. Cosmochim. Acta* 1995, 59, 5223–5231. [CrossRef]
- De Schmid, H.S. *Mica, Its Occurrence, Exploitation and Uses,* 2nd ed.; Report; Canada Department of Mines, Mines Branch: Ottawa, ON, Canada, 1912; p. 118.
- 15. Holness, M.B. Textural immaturity in cumulates as an indicator of magma chamber processes: Infiltration and crystal accumulation in the Rum Eastern Layered Intrusion. J. Geol. Soc. 2007, 164, 529–539. [CrossRef]
- Roeder, P.L.; Poustovetov, A.; Oskarsson, N. Growth forms and composition of chromian spinel in MORB magma: Diffusion-controlled crystallization of chromian spinel. *Can. Mineral.* 2001, 39, 397–416. [CrossRef]
- Bindeman, I. Oxygen isotopes in mantle and crustal magmas as revealed by single crystal analysis. In Minerals, Inclusions and Volcanic Processes (K.D. Putirka and F.J. Topley III, eds.). *Rev. Mineral. Geochem.* 2008, 69, 445–478. [CrossRef]
- 18. Kretz, R. Oxygen and carbon isotopic composition of Grenville marble, and an appraisal of equilibrium in the distribution of isotopes between calcite and associated minerals, Otter Lake area, Quebec, Canada. *Can. Mineral.* **2001**, *39*, 1455–1472. [CrossRef]
- 19. Peck, W.H.; DeAngelis, M.T.; Meredith, M.T.; Morin, E. Polymetamorphism of marbles in the Morin terrane, Grenville Province, Quebec. *Can. J. Earth Sci.* 2005, *42*, 1949–1965. [CrossRef]
- 20. Deines, P. The carbon isotope geochemistry of mantle xenoliths. Earth Sci. Rev. 2002, 58, 247–278. [CrossRef]
- 21. Moyd, L. Davis Hill near Bancroft, Ontario: An occurrence of large nepheline, biotite and albite-antiperthite crystals in calcite-cored vein-dikes. *Mineral. Rec.* **1990**, *21*, 235–248.
- 22. Joyce, D.K. Calcite vein-dikes of the Grenville geological province, Ontario, Canada. *Rocks Miner.* **2000**, *81*, 34–42. [CrossRef]
- 23. Johan, Z.; Martin, R.F.; Ettler, V. Fluids are bound to be involved in the formation of ophiolitic chromite deposits. *Eur. J. Mineral.* **2017**, *29*, 543–555. [CrossRef]
- 24. Kelemen, P.B.; Shimizu, N.; Salters, V.J. Extraction of mid-ocean-ridge basalt from the upwelling mantle by focused flow of melt in dunite channels. *Nature* **1995**, *375*, 747–753. [CrossRef]
- Chiba, H.; Chacko, T.; Clayton, R.N.; Goldsmith, J.R. Oxygen isotope fractionations involving diopside, forsterite, magnetite, and calcite application to geothermometry. *Geochim. Cosmochim. Acta* 1989, 53, 2985–2995. [CrossRef]
- 26. Wyllie, P.J.; Tuttle, O.F. The system CaO–CO₂–H₂O and the origin of carbonatites. *J. Petrol.* **1960**, *1*, 1–46. [CrossRef]
- 27. Durand, C.; Baumgartner, L.P.; Marquer, D. Low melting temperature for calcite at 1000 bars on the join CaCO₃–H₂O–some geological implications. *Terra Nova* **2015**, *27*, 364–369. [CrossRef]
- 28. Martin, R.F. The petrogenesis of anorogenic felsic magmas and AMCG suites: Insights on element mobility and mutual cryptic contamination from polythermal experiments. *Lithos* **2012**, *151*, 35–45. [CrossRef]
- 29. Czamanske, G.K.; Wones, D.R. Oxidation during magmatic differentiation, Finnmarka Complex, Oslo area, Norway. 2. The mafic silicates. *J. Petrol.* **1973**, *14*, 349–380. [CrossRef]
- 30. Schumann, D.; Martin, R.F.; Fuchs, S.; de Fourestier, J. Silicocarbonatitic melt inclusions in fluorapatite from the Yates Prospect, Otter Lake, Quebec: Evidence of marble anatexis in the Central Metasedimentary Belt of the Grenville Province. *Can. Mineral.* **2019**, *57*, 583–604. [CrossRef]
- 31. Motoyoshi, Y.; Hensen, B.J.; Matsueda, H. Metastable growth of corundum adjacent to quartz in a spinel-bearing quartzite from the Archaean Napier Complex, Antarctica. *J. Metamorph. Geol.* **1990**, *8*, 125–130. [CrossRef]
- 32. Guiraud, M.; Kienast, J.R.; Ouzegane, K. Corundum–quartz-bearing assemblage in the Ihouhaouene area (In Ouzzal, Algeria). *J. Metamorph. Geol.* **1996**, *14*, 755–761. [CrossRef]
- 33. Dalton, J.A.; Wood, B.J. The compositions of primary carbonate melts and their evolution through wallrock reaction in the mantle. *Earth Planet. Sci. Lett.* **1993**, *119*, 511–525. [CrossRef]
- 34. Wyllie, P.J.; Lee, W.J. Model system controls on conditions for formation of magnesiocarbonatite and calciocarbonatite magmas from the mantle. *J. Petrol.* **1998**, *39*, 1885–1893. [CrossRef]

- 35. Ortega-Gutierrez, F. Los marmoles intrusivos del Complejo Oaxaqueño. *Univ. Nac. Autónoma de Mex. Inst. de Geol. Rev.* 1977, 1, 28–32.
- 36. McDougall, R. Mineral highlights from the Bancroft area, Ontario, Canada. *Rocks Miner.* **2019**, *94*, 408–418. [CrossRef]
- Morteani, G.; Kostitsyn, Y.A.; Gilg, H.A.; Preinfalk, C.; Razakamanana, T. Geochemistry of phlogopite, diopside, calcite, anhydrite and apatite pegmatites and syenites of southern Madagascar: Evidence for crustal silicocarbonatitic (CSC) melt formation in a Panafrican collisional tectonic setting. *Int. J. Earth Sci.* 2013, 102, 627–645. [CrossRef]
- Martin, R.F.; Randrianandraisana, A.; Boulvais, P. Ampandrandava and similar phlogopite deposits in southern Madagascar: Derivation from a silicocarbonatitic melt of crustal origin. J. Afr. Earth Sci. 2014, 94, 111–118. [CrossRef]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).