

Article

Nd Isotope Mapping of Crustal Terranes in the Parent-Clova Area, Quebec: Implications for the Evolution of the Laurentian Margin in the Central Grenville Province

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Abstract: Over 100 new Nd isotope analyses for the central Grenville Province in the Parent-Clova region of Quebec help fill a major gap in understanding the crustal accretion history of the province. Nd model ages show that the Parent-Clova region consists of three crustal blocks: the Archean parautochthon in the north; a central block with mixed ages interpreted as an ensialic arc; and a southerly block forming an extension of the Mesoproterozoic Quebecia arc terrane. The Allochthon Boundary Thrust is believed to define the edge of the Archean parautochthon, which is bordered for a distance of 300 km by the ensialic arc block, within which model ages decrease consistently away from the craton. A similar negative correlation between Nd model age and distance from the craton is seen in published data for the Algonquin terrane in Ontario, but with a lower range of model ages. These comparisons show that in the Parent-Clova region, a Mesoproterozoic ensialic arc was established directly on the Archean margin, but further west, the Mesoproterozoic arc was built on a younger margin consisting of accreted Palaeoproterozoic arc crust. The use of large Nd data sets allows these distinct regional growth patterns to become clear and, hence, allows an understanding of Mesoproterozoic crustal evolution in the province as a whole.

Keywords: Grenville Province; Nd isotopes; model ages; ensialic arc

1. Introduction

Formed during the amalgamation of Rodinia, the Grenville Province represents a long-lived ancient orogenic belt, which comprises the southwestern margin of the Canadian Shield. New continental crust was intruded and sutured onto the Laurentian foreland for nearly a billion years until a terminal collision at 1.1 Ga halted subduction and crustal growth.

The continent-continent collision that formed the Grenville Province is analogous to that of the Himalayas [1] and resulted in considerable crustal shortening and thickening. The resulting high-grade metamorphism erased much of the evidence necessary to reconstruct the original growth history of the province and led large areas of the Grenville Province to be labeled as "seas of gneisses" [2]. However, Nd isotope analysis has been successfully used to estimate crustal formation ages for high-grade gneisses in the Grenville Province [3] and, hence, to identify several large first-order accreted terranes that were amalgamated together on the Laurentian margin over the Paleo- and Mesoproterozoic (Figure 1).

Figure 1. Map of the Grenville Province showing major terranes with distinct crustal formation ages, after Dickin [3]. Boxed area = study of Martin and Dickin [4]; ABT = Allochthon Boundary Thrust [5]; M = Manicouagan meteorite impact site (Palaeoproterozoic crust).



Dickin [3] attributed much of the Eastern Grenville Province to the accretion of three very large terranes, formed around 1.9, 1.7 and 1.5 Ga, and termed Makkovikia, Labradoria and Quebecia, respectively (Figure 1). However, isotope mapping of the western part of the province has been complicated by the establishment of long-lived Andean-type arcs on the Laurentian margin [6,7], leading to more complex mixed isotope signatures in this area (Figure 1).

The clearest evidence for such mixing was seen in the Lac St Jean region [4], represented by the boxed area in Figure 1. At that time, the adjacent Parent-Clova area to the SW was not studied in detail, due to poor road access. However, recent upgrading of forest access roads has resulted in limited blasting of road-cuts, allowing Nd isotope mapping of this region to fill one of the last remaining gaps in the crustal formation age map of the Grenville Province. This reconnaissance Nd isotope mapping will hopefully reveal major terrane boundaries within the study area, and also allow a better understanding of the geological relationships between the eastern and western parts of the province and their differing history of crustal growth.

2. Regional Geological Background

The geological context of the present study area is shown in more detail on a terrane map of the SW Grenville Province in Figure 2. As noted above, the present study area (boxed) represents the last major sampling gap for Nd data in the western part of the province, but it also falls in a kind of conceptual gap between the geological complexity of the SW Grenville Province and the somewhat simpler structure of the Central Grenville Province.

Figure 2. Map of the western Grenville Province showing the present study area (boxed), falling in a sampling gap between the established geological blocks and terranes of the Central and the SW Grenville Province. TSZ = Tawachiche Shear Zone. White = not yet understood.



Nd analysis in the Central Grenville Province by Martin and Dickin [4] showed it to consist of three major blocks or terranes. The western terrane consists of Tonalite-Trondhjemite-Granodiorite (TTG)-type Archean gneisses with homogeneous Nd isotope signatures that are interpreted as the

The eastern terrane also has homogenous Nd isotope signatures, which gave rise to a 71 point Sm-Nd isochron age of 1.51 ± 0.05 Ga [8]. This block also has TTG-type petrology and was identified by Dickin [3] as an accreted oceanic arc, termed Quebecia after Rondot [9]. Between these large terranes is a narrow block with heterogeneous Nd isotope signatures and somewhat alkaline petrology, attributed by Martin and Dickin to a Mesoproterozoic ensialic arc established on the Archean margin. The Allochthon Boundary Thrust of Rivers *et al.* [5], separating largely *in situ* parautochthonous crust to the NW from far-traveled allochthonous crust to the SE, corresponds to the edge of the Archean terrane in this area, as originally recognised from Rb-Sr dating by Frith and Doig [10].

The SW Grenville Province is more complex and is divided into several major lithotectonic terranes in Figure 2, which will be summarized briefly in order of decreasing age. In this area, Archean crust reaches as far as 150 km SE of the Grenville Front, but in some areas, it has been strongly reworked by later plutonism, and in other areas, it is covered by metasedimentary rocks that sampled material with mixed sources [3]. In some areas, Archean crust is over-ridden by the allochthonous belt, which forms large nappe lobes, but elsewhere, Archean crust is sutured against an accreted Palaeoproterozoic arc terrane with homogeneous Nd isotope signatures that gave rise to a 53 point Sm-Nd isochron age of 1.75 ± 0.05 Ga [11].

In contrast to this terrane with homogenous Nd signatures, the over-riding Allochthonous Belt, represented in this area by the Algonquin and Lac Dumoine terranes, has a heterogeneous Nd isotope signature with depleted mantle (TDM) model ages ranging from *ca*. 1.4 to 1.8 Ga [6]. The Algonquin terrane was, in turn, overthrust by the Muskoka and Parry Sound terranes with somewhat younger Nd model ages (*ca*. 1.4–1.7 Ga). Further to the SE, still younger model ages are also seen in the Mont Laurier Terrane, Central Granulite Terrane and the Adirondacks (*ca*. 1.33–1.55 Ga), attributed to crustal formation in an Elzevirian continental margin arc that gradually stepped off the earlier Mesoproterozoic margin to create a strip of juvenile crust along the edge of the continent [7,8,12].

At the peak of development of this continental margin arc, back arc spreading led to the formation of an Elzevirian back-arc rift system [13], sub-divided into an ensimatic rift zone in Ontario and an ensialic rift zone in Quebec. These zones are equivalent in extent to the so-called Composite Arc Belt of Carr *et al.* [14], but are attributed to rift-related magmatism rather than arc magmatism, consistent with the geochemistry of mafic units in this area [15].

3. Geology of the Study Area

The field area encompasses ca. $40,000 \text{ km}^2$ of south-central Quebec, extending from *ca*. 47° to $48^\circ 30'$ N and from *ca*. 73° to 75° W (Figure 2). The lack of major roads throughout this region has hindered mapping efforts, which have thus been neglected to this point. Due to the large size of the area, reconnaissance scale mapping of crustal formation ages will allow initial identification of first-order crustal terranes and investigation of the possible continuation of the ensialic arc block of Martin and Dickin [4] between Archean and Mesoproterozoic terranes to the north and south.

Previous reconnaissance scale mapping in this area was conducted by the Ministère des Ressources naturelles de la Faune et des Parcs, Gouvernement du Québec (MRNFP), leading to a series of

of the whole Grenville Province [16].

Much of the field area is dominated by basement lithologies at high metamorphic grades, including orthogneisses and minor paragneisses, whose precursors have been subjected to upper amphibolite to granulite grade metamorphism. The extent of granulite-facies metamorphism (charnockite and mangerite) is clearly indicated on maps of the area, but such variations in grade may actually be a late feature that has little significance for the earlier geological evolution of the region. Finally, a large portion has been characterized as undifferentiated or mixed gneisses, attesting to the complex geology and relative lack of geologic investigation of the region.

The Allochthon Boundary Thrust (ABT), which has been traced along much of the Grenville Province [5], is believed to cross the northern portion of the study area (heavy line in Figure 2). South of the ABT lies a band of early Mesoproterozoic mafic gneisses and amphibolites with a few identified granite intrusions generally occurring along regional fault structures. The eastern portion of the study area is dominated by a wide range of lithologies, including mixed, mafic and undifferentiated gneisses. Some anorthosite-mangerite-charnockite-granite (AMCG) suite complexes also trend along regional fault structures to the east [17]. These variable lithologies are consistent with the existence of an ensialic arc in this area, as identified to the NE by Martin and Dickin [4].

In the south, the western extent of Quebecia has been currently limited to the Tawachiche Shear Zone (TSZ in Figure 2) by both U-Pb [18] and Sm-Nd dating [3]. Further sampling to the northwest of the TSZ will be used to bridge the remaining gap in Quebecia's southwestern limit, and identify any crustal mixing [8] that may have resulted from the younger (<1.45 Ga) Elzevirian arc established on the continental margin [7].

4. Sampling and Analytical Techniques

Since the objective of this study is to characterize the protolith age of the crust as an estimate of its regional crustal formation age, the strategy adopted was to limit sampling to granitoid orthogneisses that are believed to form by anatexis of primitive arc crust. Previous studies have shown that granitoids of this type have Nd isotope signatures that are consistent and predictable, allowing reliable estimates to be determined of the formation age of the crust using the depleted mantle model of DePaolo [19]. Mafic gneisses were excluded as far as possible, because of the increased likelihood of a younger mantle-derived component in these rock-types. Metasedimentary gneisses were also excluded, because of their uncertain sedimentary provenance.

On average, 1 kg of rock was crushed, after the removal of any weathered, veined or migmatized material; and careful attention was given to obtain a fine powder that was representative of the whole rock. Major element analyses were performed by Activation Laboratories, Ancaster, Ontario, using Li-borate fusion inductively couple plasma (ICP) analysis. The accuracy of their data was ensured by the inclusion of international standards as part of the analytical protocol.

Sm-Nd analysis followed our established procedures [6]. After a four-day dissolution at 125 °C in sealed digestion vessels using HF and HNO₃, samples were converted to the chloride form before splitting and spiking. Standard cation and reverse phase column separation methods were used. Nd isotope analyses were performed on a VG Isomass 354 mass spectrometer (VG instruments, Winsford,

UK) at McMaster University using double filaments and a 4 collector peak switching algorithm, and were normalised to a ¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219. Average within-run precision on the samples was ± 0.000013 (2 σ), and an average value of 0.51185 ± 2 (2 σ population) was determined for the La Jolla standard during this work. The reproducibility of ¹⁴⁷Sm/¹⁴⁴Nd and ¹⁴³Nd/¹⁴⁴Nd is estimated at 0.1% and 0.002% (1 σ), respectively, leading to an analytical uncertainty on each model age of *ca*. 20 Myr (2 σ). Duplicate dissolutions in Table 1 support this estimate, except for two samples with anomalously old ages (#100 and #101) that may contain an inherited refractory sedimentary component.

Мар	Field	UTM N	UTM E	ABT	Nd	Sm	<u>147Sm</u>	<u>143Nd</u>	E Nd	TDM	Q	Р	Met
#	#	NAD 83	NAD 83	km	ppm	ppm	144Nd	144Nd	1.45Ga	Ga			grade
Archean													
1	CV 12	5312260	468916	-3	15.6	3.13	0.1212	0.511313	-11.9	2.87	153	-190	А
2	CV 06	5322500	472900	-7	5.3	0.62	0.0701	0.510707	-14.3	2.49	181	-181	А
3	CV 05	5327800	472800	-11	12.7	2.13	0.1013	0.510999	-14.4	2.79	156	-192	А
4	CV 01	5328100	484300	-4	21.1	3.67	0.1051	0.511082	-13.5	2.77	133	-168	А
5	PT 31	5340319	498776	-8	29.2	2.62	0.0541	0.510223	-20.8	2.71	175	-173	А
Ensiali	c West												
6	PT 29	5329575	505950	4	33.4	5.87	0.1063	0.511573	-4.1	2.08	113	-128	А
7	PT 28	5329580	507438	3	32.1	5.46	0.1027	0.511566	-3.6	2.03	136	-93	А
8	PT 27	5328314	512225	7	46.9	8.16	0.1052	0.511565	-4.0	2.08	100	-113	А
9	PT 25	5324533	515720	11	42.7	7.74	0.1095	0.511670	-2.8	2.00	186	-17	AG
10	PT 24	5319037	516678	16	49.0	8.19	0.1008	0.511595	-2.6	1.95	120	-89	G
	PT 24R				41.2	7.36	0.1079	0.511684	-2.2	1.96			
11	PT 22	5310109	522006	27	43.8	8.05	0.1110	0.511681	-2.8	2.02	157	-41	G
12	PT 21	5302873	527397	35	67.6	13.30	0.1192	0.511925	0.4	1.79	156	-17	А
13	PT 19	5293840	527596	44	15.8	3.24	0.1241	0.512041	1.8	1.69	9	-309	А
14	PT 17	5285204	526494	52	45.9	6.64	0.0874	0.511626	0.5	1.71	175	-10	А
15	PT 34	5322886	537890	19	40.8	9.91	0.1467	0.512173	0.2	1.97	19	-37	А
16	PT 38	5331126	540795	12	69.2	13.86	0.1210	0.511904	-0.3	1.87	170	-15	А
	PT 38R				66.6	13.43	0.1219	0.511906	-0.5	1.89			
17	PT 39	5334297	544032	12	29.2	4.23	0.0877	0.511467	-2.7	1.90	175	-13	G
18	PT 40	5338783	542855	10	43.2	6.85	0.0960	0.511547	-2.7	1.94	181	24	А
19	PT 42	5345715	542126	4	45.1	9.08	0.1217	0.511731	-3.9	2.17	39	-245	А
20	PT 43	5350500	543700	1	49.0	7.43	0.0917	0.511528	-2.3	1.89			G
21	PT 45	5349420	546184	4	23.7	4.58	0.1169	0.511736	-2.9	2.05	17	-284	G
22	PT 46	5346301	556317	12	58.9	9.45	0.0969	0.511612	-1.6	1.86	214	34	G
23	PT 49	5352843	571388	16	4.2	0.46	0.0659	0.511417	0.4	1.68	229	-4	G
	PT 49R				5.1	0.57	0.0678	0.511430	0.3	1.68			
24	SM 66	5324318	590040	48	105.1	17.81	0.1024	0.511814	1.4	1.68			G
25	SM 63	5337877	606147	52	27.8	6.18	0.1345	0.512183	2.6	1.65			G
26	SM 62	5339908	608634	53	45.1	8.64	0.1159	0.511957	1.7	1.69			G
27	SM 61	5340195	608862	53	48.8	10.09	0.1250	0.511977	0.4	1.83			G
28	SM 33	5350767	597347	37	43.8	7.81	0.1077	0.511693	-2.0	1.94			G
29	SM 31	5348566	608753	47	58.0	9.54	0.0994	0.511611	-2.1	1.91			AG
30	SM 53	5349001	611235	48	40.3	8.40	0.1261	0.511977	0.1	1.84			G

Table 1. Nd isotope data for the Parent-Clova area, Quebec.

Map	Field	UTM N	UTM E	ABT	Nd	Sm	<u>147Sm</u>	<u>143Nd</u>	E Nd	TDM	Q	Р	Met
#	#	NAD 83	NAD 83	km	ppm	ppm	144Nd	144Nd	1.45Ga	Ga			grade
Ensiali	ic West												
31	SM 57	5360057	610729	41	34.6	5.63	0.0984	0.511646	-1.2	1.84			G
32	SM 59	5367482	608905	35	40.7	7.93	0.1177	0.511980	1.8	1.68			AG
33	SM 30	5342182	614305	55	58.4	10.35	0.1072	0.511716	-1.5	1.89			G
34	SM 29	5339349	618111	60	61.4	10.84	0.1066	0.511784	0.0	1.79			G
35	SM 27	5337071	620546	63	61.1	12.75	0.1261	0.511989	0.4	1.83			G
36	SM 56	5355500	612300	45	21.6	4.65	0.1303	0.512145	2.7	1.64			G
37	BG 3	5374500	577300	6	20.8	2.36	0.0687	0.511291	-2.6	1.84			
38	BG 6	5358100	570800	11	57.0	9.52	0.1009	0.511715	-0.3	1.79			
39	BG 7	5349900	571200	17	52.7	7.71	0.0884	0.511554	-1.1	1.81			
Quebe	cia West												
40	PT 16	5282400	524300	56	122.1	20.70	0.1026	0.511878	2.6	1.59			А
41	PT 14	5274042	520503	61	39.0	8.44	0.1309	0.512181	3.3	1.57	193	-54	G
42	PT 12	5267045	515455	63	22.1	5.03	0.1378	0.512270	3.7	1.54	10	-184	А
43	PT 13	5263282	509264	60	44.5	8.11	0.1101	0.512050	4.6	1.46	164	-35	А
44	PT 10	5247061	507356	72	20.8	3.69	0.1072	0.511924	2.6	1.60	170	-164	А
45	PT 09	5230424	502055	82	77.6	11.34	0.0884	0.511827	4.2	1.48	130	-34	А
46	PT 08	5223870	495015	85	79.3	11.77	0.0898	0.511872	4.8	1.44	130	-12	А
47	PT 06	5212886	491489	93	9.5	2.03	0.1291	0.512164	3.3	1.58	95	-246	А
48	PT 04	5205454	488784	98	42.6	8.15	0.1156	0.512025	3.0	1.58	174	-9	А
49	LK 17	5281989	547011	62	119.6	19.19	0.0970	0.511806	2.2	1.61	189	-3	А
50	LK 15	5273224	549785	71	35.6	6.49	0.1104	0.512043	4.4	1.47	197	-32	А
51	LK 13	5268687	557192	77	111.4	17.69	0.0959	0.511909	4.4	1.46	-6	-64	А
52	LK 12	5264800	561950	85	107.1	16.28	0.0919	0.511856	4.1	1.48			А
53	LK 11	5259424	563191	88	44.8	9.45	0.1277	0.512176	3.7	1.53	165	-81	А
54	LK 10	5256375	564270	91	49.3	10.04	0.1230	0.512107	3.3	1.56	175	-87	А
55	LK 09	5250482	564596	97	71.7	11.13	0.0938	0.511901	4.7	1.45	115	-64	А
56	LK 08	5245498	566212	102	12.4	1.86	0.0909	0.511931	5.8	1.38	153	-150	А
57	LK 07	5244174	570779	105	30.5	6.11	0.1211	0.512094	3.4	1.56	184	-188	А
58	LK 04	5270000	580000	85	28.0	5.28	0.1140	0.512024	3.3	1.56			А
59	SM 67	5308878	588859	59	16.5	3.29	0.1204	0.512044	2.5	1.62			G
60	SM 15	5293515	594962	74	14.0	2.57	0.1110	0.511986	3.1	1.56			G
	SM 15R				14.5	2.70	0.1124	0.512005	3.2	1.57			
61	SM 14	5290464	597932	78	35.3	6.42	0.1099	0.511985	3.3	1.55			AG
62	SM 11	5279366	608043	94	13.1	2.26	0.1047	0.511972	4.0	1.50			А
63	SM 09	5273331	612022	101	23.7	4.06	0.1035	0.511916	3.1	1.56			А
64	SM 18	5261686	610490	109	36.4	5.71	0.0948	0.511921	4.9	1.44			А
65	SM 07	5272071	623013	109	40.6	8.69	0.1294	0.512156	3.0	1.60			AG
66	SM 06	5271843	629711	113	17.3	3.00	0.1048	0.511980	4.2	1.48			А
67	SM 04	5270537	636270	119	76.8	14.75	0.1161	0.512057	3.6	1.53			G
68	SM 03	5269598	644006	125	50.3	10.75	0.1292	0.512142	2.8	1.61			
69	SM 01	5267158	654073	134	16.1	2.71	0.1016	0.511922	3.6	1.52			G
70	SM 26	5333109	621877	67	120.0	20.75	0.1045	0.511900	2.7	1.59			G
71	SM 24	5328908	631079	77	38.2	7.90	0.1249	0.512086	2.5	1.63			G

 Table 1. Cont.

Мар	Field	UTM N	UTM E	ABT	Nd	Sm	<u>147Sm</u>	<u>143Nd</u>	E Nd	TDM	Q	Р	Met
#	#	NAD 83	NAD 83	km	ppm	ppm	144Nd	144Nd	1.45Ga	Ga			grade
Quebecia West													
72	SM 23	5311667	649863	102	32.8	6.38	0.1174	0.512073	3.6	1.53			А
73	LK 01	5199069	556421	143	35.0	7.12	0.1229	0.512117	3.5	1.55	135	-54	А
74	LK 27	5214951	548657	123	46.7	9.38	0.1215	0.512170	4.8	1.44	121	46	А
75	LK 02	5217669	560395	127	70.2	13.48	0.1160	0.512107	4.6	1.46	99	-95	А
76	LK 03	5224338	563232	122	84.2	14.99	0.1076	0.512044	4.9	1.43	170	-4	А
77	LK 20	5236188	581232	116	4.5	1.00	0.1361	0.512276	4.1	1.50	67	-243	А
78	LK 21	5236132	581708	116	20.3	4.01	0.1192	0.512145	4.7	1.44	68	-182	А
79	LK 22	5234673	586649	120	22.1	4.68	0.1279	0.512262	5.4	1.39	96	-177	А
80	LK 24	5236819	597455	123	56.2	10.21	0.1098	0.512018	4.0	1.50	175	-150	А
81	LK 26	5236356	611698	130	34.0	7.09	0.1261	0.512114	2.8	1.61	21	-197	А
82	RR 05	5233633	629851	143	7.0	1.90	0.1660	0.512595	4.8	1.42			G
83	RR 04	5232599	638010	149	14.4	1.86	0.0782	0.511728	4.2	1.48			G
84	RR 03	5232775	641429	151	46.6	8.05	0.1044	0.511967	4.0	1.50			G
85	RR 02	5231514	645627	154	50.5	9.07	0.1086	0.511986	3.6	1.53			G
86	RR 01	5229796	649883	159	31.7	7.71	0.1472	0.512460	5.7	1.37			G
87	SM 20	5297854	668804	125	34.2	8.60	0.1519	0.512378	3.2	1.64			А
88	SM 50	5339960	645205	81	133.1	21.14	0.0960	0.511868	3.6	1.52			G
Archean young													
89	CV 02	5334850	485700	-8	32.9	6.10	0.1119	0.511677	-3.1	2.05	65	-201	А
	CV 02R				38.6	6.95	0.1088	0.511641	-3.2	2.04			
90	PT 30	5332089	503285	1	23.1	3.99	0.1046	0.511400	-7.2	2.30	113	-197	G
91	BG 13	5361500	538700	-14	20.2	3.55	0.1063	0.511443	-6.6	2.28	140	-169	А
	BG 13R				20.8	3.62	0.1050	0.511451	-6.2	2.24			
Ensial	ic West, you	ıng											
92	PT 32	5310663	530916	29	21.0	3.70	0.1067	0.511968	3.6	1.53	127	-83	G
	PT 32R				24.3	4.30	0.1072	0.511993	4.0	1.50			
93	PT 36	5328510	538460	14	29.7	6.33	0.1288	0.512150	3.0	1.59	137	-131	А
94	SM 65	5332003	598295	49	18.0	4.19	0.1404	0.512352	4.8	1.43	26	-242	G
	SM 65R				19.7	4.63	0.1421	0.512373	4.9	1.42			
95	PT 33	5318600	535000	22	26.0	5.24	0.1216	0.512203	5.4	1.39			А
96	BG 4A	5365200	575200	10	32.2	5.26	0.0987	0.511846	2.7	1.58	139	-82	А
97	BG 4B	5365300	575300	10	40.5	8.21	0.1225	0.512078	2.8	1.61			А
	BG 4BR				44.0	8.82	0.1212	0.512067	2.8	1.60			
Quebe	cia West, ol	d											
98	LK 14	5269970	553081	75	51.7	8.93	0.1045	0.511649	-2.3	1.95	134	-68	А
	LK 14R				47.5	8.52	0.1083	0.511684	-2.3	1.96			
99	LK 05	5271948	574767	81	51.9	7.59	0.0883	0.511490	-2.4	1.89	205	-65	А
	LK 05R						0.0890	0.511494	-2.4	1.89			
100	SM 16	5302094	589326	65	28.6	7.95	0.1678	0.512363	0.0	2.25	110	-172	G
	SM 16R			-			0.1651	0.512354	0.3	2.17	-		
101	SM 05	5270808	634350	117	82.4	16.88	0.1237	0.511955	0.2	1.84	109	-103	А
	SM 05R				81.1	16.43	0.1224	0.512002		1.73			
102	LK 25	5236788	603276	125	77.4	15.90	0.1242	0.512005	1.1	1.78	152	-30	G

5. Nd Isotope Results

Over 100 new Nd model ages for granitoid orthogneisses from the study area are presented in Table 1. Localities are based on Universal Transverse Mercator (UTM) grid references using the 1983 North American Datum. They are plotted in Figure 3 using colours to indicate approximate ranges of model ages. Dark blue = Archean (>2.4 Ga); red, yellow and pale blue = Palaeoproterozoic (*ca.* 1.64–2.4 Ga); green and pink = largely Mesoproterozoic (1.37–1.64 Ga). Based on these colour schemes, it can be seen that samples with Archean TDM ages are restricted to the area NW of the ABT, while the line across the middle of the map separates most samples with model ages above and below 1.64 Ga. Hence, this line is argued to be a continuation of the boundary between the Eastern and Central blocks of Martin and Dickin [6], corresponding to the Quebecia and ensialic arc terranes.

Figure 3. Sample locations within the Parent-Clova region, Quebec. Dark and pale blue = ages, respectively, above and below 2.4 Ga in the Archean Parautochthon; red and pink = ages, respectively, above and below 1.64 Ga in the Ensialic Arc block; yellow and green = ages, respectively, above and below 1.64 Ga in the western extension of Quebecia.



However, these relatively broad age divisions conceal more subtle internal age variation within these terranes. Therefore, to clarify these internal variations, TDM model ages are plotted against distance from the ABT in Figure 4, in a similar manner to Martin and Dickin [4].

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This plot reveals that the central block in the present study area has exactly the same age structure as the central block of Martin and Dickin, with correlated trends of the Nd model age against distance that are completely overlapping (red circles and vertical crosses in Figure 4). Similarly, the young (southerly) terrane in the present study area (green circles) overlaps strongly with Quebecia (black diamonds). Hence, this terrane is here referred to as Quebecia West (Figure 4).

Figure 4. Plot of TDM model age *versus* distance SE of the ABT for samples of the present study (coloured spots), divided into the same three blocks that were identified by Martin and Dickin [4]. Linear regression fits are shown for published data (crosses) from the ensialic arc block [4] and the Algonquin ramp [20], along with new data for Western Quebecia.



One difference is that Western Quebecia has a larger number of samples with Nd model ages below 1.5 Ga, whereas in the main Quebecia terrane, only four such samples were seen amongst 71 with model ages in the range 1.5–1.65 Ga [8]. This is attributed to the effects of the younger Elzevirian arc, which is believed to have straddled the edge of the continent in this area, reworking the southern edge of the Quebecia terrane and generating new crust offshore, which now forms the Adirondacks [12].

In addition to the 88 samples in Table 1 that define these regular patterns, there are 14 samples that show anomalous behavior. For example, within the Western Quebecia terrane, there are five samples that show abnormally old ages. However, because rocks with these old ages are not contiguous, they are unlikely to represent specific structural features, such as tectonic windows, to an underlying thrust sheet. Instead, they are attributed to contamination of the granitoid source by inclusion of small pockets of older sediment into the melting zone.

There are also a few samples from the ensialic and Archean terranes that yield abnormally young model ages. These are attributed to younger plutons that introduced new mantle-derived material into the crust. Although these samples contribute to the geological noise, they can also yield important information. For example, the three abnormally young samples (pale blue) within the Archean terrane show the effects of mixing Archean crustal Nd with (probable) juvenile Mesoproterozoic Nd. Hence, we infer that similar mixing process gave rise to the older (*ca.* 2 Ga) model ages within the ensialic block. The fraction of old crustal Nd involved in mixing apparently decreased steadily southwards, as proposed by Martin and Dickin [4].

Six samples (coloured pink) that yield abnormally young model ages within the ensialic block are attributed to two stages of Nd mixing. The first of these stages yielded the relatively coherent signature of the Nd mixing line described above. Superimposed on this older mixing event was a more scattered younger mixing event, which introduced small amounts of new mantle-derived material into the older mixed crust of the ensialic arc block. This latter event probably represents distal plutonism related to the Elzevirian continental margin arc to the south [8].

Isotope signatures analogous to this younger mixing event were generated in crust southeast of the Algonquin Ramp in Ontario (diagonal crosses in Figure 4). This area of Ontario is part of the Algonquin Terrane that overlies the main ramp of the ABT [20] and was attributed by Dickin and McNutt [6] to Mesoproterozoic ensialic arc magmatism established on an older Palaeoproterozoic margin.

The overlapping distributions of pink circles and diagonal crosses in Figure 4 are both attributed to mixing of ensialic arc magma with an older crustal component having Nd model ages around 1.8–2 Ga. However, the origins of the older components are different in the two regions. In Ontario, the older component is attributed to an accreted Palaeoproterozoic arc with geographically homogeneous Nd signatures that yield a 1.75 Ga Sm-Nd isochron [11], as described in the introduction. In contrast, the older component in the present study area was itself the product of earlier mixing, demonstrated by its highly variable model age structure.

The calculation of model ages for mixed components involves extrapolation from the time of mixing to the apparent intersection with the mantle growth curve [21]. Hence, this can cause error magnification and, therefore, increased data scatter. To overcome this problem, an alternative data presentation involves plotting epsilon Nd values calculated at the estimated time of mixing. It is not necessary to know the precise time of mixing, because the narrow range of Sm/Nd ratios in granitoid rocks causes most Nd isotope growth lines to be sub-parallel. Hence, the epsilon model is quite insensitive to the exact time (t) chosen, provided this is the same for all samples. The result (Figure 5) effectively reproduces the effects seen in Figure 4, but with less scatter about the mixing lines. The result is strong support for the distance-modulated crustal mixing model.

The epsilon *versus* distance plot can also be used to test another feature of the sample suite, namely the effect of metamorphic grade. The study area displays variable metamorphic grade from amphibolite-facies to granulite-facies (A and G, respectively, in Table 1). It is possible that the variable grade of metamorphism could have affected the closed-system assumption inherent in Nd isotope mapping. However, granulite-facies samples (shown in darker red and green) show no consistent difference from amphibolite-facies samples. Hence, it is argued that metamorphic grade has not affected the Sm-Nd closed-system assumption in the large whole-rock samples analysed.

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Figure 5. Plot of ε Nd values *versus* distance SE of the ABT, distinguishing between amphibolite facies and granulite facies gneisses.



6. Petrochemical Data

In order to compare the petrology of the analysed samples with those of the surrounding region, major element analysis was performed on selected samples. These data were used to determine the quartz (Q) and plagioclase (P) indices of Debon and LeFort [22], which are intended to classify granitoid rocks following Streckeisen [23], but using whole-rock chemical data. The new data (Table 1) are plotted in Figure 6, along with data from Martin and Dickin [4].

The results in Figure 6 show that the terranes identified by Martin and Dickin [4] continue to the west with similar petrology. Thus, the Archean samples in both areas are restricted to the quartz diorite and tonalite fields, whereas the ensialic arc in both areas trends across the middle of the diagram from diorite to granite, similar to the Blanco Batholith in Peru, which provides a modern analogue of continental arc magmatism [24]. However, whereas Quebecia samples are largely restricted to the tonalite-granodiorite-monzogranite fields, the western extension of Quebecia is more variable, with scattered samples in the lower part of the diagram. This is consistent with the reworking of the western extension of Quebecia by the Elzevirian arc, which yielded several monzonitic to syenitic rocks in the Mont Laurier area to the SW [8].

Figure 6. Petrochemical grid after Streckeisen [23] for newly collected samples, compared with the Archean and ensialic arc blocks of Martin and Dickin [4]. TN, tonalite; GD, granodiorite; MG, monzogranite; GR, granite; QD, quartz diorite; QMD, quartz monzodiorite; QM, quartz monzonite; QSY, quartz syenite; DI, diorite; MD, monzodiorite; MZ, monzonite; SY, syenite.



7. Discussion

New Nd data from the Parent-Clova region of south-central Quebec help to fill in a major gap in the crustal formation age map of the Grenville Province. They show clearly that the ensialic arc block of Martin and Dickin [4] continues a further 100 km to the SW, forming an almost parallel-sided strip between Archean crust and the Quebecia terrane along a distance of over 300 km (Figure 7).

The positive correlation between epsilon (1450 Ma) values and the distance from the ABT in the ensialic arc block provides strong evidence that this is an isotopic mixing line, and because the mixing line projects towards the compositions of scattered Proterozoic plutons within the Archean terrane (Figure 5), this suggests strongly that the crustal end-member of the mixing line was Archean. Hence, the mixing line suggests that Mesoproterozoic crustal growth occurred directly on the Archean margin in the present study area, in the absence of the accreted Palaeoproterozoic arc crust.

However, around 76° west, there is an important change in the nature of the Laurentian margin. From this point westwards, Archean crust was fringed by an accreted Palaeoproterozoic arc named Barilia by Dickin [3]. This transition has been emphasized in Figure 7 by leaving the Archean crust west of 76° longitude un-coloured. South of the Palaeoproterozoic margin in Ontario, the Algonquin

terrane represents an ensialic arc analogous to the central block of Martin and Dickin [4], forming a similar mixing line on the epsilon Nd *versus* distance plot. The samples that gave rise to this mixing line came from the area shaded dark pink in Figure 7. However, the Algonquin mixing line projects towards a Palaeoproterozoic rather than an Archean end-member (Figures 4 and 5). Hence, we can see that a Mesoproterozoic ensialic arc was established along this whole margin, but it crossed from Archean crust in the east to Palaeoproterozoic crust in the west.

Figure 7. Map of the western Grenville Province showing the change in the age of the Mesoproterozoic Laurentian margin from Archean (blue) in the central Grenville Province to Palaeoproterozoic (orange) in the SW. Red = ensialic arc established on Archean margin (present study area); pink = ensialic arc established on Palaeoproterozoic crust (dark pink = data that generated the Algonquin mixing lines in Figures 4 and 5); pale green = ensialic arc established on the accreted Mesoproterozoic margin; darker green = ensialic arc established on the older Mesoproterozoic ensialic arc.



It was suggested by Martin and Dickin [4] that the ensialic arc magmatism that gave rise to the Central Block occurred due to a subduction flip *after* the accretion of Quebecia. However, the new data presented here show that the reworking of Quebecia in the Elzevirian arc gave rise to a much more scattered mixing signature than the more regular mixing line seen in the Central Block. Therefore, we now suggest that an early Mesoproterozoic ensialic arc was established on the Laurentian margin as part of the Pinwarian magmatic event [25], before the accretion of Quebecia (Figure 8).

In view of the isotopic homogeneity and TTG-type petrology of the Quebecia terrane, Dickin [3] proposed that this was an accreted oceanic arc. An alternative possibility proposed by Rivers and Corrigan [7] is that the ensialic arc that gave rise to the Central Block continued to step further away from the continent, so that it generated juvenile ensimatic crust off-shore. However, in the Manicouagan area, homogeneous Mesoproterozoic arc crust abuts directly against Palaeoproterozoic crust [26], suggesting that in that area, Quebecia was a discrete accreted terrane. In that case, a possible scenario that could explain crustal evolution in the present study area would be two subduction zones, as shown in Figure 8.

Figure 8. Cartoon to show proposed early ensialic arc established on the Laurentian margin during the Pinwarian event, followed by more scattered plutonism of the composite margin during the Elzevirian. Red shading indicates crust with mixed isotopic signatures formed in the ensialic arc block.



Another reason for believing that Quebecia is a discrete accreted terrane is that no such crustal unit is seen in Ontario. Here, it seems that the (Pinwarian) ensialic arc that gave rise to the Algonquin Terrane was followed by continued ensialic arc magmatism on the continental margin, forming the Muskoka Terrane [6,20,27].

Slagstad *et al.* [27] suggested that a 1.55 Ga TDM boundary line, identified in the U.S. Central Plains by van Schmus *et al.* [28], could be traced through the Muskoka terrane of the Grenville Province. However, the data presented here, building on the study of Dickin *et al.* [20], show that no meaningful 1.55 Ga TDM boundary can be traced through Ontario, because the crustal context in Ontario and western Quebec is different from the Central Plains.

Van Schmus *et al.* [28] interpreted the 1.55 Ga TDM line as "a fundamental crustal feature representing the southeastern limit of Palaeoproterozoic crust in Laurentia". This older Laurentian crust is relatively homogeneous in the Central Plains region, with an average TDM age of 1.7 Ga over large areas. However, the crust to the south of the line is even more homogeneous, with an average TDM age of 1.50 Ga that is barely older than the U-Pb ages of these rocks. Hence, Van Schmus *et al.* [28] suggested that this younger crust "could consist of one or more juvenile terranes accreted to the

southeastern margin of early Mesoproterozoic Laurentia". The 1.55 Ga TDM boundary, therefore, approximates a crustal suture line.

A similar scenario to this is seen in eastern Quebec (Figure 1), where the homogeneous juvenile Quebecia terrane (TDM 1.55 Ga) is juxtaposed against the Palaeoproterozoic Labradoria terrane (TDM 1.75 Ga) along a sharp boundary line [3]. However, the situation in Ontario is quite different, because "primary Palaeoproterozoic crust" (with an average TDM age of 1.9 Ga) is here fringed by the Algonquin ensialic arc mixing zone, which was itself reworked by Elzevirian continental arc magmatism. Therefore, in Ontario, the edge of primary Palaeoproterozoic crust is best approximated by a 1.8 Ga demarcation line, which also corresponds to the location of the ABT [11]. In contrast, a 1.55 Ga age cut-off runs through the middle of the mixing line in the Algonquin ramp, as indicated by the black horizontal bar in Figure 4.

It is not surprising that suture boundaries of the type identified by van Schmus *et al.* [28] cannot be traced across a whole continent. Most arc systems have a finite geographical extent, so that long-lived active continental margins are expected to periodically break down into separate segments, some of which are characterized by the accretion of large arc terranes, while others are characterized by long-lived ensialic arc subduction zones. Both types are here demonstrated on the Laurentian margin.

8. Conclusions

New Nd data for the Parent-Clova region of Quebec fill a major gap in understating between the geological evolution of the eastern and western Grenville Province. The Parent-Clova area contains a 60 km-wide zone of ensialic arc crust, located between the Archean craton to the north and an accreted Mesoproterozoic arc to the south. This ensialic arc extended NE–SW for a distance of 300 km along the Archean margin, before crossing onto accreted Palaeoproterozoic crust in western Quebec and Ontario. These inferences have been made possible by the analysis of large Nd data sets, which reveal distinct Nd isotope mixing zones on the edge of the Archean and Palaeoproterozoic margins, along with other areas of homogeneous crust attributed to accreted oceanic arcs.

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Conflict of Interest

The authors declare no conflict of interest.

References

 Easton, R.M. The Grenville Province and the Proterozoic History of Central and Southern Ontario. In *Geology of Ontario*; Special Paper 4; Ontario Geological Survey: Toronto, Canada, 1992; Part 2, pp. 714–904.

- 2. Davidson, A. New Interpretations of the Southwestern Grenville Province. In *The Grenville Province*; Special Paper 31; Moore, J.M., Davidson, A., Baer, A.J., Eds.; Geological Association of Canada Publisher: St John's, Canada, 1986; pp. 61–74.
- Dickin, A.P. Crustal formation in the Grenville Province: Nd-isotope evidence. *Can. J. Earth Sci.* 2000, *37*, 165–181.
- 4. Martin, C.; Dickin, A.P. Styles of crustal formation on the southeast margin of Laurentia: Evidence from the central Grenville Province northwest of Lac St.-Jean, Quebec. *Can. J. Earth Sci.* 2005, *42*, 1643–1652.
- 5. Rivers, T.; Martignole, J.; Gower, C.F.; Davidson, A. New tectonic divisions of the Grenville Province, southeastern Canadian Shield. *Tectonics* **1989**, *8*, 63–84.
- Dickin, A.P.; McNutt, R.H. Nd Model-Age Mapping of Grenville Lithotectonic Domains: Mid-Proterozoic Crustal Evolution in Ontario. In *Mid-Proterozoic Laurentia–Baltica*; Special Paper 38; Gower, C.F., Rivers, T., Ryan, B., Eds.; Geological Association of Canada Publisher: St John's, Canada, 1990; pp. 79–94.
- 7. Rivers, T.; Corrigan, D. Convergent margin on southeastern Laurentia during the Mesoproterozoic: Tectonic implications. *Can. J. Earth Sci.* **2000**, *37*, 359–383.
- 8. Dickin, A.P.; McNutt, R.H.; Martin, C.; Guo, A. The extent of juvenile crust in the Grenville Province: Nd isotope evidence. *Geol. Soc. Am. Bull.* **2010**, *122*, 870–883.
- Rondot, J. Geosutures dans le Grenville [in French]. In *The Grenville Province*; Special Paper 31; Moore, J.M., Davidson, A., Baer, A.J., Eds.; Geological Association of Canada Publisher: St John's, Canada, 1986; pp. 313–325.
- Frith, R.A.; Doig, R. Pre-Kenoran tonalitic gneisses in the Grenville Province. *Can. J. Earth Sci.* 1975, *12*, 844–849.
- 11. Dickin, A.P.; Moretton, K.; North, R. Isotopic mapping of the Allochthon Boundary Thrust in the Grenville Province of Ontario, Canada. *Precambrian Res.* **2008**, *167*, 260–266.
- 12. Daly, J.; McLelland, J. Juvenile Middle Proterozoic crust in the Adirondack highlands, Grenville Province, north-eastern North America. *Geology* **1991**, *19*, 119–122.
- 13. Dickin, A.P.; McNutt, R.H. The Central Metasedimentary Belt (Grenville Province) as a failed back-arc rift zone: Nd isotopic evidence. *Earth Planet. Sci. Lett.* **2007**, *259*, 97–106.
- 14. Carr, S.D.; Easton, R.M.; Jamieson, R.A.; Culshaw, N.G. Geologic transect across the Grenville orogen of Ontario and New York. *Can. J. Earth Sci.* **2000**, *37*, 193–216.
- Smith, T.E.; Holm, P.E. The geochemistry and tectonic significance of pre-metamorphic minor intrusions of the Central Metasedimentary Belt, Grenville Province, Ontario. *Precambrian Res.* 1990, 48, 341–360.
- 16. Davidson, A. Geological Map of the Grenville Province, Canada and Adjacent Parts of the United States of America; Geological Survey of Canada: Ottawa, Canada, 1988; Map 1974A, scale 1:2000000.
- Davidson, A. An Overview of Grenville Province Geology, Canadian Shield. In *Geology of the* Precambrian Superior and Grenville Provinces and Precambrian Fossils in North America; Geology of Canada 7; Lucas, S.B., St-Onge, M.R., Eds.; Geological Survey of Canada: Ottawa, Canada, 1988; Chapter 3, pp. 205–270.

- 18. Corrigan, D.; van Breemen, O. U-Pb age constraints for the lithotectonic evolution of the Grenville Province along the Mauricie transect, Quebec. *Can. J. Earth Sci.* **1997**, *34*, 299–316.
- 19. DePaolo, D. J. Neodymium isotopes in the Colorado Front Range and crust-mantle evolution in the Proterozoic. *Nature* **1981**, *291*, 193–196.
- Dickin, A.P.; Cooper, D.; Guo, A.; Hutton, C.; Martin, C.; Sharma, K.N.M.; Zelek, M. Nd isotope mapping of the Lac Dumoine thrust sheet: Implications for large scale crustal structure in the SW Grenville Province. *Terra Nova* 2012, *24*, 363–372.
- 21. Arndt, N.T.; Goldstein, S.L. Use and abuse of crust-formation ages. Geology 1987, 15, 893-895.
- 22. Debon, F.; LeFort, P. A chemical-mineralogical classification of common plutonic rocks and associations. *Trans. Roy. Soc. Edinb. Earth Sci.* **1983**, *73*, 135–149.
- 23. Streckeisen, A.L. Plutonic rocks. Classification and nomenclature recommended by the IUGS subcommission on the systematics of igneous rocks. *Geotimes* **1973**, *18*, 26–30.
- Atherton, M.P.; McCourt, W.J.; Sanderson, L.M.; Taylor, W.P. The Geochemical Character of the Segmented Peruvian Coastal Batholith and Associated Volcanics. In *Origin of Granite Batholiths: Geochemical Evidence*; Atherton, M.P., Tarney, J., Eds.; Shiva Pub.: Orpington, UK, 1979.
- Gower, C.F. The Evolution of the Grenville Province in Eastern Labrador, Canada. In *Precambrian* Crustal Evolution in the North Atlantic Region; Special Publication 112; Brewer, T.S., Ed.; The Geological Society of London: London, UK, 1996; pp. 197–218.
- 26. Thomson, S.; Dickin, A.P.; Spray, J.G. Nd isotope mapping of Grenvillian crustal terranes in the vicinity of the Manicouagan Impact Structure. *Precambrian Res.* **2011**, *191*, 184–193.
- 27. Slagstad, T.; Culshaw, N.G.; Daly, J.S.; Jamieson, R.A. Western Grenville Province holds key to midcontinental Granite-Rhyolite Province enigma. *Terra Nova* **2009**, *21*, 181–187.
- Van Schmus, W.R.; Bickford, M.E.; Turek, A. Proterozoic Geology of the East-Central Midcontinent Basement. In *Basement and Basins of Eastern North America*; Special Paper 308; van der Pluijm, B.A., Catacosinos, P.E., Eds.; Geological Society of America: Dunver, CO, USA, 1996; pp. 7–32.

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