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Pb Isotope Mapping of Paleoproterozoic Gneisses in the SW Grenville Province: Evidence for a Cryptic Continental Suture

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Abstract: New whole-rock lead (Pb) isotope analyses are presented in this study for granitoid orthogneisses from the Southwest Grenville Province in Ontario and Western Quebec. These data are used to test the location of a cryptic Archean-Proterozoic suture proposed on the basis of neodymium (Nd) isotope mapping. Immediately south of the inferred suture boundary, Pb isotope results show a crustal component derived solely from a juvenile Paleoproterozoic mantle source. These data are distinctly different from the reworked Archean craton to the northwest and strongly support the boundary derived from Nd isotope data. Pb signatures in the Paleoproterozoic crust suggest a southerly increase in magmatic reworking due to intensive plutonism during the late Paleoproterozoic and early Mesoproterozoic periods. The accretion of a juvenile arc to the Archean margin during the Penokean event (ca. 1.85 Ga) would have triggered subduction-zone reversal and the development of a long-lived ensialic arc on the composite margin. This was expressed as a 1.75 Ga Killarnian magmatic event and subsequent early Mesoproterozoic magmatism. This tectonic model for the Southwest Grenville Province shows that its crustal evolution is consistent with the Paleoproterozoic Makkovik-Ketilidian Orogen of Labrador and Southern Greenland. Hence, the application of whole-rock Pb isotope data in conjunction with Nd model ages provides data useful for mapping the extent of crustal terranes of differing age, which is essential for modeling the tectonic evolution of complex ancient accretionary orogens.

Keywords: applied isotope geochemistry; Pb isotopes; Grenville Province; crustal evolution; Paleoproterozoic

1. Introduction

The Great Proterozoic Accretionary Orogen (GPAO) along the southeast margin of Laurentia represents a major crust-forming event between 2.0 and 1.0 Ga [1,2]. Evidence of Paleoproterozoic crustal growth during this period has been recorded in various regions such as Colorado, Wisconsin, Labrador, and Southern Greenland [3–6]. The Grenville Province represents a long-lived ancient orogenic belt that contains remnants of Proterozoic crust accreted to the southeastern Laurentian margin during the GPAO (Figure 1a). However, the Archean-Proterozoic boundary in the Grenville Province remains poorly defined due to high-grade metamorphism associated with the 1.2−1.0 Ga Grenville orogeny, which obscured much of the pre-Grenvillian history of the region.

This study uses whole-rock lead (Pb) isotope analyses to constrain the Paleo- to Mesoproterozoic crustal evolution of the Southwest Grenville Province. The Pb isotope systematics of ancient crustal rocks are generally more complex than samarium-neodymium (Sm-Nd) isotope systematics in large whole-rock samples. However, whole-rock Pb isotope analysis can provide valuable additional information about crustal formation and differentiation, provided large sample suites are used to overcome the geological complexities inevitable in old terranes with complex evolution histories [7]. A study of crustal formation in the Makkovik Province of Labrador demonstrated the usefulness of combined Pb and Nd isotope analysis [6]. The integration of these isotopic tracers can assist with mapping the extent of cryptic terrane boundaries common in many accretionary orogens, which is essential to advancing our understanding of the tectonic framework of a region.

Across the Grenville Province, many crustal terranes have been mapped using Nd isotope data to determine the crustal formation ages of these rocks and the boundaries between them [8]. One of these terranes in Ontario and Western Quebec is thought to be a Paleoproterozoic arc that was accreted to the southern margin of Laurentia [9,10]. However, some authors suggested that this terrane actually consists of Archean crust that was magmatically reworked in the Mesoproterozoic [11]. Since the uranium (U)-lead (Pb) isotope system has significantly different chemical behavior than the Sm-Nd system, Pb isotope analysis provides an independent method for testing the results of Nd isotope analysis and constraining the location and origin of this cryptic Paleoproterozoic arc terrane.

2. Previous Isotopic Tracer Studies

Archean and Paleoproterozoic rocks in the Grenville Province (yellow shading, Figure 1b) are exposed in the Parautochthonous Belt that extends from Lake Huron to SE Labrador [12]. This Archean-Paleoproterozoic margin can be linked with the bordering Makkovik Province (Figure 1c), which contains remnants of Paleoproterozoic crust accreted to the Archean craton during the 1.9−1.8 Ga Makkovikian orogeny [6,13,14].

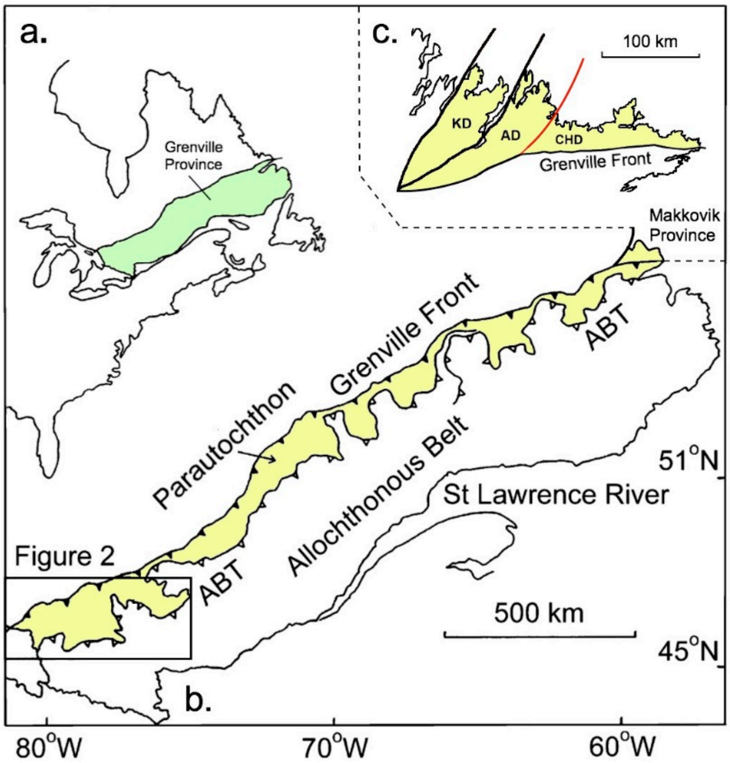

Figure 1. View of the southeast Canadian Shield showing: (**a**) the location of the Grenville Province in Eastern Canada (green shading); (**b**) major tectonic belts of the Grenville Province as determined by Rivers et al. [12]: Allochthon Boundary Thrust (ABT) and Archean and Paleoproterozoic crust (yellow shading); and (**c**) the tectonic domains of the Makkovik Province: Aillik domain (AD), Archean-Proterozoic suture (red line), Cape Harrison domain (CHD), and Kaipokok domain (KD) [6,15].

In Eastern Labrador, a combination of whole-rock Pb and Nd isotope data were used in a reconnaissance study of the Makkovik Province to interpret the crustal formation history of this region during the Paleoproterozoic era [6]. Nd isotope data for the Cape Harrison domain yielded a good Sm-Nd errorchron with an age of 1.95 ± 0.1 Ga (2σ) and an average T_{DM} age of 2.0 Ga. This suggests that juvenile Makkovik crust was generated in an oceanic arc during a single crust-forming event shortly before being accreted to the Laurentian margin at 1.9 Ga. Likewise, Pb isotope data show Paleoproterozoic crustal signatures for the Cape Harrison domain that are quite different from the Archean signatures of the Aillik domain, but similar to the Ketilidian mobile belt of Greenland [16]. Citing the Nd data of Kerr and Fryer [13], Moumblow et al. [6] defined the boundary between the Aillik and Cape Harrison domains as a cryptic Archean-Proterozoic suture (red line, Figure 1c).

In the SW Grenville Province, studies by Dickin and McNutt [9,17] and Dickin [10] linked the southern limit of Archean basement in Ontario to a sharp decrease in Nd model ages, approximately 60 km SE of the Grenville Front (Figure 2). This break in model ages was equated with a cryptic collisional suture (red line, Figure 2) between the Archean foreland and an accreted Paleoproterozoic arc. On the south side of the boundary, ca. 1.90 Ga Nd model ages were interpreted as the crustal extraction age of an oceanic arc formed over a southerly dipping subduction zone [9]. Dickin [8] named this arc "Barilia" based on the location of the U-Pb dated material in the Pointe au Baril (PB) area (Figure 2).

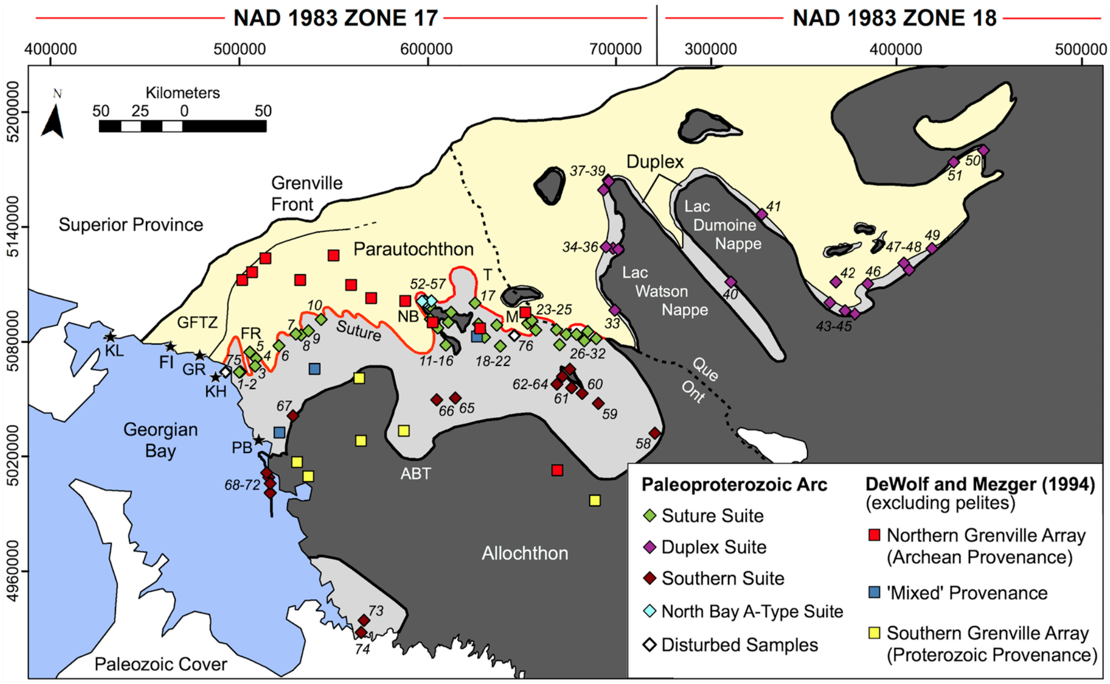

Figure 2. Map of the Southwest Grenville Province and its major tectonic units. Boundaries: Allochthon Boundary Thrust (ABT), Archean parautochthon (yellow shading), Archean-Proterozoic suture (solid red line), Grenville Front Tectonic Zone (GFTZ), and Paleoproterozoic parautochthon (light grey shading). Locations: French River (FR), Mattawa (M), North Bay (NB), and Temiscaming (T). Plutons: Fox Islands (FI), Grondine (GR), Key Harbor (KH), Killarney (KL), and Pointe au Baril (PB). Boundaries established by Dickin et al. [18].

Questioning this interpretation, DeWolf and Mezger [11] presented Pb isotope analyses on feldspars from a variety of rock types spanning across the proposed Archean-Proterozoic suture (squares, Figure 2). They claimed that several samples from the south of the suture had Pb compositions that were indicative of Archean rather than Proterozoic provenance. However, Dickin [19] argued that the discrepancies between Nd and Pb isotope data were due to a lack of consideration of the geologic context of the samples analyzed by DeWolf and Mezger [11], which included pelites, amphibolites, pegmatites, and granites, as well as the quartzo-feldspathic gneisses that are thought to form the oldest crustal basement in the study area.

Conversely, Pb isotope analysis of plutonic orthogneisses that are representative of average crust can be used effectively to test the location of the Archean-Proterozoic suture proposed on the basis of Nd isotope mapping. When used in conjunction with Nd isotope data, Pb signatures of orthogneisses can provide information regarding the timing of magma extraction from the mantle, thus differentiating reworked Archean crust from Paleoproterozoic crust derived solely from a juvenile mantle-derived source. Therefore, we contribute new whole-rock Pb isotope data for the Paleoproterozoic crust across the SW Grenville Province to place additional constraints on the Proterozoic history of the region.

3. Regional Geological Background: SW Grenville Province

The Grenville Province is a one-billion-year-old orogenic belt in the SE Canadian Shield that contains older reworked crustal terranes of Archean to Mesoproterozoic age that were metamorphosed and tectonized during the Grenville Orogenic Cycle [12,20]. The Grenville Front marks the northern limit of a series of northwest-directed thrust sheets that telescoped the earlier Archean-Paleo-Mesoproterozoic margin of Laurentia (Figure 2).

To the south of the Grenville Front, Rivers et al. [12] divided the province into two major longitudinal belts: the parautochthonous and allochthonous belts (Figure 2). The Allochthon Boundary Thrust (ABT) represents a major thrust zone that separates the parautochthonous belt to the northwest from the overriding allochthonous terranes to the southeast (Figure 2). The parautochthonous belt comprises part of the Laurentian foreland that was highly metamorphosed and tectonized during the 980 Ma Rigolet event [20], but remained relatively *in situ* compared to the overriding allochthonous terranes during the 1080−1040 Ma Ottawan collisional event.

Nd isotope mapping in the SW Grenville Province revealed three distinct T_{DM} model age groups in the parautochthonous belt [8], which correlate with those mapped across the Makkovik Province [6,13]. In the Makkovik Province, these distinct age suites are represented by (1) Archean model ages (>2.5 Ga) attributed to metamorphosed or re-melted foreland crust, (2) intermediate model ages (2.49–2.15 Ga) attributed to Proterozoic magmatism with a variable Archean crustal Nd component, and (3) Paleoproterozoic model ages (<2.14 Ga) attributed to juvenile Makkovikian crust. Paleoproterozoic T_{DM} ages are uniform across the Cape Harrison domain SE of the Archean-Proterozoic suture, indicating that the Cape Harrison domain represents an accreted Paleoproterozoic arc [6,13].

Similarly, the first age suite in the SW Grenville Province is located directly south of the Grenville Front with crustal formation ages older than 2.5 Ga (yellow shading in Figure 2). These T_{DM} ages are attributed to metamorphosed equivalents of the Archean Superior Province basement [8]. Reworking of the Laurentian foreland during the Mesoproterozoic subjected the relatively pristine Archean basement to extensive plutonism and migmatization. The mixing of Archean and Mesoproterozoic magmatic sources led to the generation of a second (intermediate) age suite composed of reworked Archean crust with Nd model ages from 2.5 to 2.0 Ga [8,21]. The third age suite was recognized south of the reworked Archean suite, and yields a narrow range of T_{DM} ages from 2.0–1.8 Ga, with an average of 1.9 Ga. This younger crustal belt (pale grey in Figure 2) was attributed to a Paleoproterozoic juvenile arc terrane accreted onto the Laurentian margin during the 1.85 Ga Penokean orogeny. A collisional suture separates this Paleoproterozoic crust from the reworked Archean margin, which has been mapped in detail across the SW Grenville Province [10,21–23] (Figure 2).

In Ontario, the parautochthon shows a widespread episode of Proterozoic granitoid plutonism, likely emplaced during the Killarnean magmatic event. Plutonic rocks of this 1.75–1.70 Ga suite include the Killarney granite north of the Grenville Front, the Grondine and Fox River complexes within the Grenville Front Tectonic Zone, and a 1.74 Ga granitoid orthogneiss near Pointe au Baril [24–26] (Figure 2). In addition, the petrology of the Key Harbor gneiss association reveals a suite of 1.70 Ga plutonic rocks intruded into previously metamorphosed and migmatized gneissic country rocks [27]. This metamorphosed country rock suggests a significant geological history prior to 1.70 Ga. This widespread episode of Proterozoic reworking on the continental margin in Ontario is comparable with the 1.65 Ga Labradorian orogenesis in Southeastern Labrador that significantly reworked Makkovik crust south of the Grenville Front [28].

In Western Quebec, the allochthon was thrust northward over the Archean parautochthon such that the complex surface trace of the ABT delineates the footwall of two major NW trending nappes, the Lac Watson and Lac Dumoine terranes (Figure 2). These thrust sheets were found to include an upper and lower structural deck. The upper (Mesoproterozoic) thrust deck is allochthonous, whereas the lower deck is a slice of Paleoproterozoic crust that was entrained onto the bottom of the allochthon. This is demonstrated by the 2.0–1.8 Ga crustal formation ages in a narrow strip of crust sandwiched between Archean and Mesoproterozoic aged crust. This caused the Archean-Proterozoic boundary to closely follow the lobate shape of the ABT, forming a tectonic duplex [29] (Figure 2).

4. Sampling and Analytical Methods

Whole-rock Pb isotope data were determined for 83 granitoid orthogneisses from across the SW Grenville Province to test the variability of the Pb isotope signatures in juvenile Paleoproterozoic crust. UTM grid references are given in Table 1, and localities are numbered in Figure 2 based on the number (#) column in Table 1. Samples 1–39 and 52–76 are from Zone 17, whereas 40–51 are from zone 18. Analyzed samples were grey gneisses with a minimum of migmatite that were selected as the oldest units present within each outcrop. All samples have T_{DM} ages in the range 2.0–1.85 Ga, which are quoted in Table 1 from published data using the depleted mantle model of DePaolo [30].

Much of the study area has never been subject to modern field mapping. For areas such as the shores of Georgian Bay that have been mapped in detail [31], most Paleoproterozoic rocks are grouped into gneiss associations because plutonic boundaries within the oldest crustal units are unclear. Plutonic boundaries are clearer for cross-cutting Mesoproterozoic granitoids, which are often megacrystic [31]. However, these lithologies were avoided as much as possible in this study, since they do not represent the earliest arc crust.

Pb isotope analysis largely followed the procedures of Dickin [32] using finely powdered whole-rock samples. In that study, all samples were leached before dissolution using warm 6 M HCl overnight prior to dissolution in order to remove sulfide phases that may contain remobilized Pb. However, this process may also leach radiogenic Pb from U-rich minerals such as biotite. Therefore, in the present study, a subset of samples was analyzed both with and without leaching (Table 1) to test the effect of this treatment. No significant difference was observed between the Pb ratios of the unleached samples and their leached counterparts, with all samples falling within the geologic scatter of the main arrays (Figure 3). Therefore, in the present study, the majority of samples were unleached.

After Savillex "bomb" dissolution for four days in HF and HNO_3 followed by HCl, Pb extraction followed standard techniques, using miniature anion exchange columns eluted with HBr and HCl. Samples were loaded with silica gel and phosphoric acid onto single Re filaments and analyzed on a VG 354 mass spectrometer at McMaster University. Average within-run precision on samples was 0.02% (1σ), with the reproducibility of fractionation-corrected Pb isotope ratios in Table 1 estimated at 0.1% (2σ). All data were fractionation corrected (average 0.12% per amu) based on frequent analysis of NBS 981 using the reference values of Todt et al. [33].

Table 1. Lead (Pb) isotope data for samples from the SW Grenville Paleoproterozoic parautochthon.

#	Sample ID	UTM N NAD 83	UTM E NAD 83	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	T_{DM} (Ga)
			Suture Suite				
1	KR3	5081200	524600	17.672	15.470	38.033	1.86 [10]
2	KR4	5081600	525400	18.093	15.513	37.494	1.91 [10]
3	GF67	5085700	532600	17.018	15.369	36.967	1.91 [10]
4	GF63	5089600	532600	18.480	15.562	38.159	1.92 [10]

Table 1. *Cont.*

#	Sample ID	UTM N NAD 83	UTM E NAD 83	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	T_{DM} (Ga)
			Suture Suite				
5	PW5	5092500	528600	17.039	15.419	37.764	1.91 [10]
6	FE11.4	5098200	543600	17.479	15.373	37.197	2.00 [10]
7	NV11	5105700	551600	17.611	15.441	37.439	1.86 [10]
8	NV25	5105700	554600	18.645	15.554	38.545	1.86 [10]
9	NV1	5108500	558100	17.474	15.426	37.207	1.88 [10]
10	NV17	5115400	564000	18.754	15.537	37.538	1.98 [23]
11	PO12	5112160	632250	17.314	15.406	36.439	1.98 [23]
12	BO23	5120500	626600	17.357	15.365	37.462	1.88 [34]
13	BO85	5124500	621900	17.643	15.389	37.149	1.89 [34]
14	BO70	5131500	620600	17.658	15.459	37.237	1.92 [34]
15	BO43	5124300	631700	17.831	15.452	37.373	1.95 [34]
16	BO 34	5129800	632500	17.323	15.412	38.119	1.88 [34]
17	BO8	5136500	644300	18.370	15.519	38.948	1.88 [34]
18	BO5	5125800	647900	16.405	15.288	35.831	1.95 [21]
19	BO1	5122600	649200	16.024	15.282	35.829	1.93 [21]
20	BO2	5119500	652200	16.108	15.255	35.867	1.95 [21]
21	MT88	5126700	657800	18.544	15.544	39.084	1.86 [21]
22	TA32	5116000	661300	16.123	15.307	35.963	1.93 [21]
23	MT2	5130300	674000	18.212	15.537	37.941	1.88 [21]
24	MT55	5132100	676100	17.833	15.479	40.252	1.86 [21]
25	TG14	5127330	678812	17.752	15.478	37.705	1.90 [23]
26	TG13	5121531	692799	16.464	15.294	36.723	1.91 [23]
27	TA3	5129300	689900	17.130	15.361	37.413	1.94 [21]
28	MT71	5127600	695500	16.534	15.309	37.070	1.94 [21]
29	MT68	5128500	700900	16.143	15.235	36.562	1.93 [21]
30	MT5	5125700	705500	15.800	15.205	35.651	1.92 [21]
31	TA21	5130800	706700	15.938	15.219	37.431	1.92 [21]
32	MT65	5127800	711800	18.814	15.524	40.256	1.88 [21]
			Duplex Suite				
33	DR25	5144300	719400	16.754	15.355	36.962	1.97 [35]
34	LF2	5176800	709700	17.040	15.346	36.854	1.96 [35]
35	LF8	5176700	713400	18.057	15.513	38.697	1.99 [35]
36	LF10	5176600	716400	16.574	15.262	37.037	1.96 [35]
37	LW13	5212227	705282	16.871	15.360	37.379	1.90 [23]
38	LW12	5211586	705669	16.052	15.239	36.361	1.96 [23]
39	LW4	5206556	703599	17.631	15.423	37.041	1.93 [23]
40	MZ7	5164763	319468	15.964	15.205	36.840	1.93 [31]
41	LB2	5202110	333410	16.790	15.306	37.480	1.95 [31]
42	LV3	5169100	376100	16.158	15.246	36.615	1.93 [22]
43	MAW9	5158000	373700	17.066	15.404	38.076	1.93 [22]
44	MAW6	5153000	387700	16.817	15.346	36.951	2.00 [22]
45	MAW8	5154300	382200	16.322	15.321	36.962	1.87 [22]
46	LV2	5169500	393500	16.037	15.254	37.201	1.98 [22]
47	Vo163.2	5182100	412200	16.199	15.338	36.165	1.91 [22]
48	RB2	5178700	415300	16.590	15.396	36.479	1.96 [22]
49	BR90.9	5190900	426700	17.083	15.386	38.641	-
50	ZP12	5245400	450600	15.877	15.195	36.871	1.89 [22]
51	ZP 9	5237800	435000	20.541	15.717	41.054	1.85 [22]
			North Bay A-Type Suite				
52	CH28	5133900	617700	17.653	15.342	37.150	1.91 [36]
53	NB102	5134200	621000	16.598	15.223	36.247	1.89 [36]
54	NB12	5132800	619600	17.738	15.327	37.736	1.93 [36]
55	NB6	5133200	616000	16.565	15.250	36.201	1.95 [36]
56	BO69	5132700	618700	17.329	15.298	37.495	1.93 [34]
57	BO67	5133300	617700	17.146	15.295	36.377	2.04 [34]

Table 1. *Cont.*

#	Sample ID	UTM N NAD 83	UTM E NAD 83	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	T_{DM} (Ga)
				Southern Suite			
58	AG6	5081460	284800	17.090	15.399	38.309	1.96 [31]
59	AG1	5093890	718150	17.048	15.424	37.575	1.97 [31]
60	AQ35	5097900	708700	16.508	15.326	36.970	1.94 [18]
61	AQ42	5100000	702700	17.192	15.453	38.382	1.92 [18]
62	AQ6	5100600	694400	16.643	15.336	37.430	1.90 [18]
63	AQ4	5105250	696850	16.431	15.317	36.625	1.92 [18]
64	AQ10	5109600	700250	17.211	15.412	37.677	1.92 [18]
65	KW3	5085000	641500	16.180	15.325	36.697	1.96 [23]
66	KW1	5082600	631700	16.811	15.331	36.367	1.98 [23]
67	SB56.7	5062650	556670	17.126	15.397	36.384	2.00 [37]
68	SH2	5030600	547300	16.882	15.352	36.361	1.90 [38]
69	SH9A	5025300	549900	16.420	15.334	35.960	1.87 [38]
70	SH12	5028400	548700	17.907	15.488	38.286	1.93 [38]
71	SI11	5020360	550730	17.200	15.420	37.856	1.95 [38]
72	SI12	5020470	550700	17.508	15.444	37.700	1.91 [38]
73	GH14	4954406	610035	18.699	15.537	37.302	1.87 [39]
74	GH9	4961020	610588	16.852	15.357	36.710	1.88 [39]
				Disturbed Samples			
75	KR11	5080100	517400	23.603	15.972	36.967	1.92 [10]
76	TG17	5122757	667988	21.338	15.582	38.287	1.98 [23]
				Leached Duplicates			
	NB6	5133200	616000	16.403	15.238	35.734	1.95 [32]
	ZP12	5245400	450600	15.833	15.209	35.891	1.89 [22]
	BO2	5119500	652200	15.821	15.200	35.531	1.95 [21]
	MT5	5125700	705500	15.666	15.189	35.394	1.92 [21]
	BO67	5133300	617700	17.298	15.304	35.843	2.04 [34]
	LW12	5211586	705669	15.966	15.232	35.661	1.96 [23]
	MZ7	5164763	319468	15.648	15.156	35.686	1.93 [31]

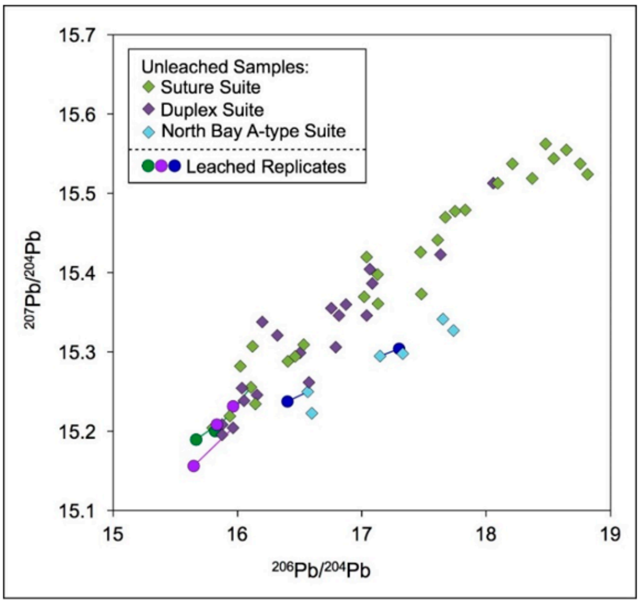

Figure 3. Pb-Pb isochron diagram showing the Pb ratios of replicated leached duplicates relative to their unleached counterparts. Leached-unleached pairs (with tie lines) are plotted with unleached samples from the corresponding Suture, Duplex, and A-type suites (Table 1).

5. Results

Sample localities are plotted in Figure 2 and are subdivided into four suites based on their geographical location. These suites include: (1) the Suture Suite (green diamonds) attributed to samples along the southern margin of the Archean-Proterozoic suture, (2) the Duplex Suite (purple diamonds) attributed to samples in the narrow duplex of Paleoproterozoic crust in Quebec adjacent to the ABT, (3) the Southern Suite (red diamonds) attributed to samples from the southern Paleoproterozoic parautochthon, and (4) the North Bay A-type suite (light blue diamonds) attributed to samples from the North Bay orthogneiss of Holmden and Dickin [36] with anorogenic chemistry. Samples disturbed during younger Grenvillian orogenesis are indicated as white diamonds. Sample localities for feldspar separates analyzed by DeWolf and Mezger [11] are also indicated as squares in Figure 2; however, their pelites were excluded as their provenance is unknown.

Whole-rock Pb isotope data from the SW Grenville Province are plotted on a series of Pb-Pb isochron diagrams following the symbology established in Figure 2. As discussed above, the Pb data in Figure 3 are presented to show the relatively limited effect of leaching prior to analysis. In subsequent Figures 4–7, a single-stage Pb mantle growth curve is plotted using a typical Proterozoic mantle value of 8.0 as a reference for assessing the petrogenesis of the samples [16].

In the following presentation of data, the Paleoproterozoic Suture Suite is believed to have had the simplest geological history, and is therefore presented as the normative data set, with which the other suites are compared. Gneisses from this suite lie immediately south of the proposed Paleoproterozoic suture but avoid secondary geological features that are identified in the other suites (see below). They define a strong array (Figure 4) that is collinear with published Pb data from the juvenile Makkovik Province [6] (orange circles). The Pb signatures from the juvenile Makkovik suite demonstrate a crustal component derived solely from a Paleoproterozoic mantle-derived source resembling the ca. 1.9–1.75 Ga Ketilidian mobile belt of Greenland [16] (light blue circles).

Assuming closed-system Pb isotope evolution, samples from the Paleoproterozoic Suture Suite fall along a 1.74 Ga reference isochron with a similar degree of geologic scatter as the juvenile Makkovik array. The Pb-Pb slope age of ca. 1.74 Ga for the Suture Suite is consistent with the whole-rock Sm-Nd isochron age for the Paleoproterozoic terrane determined by Dickin et al. [37]. It is also consistent with the age of Killarnean plutonism dated at 1742 $\pm$ 1.4 Ma by van Breemen and Davidson [24].

Although the Suture Suite is collinear with the Makkovik and Greenland arrays, it is much less radiogenic. In particular, the lower end of the Suture Suite lies only half as far from the growth curve as the least radiogenic Makkovik samples, implying 50% lower time-integrated U/Pb values. This suggests that U-depletion occurred early in the history of these samples, probably due to high-grade metamorphism during arc accretion, which is therefore interpreted as a crustal accretion–differentiation super-event [7]. This suggests that the rocks presently at the surface in the accreted arc terrane were exhumed from the deep crust during the Paleoproterozoic, long before the Grenville orogeny. If these samples lost much of their uranium during a Paleoproterozoic metamorphic event, this can explain why they were relatively immune to disturbance during the Grenville orogeny. In contrast, two samples that lie well outside the main array are attributed to secondary uranium enrichment during Grenvillian orogenesis (white diamonds, Figure 4).

The Duplex Suite (purple diamonds) defines an array that is strongly collinear with the Suture Suite on a Pb-Pb isochron diagram (Figure 5). This supports the contention that the Paleoproterozoic duplex is derived from crust that is essentially the same as the main Paleoproterozoic terrane south of the suture. Since the duplex was entrained onto the base of the Mesoproterozoic allochthon, this implies that it was exhumed from deeper levels of the crust in the Grenville orogeny. However, the similar range of Pb isotope ratios in the Suture and Duplex suite samples implies a similar range of U/Pb ratios in the two suites. This suggests that the accreted Paleoproterozoic arc terrane was already exhumed from the lower crust during arc accretion, so that no further decrease in Pb isotope ratios could result from further Grenvillian exhumation.

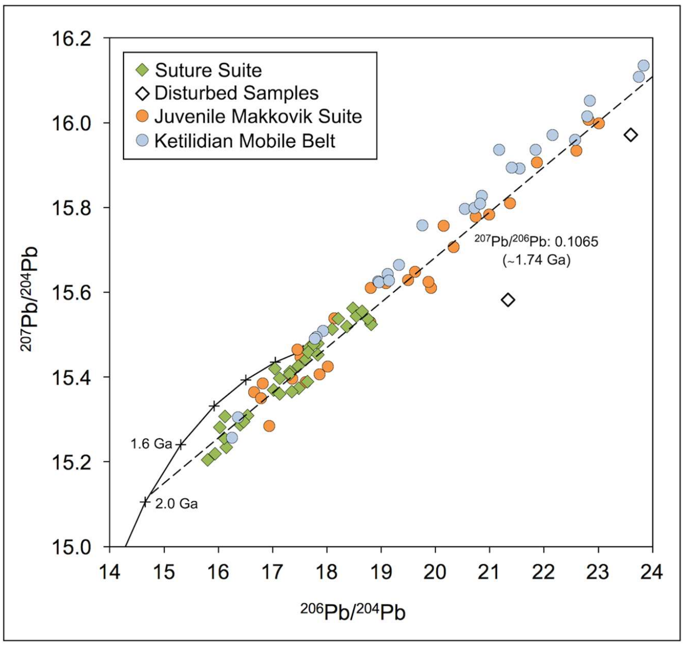

Figure 4. Pb-Pb isochron diagram showing samples from the Paleoproterozoic Suture Suite and disturbed samples, compared with published data from the juvenile Makkovik Province [6] and the Ketilidian Mobile belt [16].

In contrast to the strong collinearity of these two suites, the North Bay A-type suite (light blue diamonds) scatters below the 1.74 Ga regression line (Figure 5) implying a period of Grenvillian magmatism that reworked the parautochthon in this region. On the other hand, the regression line for the North Bay A-type array projects back to the growth curve, yielding a Paleoproterozoic Pb model age that is consistent with the Suture and Duplex suites.

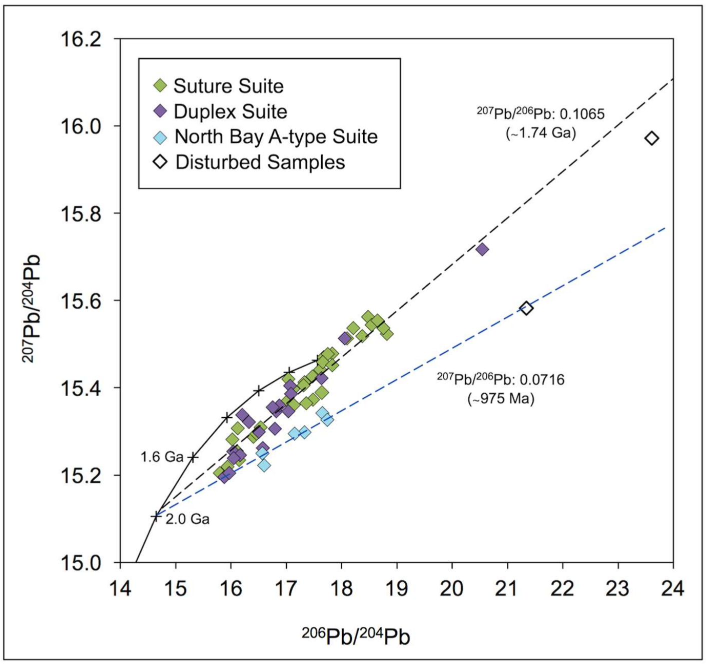

Figure 5. Pb-Pb isochron diagram showing Paleoproterozoic samples from the Duplex Suite and North Bay A-type suite, compared with the Suture Suite and disturbed samples. Pb data are plotted against the 1.74 Ga reference line from Figure 4 (black dotted line).

Pb signatures for gneisses from the Southern Suite are shown by red diamonds in Figure 6. Based on their location nearer the original edge of the Proterozoic continental margin, it was anticipated that these samples may have undergone a greater degree of late Paleoproterozoic magmatic reworking [38]. To test this idea, they are compared in Figure 6 with the Suture Suite, and with published Pb isotope data from Loewy et al. [40] for samples with Labradorian (1.65 Ga) intrusive ages (black circles). The Labradorian suite represents late Paleoproterozoic magmatism that extensively reworked older Makkovikian crust [28]. The Southern Suite from Ontario lies slightly above the Suture Suite in Figure 6, and overlaps with the Labradorian suite, supporting the model of younger reworking of these samples during the late Paleoproterozoic or Mesoproterozoic.

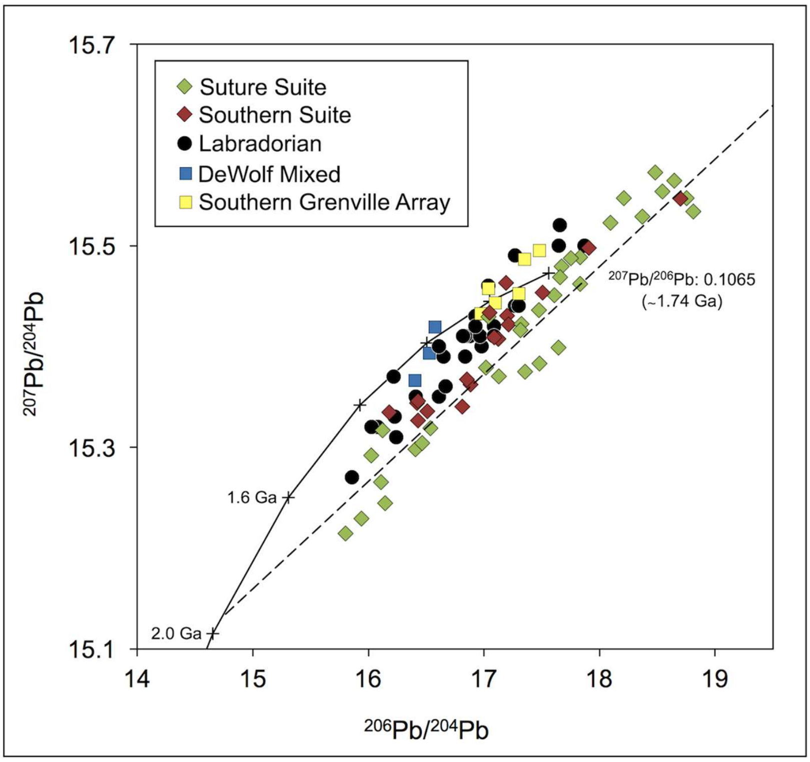

Figure 6. Pb–Pb isochron diagram showing Pb data from the Suture Suite and Southern Suite compared with published Pb data from the Labradorian array [40], the Southern Grenville Array of DeWolf and Mezger [11], and samples they attributed to mixed Archean—Proterozoic provenance. Pb data are plotted against the 1.74 Ga reference line from Figure 4. Axes adjusted relative to Figures 4 and 5.

The Southern Grenville Array of DeWolf and Mezger [11] falls within the Labradorian array when plotted on Figure 6 (yellow squares). Gneisses from the Southern Grenville Array represent allochthonous crust just south of the ABT in Ontario. Likewise, the 'transitional' samples of DeWolf and Mezger [11] have Pb isotope ratios that overlap with the Labradorian array, thus resembling Paleoproterozoic arc crust that was reworked extensively during the early Mesoproterozoic (blue squares).

Pb isotope ratios for gneisses from the Archean parautochthon of Ontario [32] are plotted on the Pb–Pb isochron diagram in Figure 7 (black crosses). As expected, the Archean suite yields a much steeper array than the Paleoproterozoic Suture Suite and juvenile Makkovik suite, but has a similar distribution to galena ores [41] from the Aillik domain of the Makkovik Province (blue crosses). The composition of these ores was attributed by Wilton [41] to remobilized Archean Pb.

Dickin [32] interpreted the Archean array from the Ontario parautochthon as a transposed 2.7–1.1 Ga paleoisochron. However, unleached samples of Archean crust yield a somewhat lower slope age, much nearer the 2.75 Ga age of Superior Province basement [42]. This suggests that the steeper slope of the transposed paleoisochron produced by leached samples was partly an analytical artefact. Samples with high U/Pb ratios are much more susceptible to U mobilization during a secondary metamorphic event. When the samples with highest $^{207}Pb/^{206}Pb$ ratios are removed from the regression (open red diamonds), the remainder of the suite yields a single-stage Pb/Pb age of 2.96 Ga that is closer to the Sm-Nd age. Therefore, we surmise that samples with high $^{207}Pb/^{206}Pb$ ratios suffered selective leaching of Pb from secondary sites containing remobilized U.

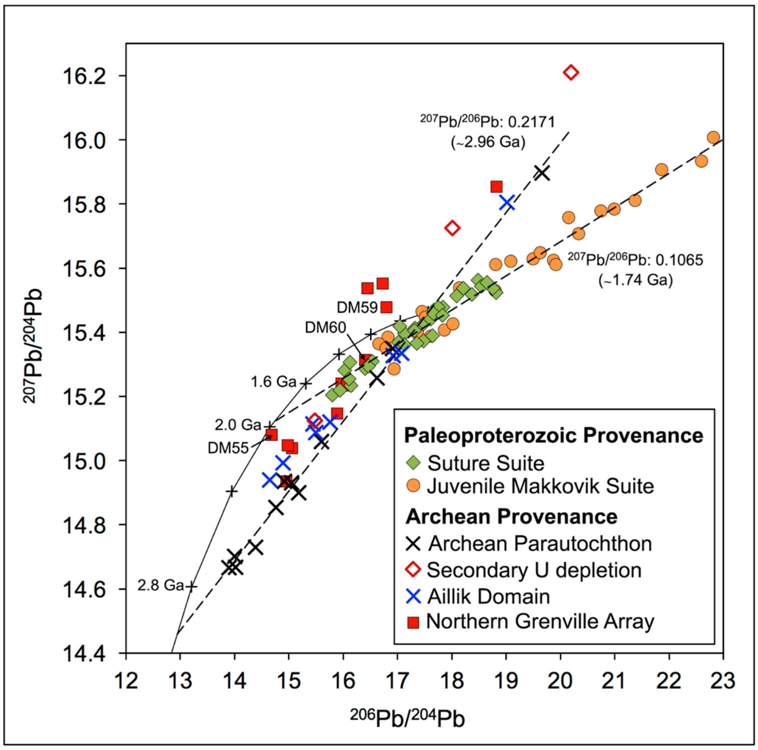

Figure 7. Pb–Pb isochron diagram of published Pb data for orthogneisses from the Archean parautochthon in Ontario [32], Northern Grenville Array of DeWolf and Mezger [11], and Galena separates from the Aillik domain in the Makkovik Province [41] demonstrating Pb arrays that project back to the Archean. Published Pb data is plotted against Paleoproterozoic samples from the Suture Suite and the juvenile Makkovik Province [6] for reference. Axes adjusted relative to Figures 4 and 5.

Archean samples from the Northern Grenville Array of DeWolf and Mezger [11] lie to the left of the whole-rock array of Dickin [33], as expected for feldspar separates (red squares in Figure 7). However, the feldspar data actually show more scatter than unradiogenic whole-rock data. This shows that suitably selected whole-rock samples show more coherent Pb ratios than feldspar separates from a wide variety of rock types. The new whole-rock Pb isotope data show a clear distinction between Archean and Paleoproterozoic crust in the SW Grenville Province that is comparable with the distinction between the reworked Archean margin and accreted juvenile Makkovik crust in Labrador.

When plotted on a thorogenic versus uranogenic Pb diagram (Figure 8), gneisses from the four Proterozoic Grenville suites show more scatter than was observed for uranogenic data alone. This is normal, but the Ontario samples also show some distinction from the juvenile Makkovik suite. The higher uranogenic/thorogenic Pb ratios in the latter suite may indicate more intensive ensialic arc reworking, since their Pb signatures match those of disturbed samples from Ontario attributed to secondary U enrichment. However, Makkovik ensialic arc reworking probably occurred soon after crustal extraction, so that the uranogenic Pb isotope systematics were not disturbed. In contrast, the samples with high uranogenic/thorogenic Pb signatures from the SW Grenville province also have abnormal uranogenic Pb isotope ratios and therefore were probably disturbed much later, during younger Grenvillian orogenesis.

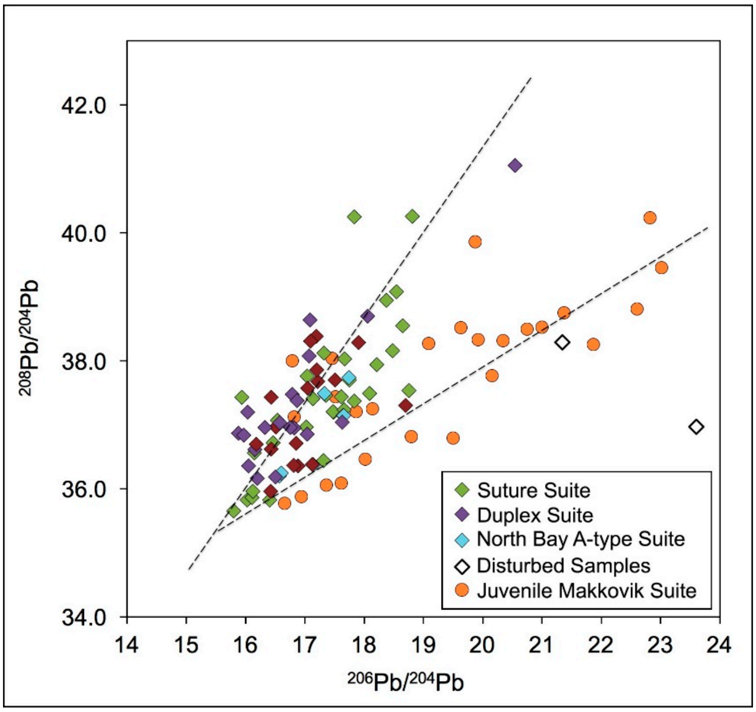

Figure 8. Plot of thorogenic versus uranogenic Pb showing Proterozoic samples from the four SW Grenville suites compared with published data from the juvenile Makkovik Province [6].

6. Lithochemical Data

Major element data were available for a subset of the samples analyzed. Although the data are limited, it is thought that they are representative of the suite as a whole. This is because samples without major element data were collected to give more detailed geographical coverage of terrane boundaries, but with the same petrological selection criteria (preference for grey gneisses with apparent granodioritic affinity).

The petrology of Paleoproterozoic crust across the SW Grenville Province can be characterized using the petrochemical Streckeisen grid of Debon and LeFort [43] (Figure 9). The aim of this diagram is to describe the petrological affinity of each sample using their Q (quartz) and P (plagioclase vs. K-feldspar) indices based on major-element chemistry. Archean gneisses from western Quebec trend across the left of the diagram, through the quartz diorite and tonalite fields (black crosses, Figure 9). This reference suite represents lateral equivalents of Superior Province crust, whose petrological signatures are attributed to the accretion of oceanic arc fragments during the Kenoran orogeny [22]. In contrast, the juvenile Makkovik suite shows a more alkaline character, and trends diagonally across the middle of the diagram. Samples from this reference suite are characteristic of a more mature continental arc setting, as these gneisses were formed from ensialic arc magmatism, following the accretion of a juvenile Makkovikian arc to the Archean continental margin [6].

Major element whole-rock data for the Proterozoic Grenville samples were obtained from the published sources indicated in Table S1. A significant overlap with the juvenile Makkovik suite shows that the Proterozoic gneisses analyzed in this study have a more alkaline character than the Archean crust. This is indicative of reworking of the accreted Paleoproterozoic terrane by ensialic arc magmatism during the late Paleoproterozoic and early Mesoproterozoic. Samples from the North Bay A-type suite cluster within the granite field, which is indicative of their more evolved geologic history [36].

Trace element identification, using Y versus Nb, and Y and Nb versus Rb discrimination diagrams, supports an ensialic arc environment for the Paleoproterozoic Grenville gneisses (Figure 10; Table S1). In both plots, samples from the Paleoproterozoic Grenville suites lie mainly within the volcanic arc granite field (VAG) overlapping the juvenile Makkovik suite. This is consistent with previous interpretations that these gneisses were once part of an island arc that was magmatically reworked in a continental arc setting [17]. Three samples from the North Bay A-type suite with higher Y and Nb contents (53, 55, 56, light blue diamonds) lie in the within-plate granite field (WPG). These samples are part of the North Bay area orthogneisses and are therefore representative of younger plutonic rocks with disturbed Pb signatures [36].

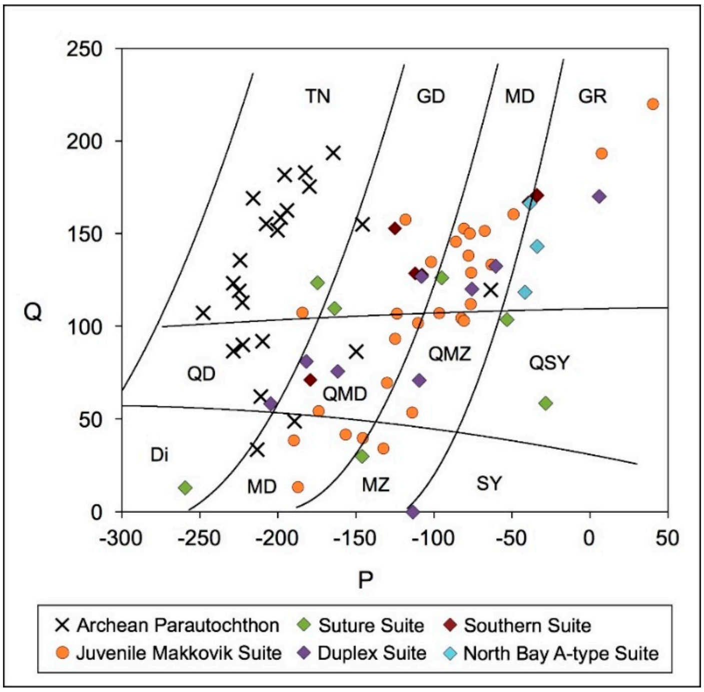

Figure 9. Petrochemical grid of Debon and LeFort [43] for the chemical Streckeisen classification of granitoid rocks. Q, 1/3 Si-(K + Na + 2/3Ca); P, K-(Na + Ca). Tonalite (TN), granodiorite (GD), monzogranite (MG), granite (GR), quartz diorite (QD), quartz monzodiorite (QMD), quartz monzonite (QMZ), quartz syenite (QSY), diorite (DI), monzodiorite (MD), monzonite (MZ), and syenite (SY). Published data for the Archean parautochthon [22] and juvenile Makkovik Province [6].

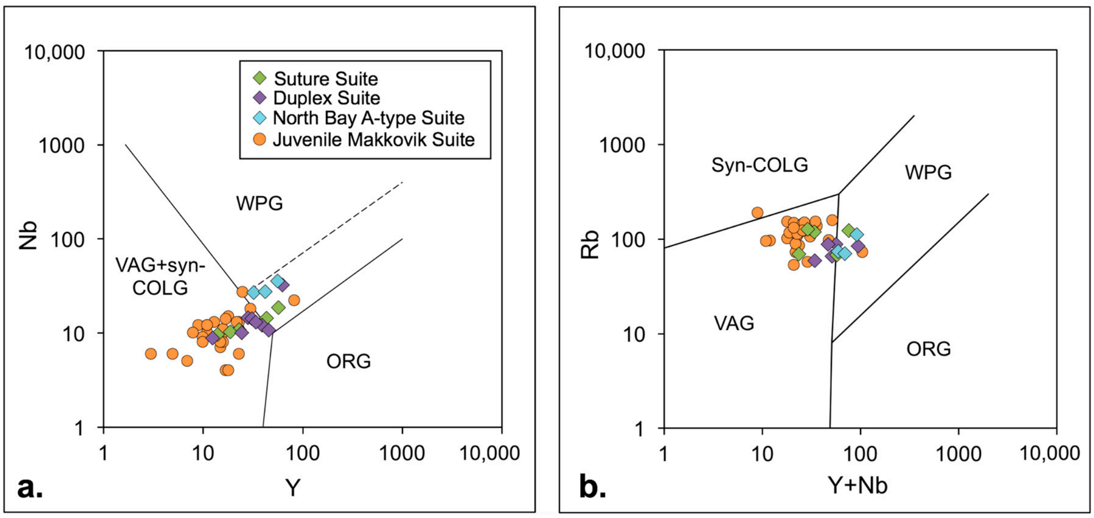

Figure 10. Discrimination diagrams of: (**a**) yttrium (Y) versus Nb and (**b**) Y and Nb versus Rb after Pearce et al. [44]. Volcanic arc granites (VAG), syn-collisional granites (Syn–COLG), orogenic granites (ORG), and within plate granites (WPG). Published data for the juvenile Makkovik Province [6].

7. Discussion and Conclusions

Isotopic data from Wisconsin, Labrador, and Southern Greenland suggest an Archean-Paleoproterozoic collisional regime along the Laurentian continental margin between 2.0 and 1.8 Ga [4,6,16]. Whole-rock Pb-Pb data presented in this study differentiate Proterozoic juvenile crust in the SW Grenville Province of Ontario from the Archean craton and suggest a solely Proterozoic crustal source for Pb in the four Proterozoic Grenville suites discussed above. Therefore, the following discussion will focus on the Proterozoic Pb history of the region and the tectonic inferences that can be drawn.

7.1. Southern Extent of Archean Basement

Three samples analysed by DeWolf and Mezger [11] with suggested mixed Pb provenance (DM46, DM53, and DM57; Figure 11) have Pb isotope ratios that lie alongside the Proterozoic array in Figure 6. This is significant as all three samples lie within our Paleoproterozoic terrane. However, DeWolf and Mezger [11] claimed that three samples of possible Archean provenance lie to the south of our proposed Archean-Proterozoic suture (DM55, DM59, and DM60; Figure 11). They proposed a boundary for the southern extent of "Archean crustal influence" based on their Pb data on feldspars (blue dotted line, Figure 11). However, the Pb composition of sample DM60 plots collinear with our Proterozoic data in Figure 7. A Proterozoic provenance for this sample is almost inevitable as it is located south of the ABT in the Mesoproterozoic allochthonous belt [18].

Of the two other samples in question, DM59 is located in the city of North Bay. Moore and Dickin [23] showed that a lobe of Archean crust extends southward across Lake Nipissing in this vicinity (Figure 11). Hence this sample might be from the edge of Archean basement to the west of the North Bay allochthonous klippe. Based on its locality, the final sample with possible Archean affinity (quartzofelspathic gneiss DM55) is inferred to represent a screen of country rock within the Mesoproterozoic Bonfield Batholith. However, the Pb ratio of this sample is questionable, since it lies to the left of the main Archean data array in Figure 6. Overall, we conclude that there is a lack of any clear Archean Pb signatures south of the suture delineated based on Nd isotope mapping. This suggests that there was no Archean basement below the Paleoproterozoic arc terrane at the time of crustal formation. This is comparable to the accreted juvenile arc in the Makkovik Province [6].

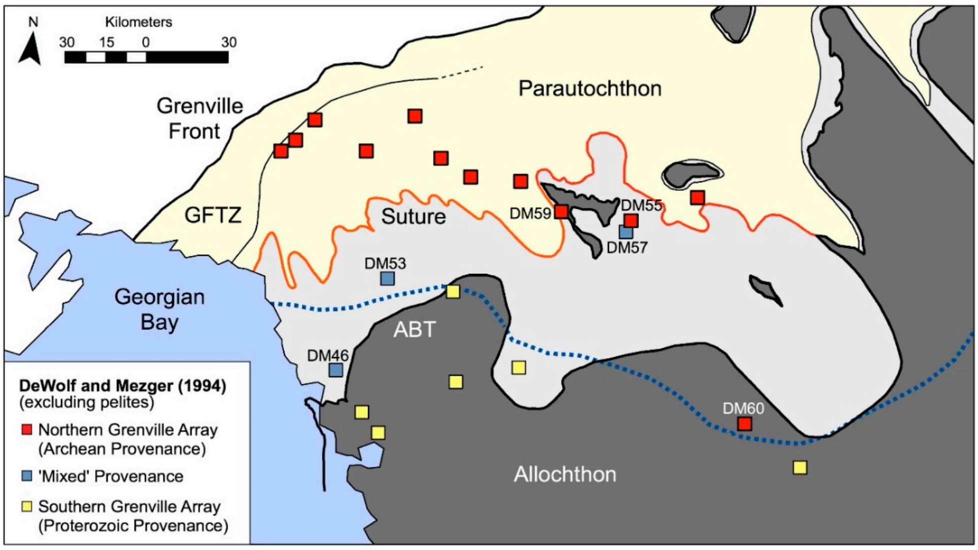

Figure 11. Map of the SW Grenville Province showing sample localities of DeWolf and Mezger [11] with their boundary for the southern limit of Archean crustal material (blue dotted line). Other boundaries and terranes determined by Dickin et al. [18]: Allochthon Boundary Thrust (ABT), Archean parautochthon (yellow shading), Archean-Proterozoic suture (solid red line), and Paleoproterozoic parautochthon (light grey shading). Grenville Front Tectonic Zone (GFTZ).

7.2. Paleoproterozoic Evolution of the SW Grenville Province

Ketchum et al. [14] attributed the Makkovik Province to a 1.9 Ga arc accretion event, caused by the attempt to subduct the Archean margin under a ca. 2 Ga oceanic arc. They proposed that arc accretion was followed by subduction-flip, establishing an ensialic arc on the new margin. This model was supported by Moumblow et al. [6], but they rejected a second arc accretion event suggested by Ketchum et al. [14], since there is no evidence for two distinct arcs within the Cape Harrison domain.

One piece of evidence that strongly supports the initial attempt to subduct the continent under the arc and not vice-versa is the preservation of pre-1.9 Ga passive margin sedimentary sequences on the foreland side of the Makkovik orogen. These sediments would likely have been destroyed if subduction was initiated under the Archean margin because this would have led to the uplift and erosion of the margin. In contrast, arc accretion on the Archean margin depressed the craton edge, preserving its older passive margin supracrustal sequences.

After arc accretion, depression of the craton margin led to the development of a retro-arc foreland basin over the older supracrustal sequence. Development of this foreland basin was facilitated by a relaxation in the compressive stress across the orogeny after the initiation of cratonward subduction. However, this relaxation of stress only lasted for ca. 20 Ma, after which the compressive regime returned, perhaps associated with a shallowing of the subduction angle.

The subduction-flip model for the Makkovik Province makes it almost identical to the Paleoproterozoic evolution of the SW Grenville Province proposed by Dickin and McNutt [17]. This model is therefore summarized here (Figure 12) to emphasize the detailed evidence in support of the arc-accretion subduction-flip model.

Early stages of Paleoproterozoic crustal evolution in the SW Grenville Province began with the southeastward subduction of oceanic crust beneath an approaching outboard arc prior to the Penokean event (Figure 12a). Southerly dipping subduction accounts for the lack of any Penokean-aged plutonism (ca. 1.9−1.8 Ga) in the Archean foreland [9,25].

The attempt to subduct the foreland margin under an accreted arc (Figure 12b) can explain the preservation of radiogenic upper crustal Pb signatures [32] immediately north of the Archean-Proterozoic suture in the French River (FR) area of Ontario (Figure 2). Conversely, unradiogenic Pb signatures in the accreted Penokean arc provide evidence for deep exhumation of the core of the arc after accretion due to back-thrusting in the arc (Figure 12c) [45]. Hence, the Paleoproterozoic Pb data from south of the suture strengthen the argument of Dickin [32], which states that the Archean margin was over–ridden during the Paleoproterozoic by a Penokean arc, causing differential uplift on opposite sides of the suture [45].

Nd model ages across the Grenville parautochthon distinguish crust of Archean provenance northwest of the suture from crust with Paleoproterozoic provenance to the southeast. This is supported by the new Pb data in Figure 7 that illustrate a clear distinction between Archean and Proterozoic crustal signatures north and south of the suture, respectively. These breaks in Nd and Pb isotopic signatures are consistent with those across the Archean-Proterozoic boundary in the Makkovik Province, which was interpreted as a cryptic suture between the Laurentian margin and an accreted Paleoproterozoic arc [6]. Both sutures are cryptic due to the intensity of ensialic arc plutonism after arc accretion. In both cases, there are no recognized *in situ* vestiges of the original arc, but it is preserved in the isotope signatures of the ensuing ensialic arc plutonism.

Metasedimentary gneisses containing abundant quartzite overlie the Archean margin near the French River, Temiscaming, and the Ontario-Quebec border north of Mattawa [21,23,32] (Figure 2). Nd isotope evidence [36] reveals a range of isotopic compositions for these rocks, attributed to mixing of sediment from Archean and Paleoproterozoic sources. The accretion of a Penokean arc would have caused loading of the continental margin and subsequent depression in the back–arc region, forming a foreland basin (Figure 12c). A similar scenario is observed behind the accretionary margin of the Makkovik Province in which the supracrustal units from the Aillik Group were deposited in a retro–arc basin ca. 1.86−1.85 Ga [6,14].

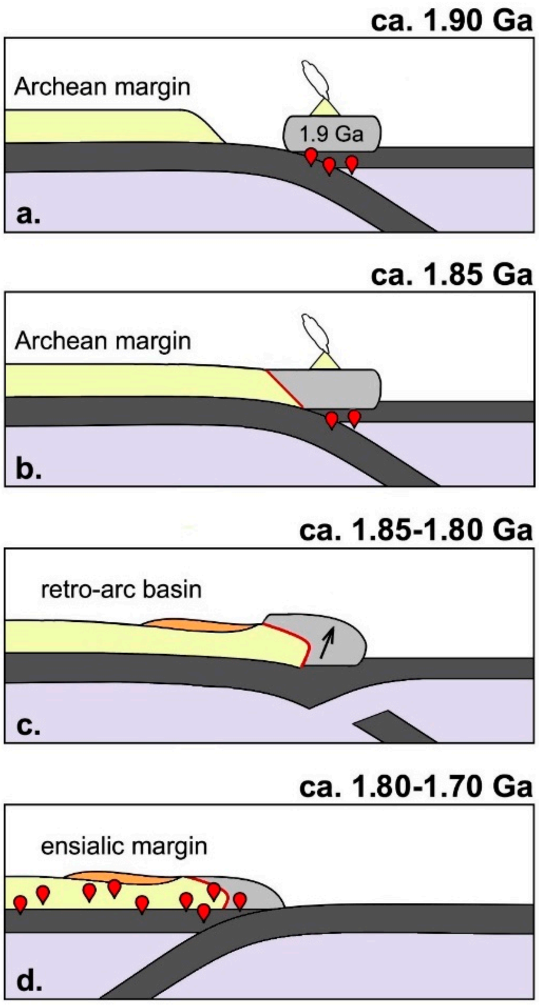

Figure 12. Proposed model for the Paleoproterozoic evolution of the SW Grenville Province based on the interpretation of Dickin and McNutt [17].

Evidence for a Paleoproterozoic crustal source in the SW Grenville province is further supported by the Kiosk quartzite south of the proposed Penokean arc. Detrital zircons in this unit reveal a frequency maximum U-Pb age of 1850 Ma [46]. The abundance of Paleoproterozoic zircons suggests inheritance from a nearby Penokean terrane, thus validating our model for the accretion of a Penokean arc in the SW Grenville Province around 1.85 Ga.

Following the accretion of the Penokean arc to the Archean craton, a flip to cratonward subduction resulted in the formation of a long-lived ensialic margin on the Archean-Paleoproterozoic margin (Figure 12d). This change in subduction direction is constrained by the timing of igneous activity on the Archean-Paleoproterozoic composite margin dated to ca. 1.75−1.7 Ga [24,26]. These intrusions, corresponding to the Killarnean magmatic event, are analogous to the timing of long-lived ensialic arc activity in the Makkovik Province [6]. Extensive Killarnean plutonism south of the Penokean suture is reflected in the Pb-Pb slope age for the Paleoproterozoic Grenville arrays. However, an average ca. 1.90 Ga Nd model age for crust south of the suture emphasizes the melting of mafic rock at the base of the Penokean arc rather than juvenile mantle-derived magmatism [17,37].

The strongly overlapping Pb signatures in the Suture Suite and the Duplex Suite (Figure 5) suggest a similar origin of the Paleoproterozoic crust in Ontario and Western Quebec. However, the Archean-Proterozoic boundary in Western Quebec represents a Grenvillian thrust zone rather than a collisional suture. The thin sliver of Paleoproterozoic crust sandwiched between the Archean

Parautochthon and ABT can be interpreted as a tectonic duplex that was entrained onto the base of the allochthon from buried Paleoproterozoic parautochthonous basement further south [29].

The chemistry of the locally-distributed North Bay A-type suite (Figure 2) suggests a complex geologic history for the crust between the North Bay klippe and the Archean-Proterozoic suture. However, the Pb isotope data indicate no detectable Archean inheritance for these samples. The anorogenic nature of the North Bay A-type suite is likely the result of post-tectonic magmatism on the accreted Paleoproterozoic continental margin. However, further investigation is necessary to better understand the post–Paleoproterozoic history of this orthogneiss suite.

Overall, the Pb isotope signatures presented here show evidence of juvenile crustal addition and extensive magmatic reworking during the late Paleoproterzoic and early Mesoproterozoic eras. This suggests that the SW Grenville Province shares a similar Proterozoic evolution with the Makkovik-Ketilidian orogeny to the northeast [6,16]. The addition of a Penokean arc to the Laurentian margin was followed by a span of nearly 500 million years of intermittent ensialic arc magmatism and crustal growth, which was brought to an end during the terminal Grenville orogeny [17].

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3263/8/7/247/s1, Table S1: Published major and trace element data.

Author Contributions: G.A.A. and A.P.D. conceived, designed, and performed the experiments; G.A.A. analyzed the data, wrote the paper, and prepared the figures.

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