

A trace element and chemical Th–U total Pb dating study in the lower Belt-Purcell Supergroup, Western North America: Provenance and diagenetic implications

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Abstract

Comprehensive geochemical and monazite chemical age data on the Mesoproterozoic Belt-Purcell Supergroup reveals information on provenance age(s), and the sources of interbedded argillites and sandstones. Compliance of rare earth element (REE) and multi-element patterns of argillites to post-Archean upper continental crust (PA-UCC), and Cr–Ni, and Th/Sc–Sc systematics are consistent with a dominantly post-Archean source area. Sandstones have the same geochemical fingerprint as argillite for the Appekunny and Grinnell formations in the lower Belt-Purcell Supergroup sequence, albeit variably depleted by detrital quartz. Sandstone developed in a separate high-energy environment, and argillite and sandstone became interbedded during storms, accounting for the sharp interbedding of the two facies.

Detrital monazite chemical Th–U total Pb ages from the Appekunny and Grinnell sandstones, and argillites of the former, cluster at ~1700 Ma. Paleocurrents and chemical ages support a Laurentian Paleoproterozoic provenance, likely the Yavapai, Mazatzal and Central Plains provinces. Other potential sources could have been terranes at ~1875–1750 Ma that cooled through the blocking temperature of monazite ~1700 Ma such as the Wyoming Province. Rare >2500 Ma monazite ages in argillite and sandstone stem for minor contributions from Archean terrane(s).

Diagenetic overprint in the Belt-Purcell rocks is widespread and displayed geochemically as heavy REE enrichment relative to light REE, normalized to PA-UCC. There are two populations of monazites: the first has detrital textures, with chemical ages >~1400 Ma, higher ThO₂ and Y, and lower LREE/HREE content than <~1400 Ma monazites with euhedral texture, ages up to ~900 Ma post-deposition, with lower ThO₂ and Y, and higher LREE/HREE content. The second population is interpreted as the product of protracted migration of basinal brines that mobilized HREE, as documented in several Proterozoic sedimentary basins. © 2005 Elsevier B.V. All rights reserved.

Keywords: Mesoproterozoic; Sedimentary rocks; Belt-Purcell Supergroup; Provenance; Diagenesis; Monazite; Chemical age

1. Introduction

The Belt-Purcell Supergroup is a Mesoproterozoic, dominantly siliciclastic, sedimentary sequence ~15–20 km thick, located in northwestern Montana and southern Alberta and British Columbia. This

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Supergroup was deposited at ~ 1470 – 1400 Ma as part of a series of intracontinental rifts (e.g., Höy, 1989; Chandler, 2000; Lydon, 2000; Poage et al., 2000) that developed as the Mesoproterozoic supercontinent Columbia dispersed (Zhao et al., 2004; Rogers-John and Santosh, 2004). The provenance of the Belt-Purcell Supergroup has been controversial, and addressed both from sedimentological and stratigraphic criteria, as well as geochronological data on detrital zircons and monazites (e.g., Harrison, 1972; Frost and Winston, 1987; Winston, 1990; Ross et al., 1992; Whipple et al., 1997; Ross and Villeneuve, 2003). Paleocurrents and geographic variations in the stratigraphic thickness of several formations are consistent with an eastern source in Laurentia, and in other formations a separate western provenance. Specifically, in the lower Belt-Purcell sequence, sandstones were interpreted to have a provenance in Laurentia to the southeast, whereas argillites (fine-grained sedimentary rock that includes shale, mudstone, siltstone, and claystone) were transported from a western catchment (Winston, 1990; Link, 1997; Whipple et al., 1997) that, depending on paleoreconstructions of Columbia, could be Paleo- or Mesoproterozoic terranes of

Australia or East Antarctica that match the age of detrital minerals in the lower Belt-Purcell sequence (1920–1460 Ma and less abundant Archean ages; Ross et al., 1992; Ross and Villeneuve, 2003).

The rare earth elements (REE), Th, Y, Co, and Sc are in many cases preserved when transferred from provenance areas into the sedimentary budget of many siliciclastic sequences. Consequently they preserve the geochemical fingerprint of the source areas, and have been used in many geochemical studies to address provenance (e.g., Taylor and McLennan, 1995; Fralick and Kronberg, 1997; Fralick, 2003; McLennan et al., 2003). Accordingly, this paper builds on the existing sedimentological and stratigraphic literature on the Belt-Purcell Supergroup, and geochronological studies of detrital minerals. New high-precision geochemical analyses of extensive argillites and sandstones are reported from the Appekunny and Grinnell formations (Ravalli Group; Fig. 2A) at Waterton-Glacier International Peace Park, as one proxy of their provenance, inasmuch as there are few modern high precision analyses of this part of the Belt-Purcell sedimentary rocks. The Appekunny and Grinnell formations were selected as they are characterized by well-developed interbedding of sandstones and argillites. To complement

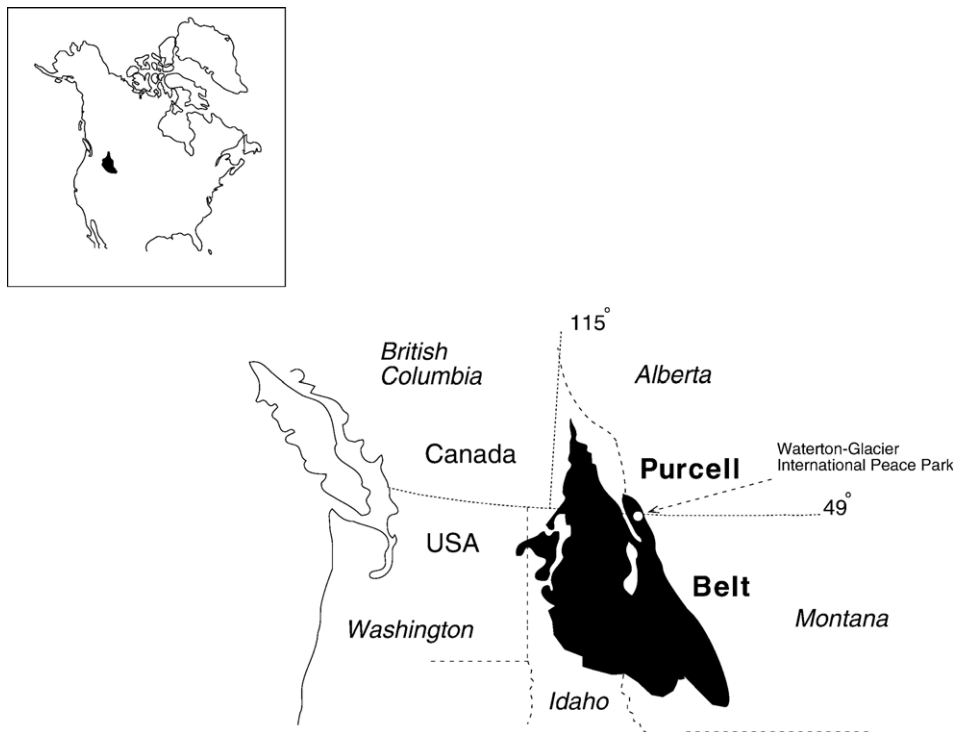


Fig. 1. Generalized geographic location of the Belt-Purcell Supergroup outcrops spanning the Canada–USA border.

the whole rock geochemistry, chemical Th–U total Pb ages of monazite grains from both facies of the same stratigraphic levels have been measured, to build on previous studies of detrital zircons and monazites of sandstones of the Belt-Purcell Supergroup (cf. Ross et al., 1991, 1992; Ross and Villeneuve, 2003).

2. Geologic setting

The preserved Belt-Purcell sedimentary sequence extends 500 km from southwestern Montana, where it is known as the Belt Supergroup, to southeastern British Columbia, where it is referred to as the Purcell

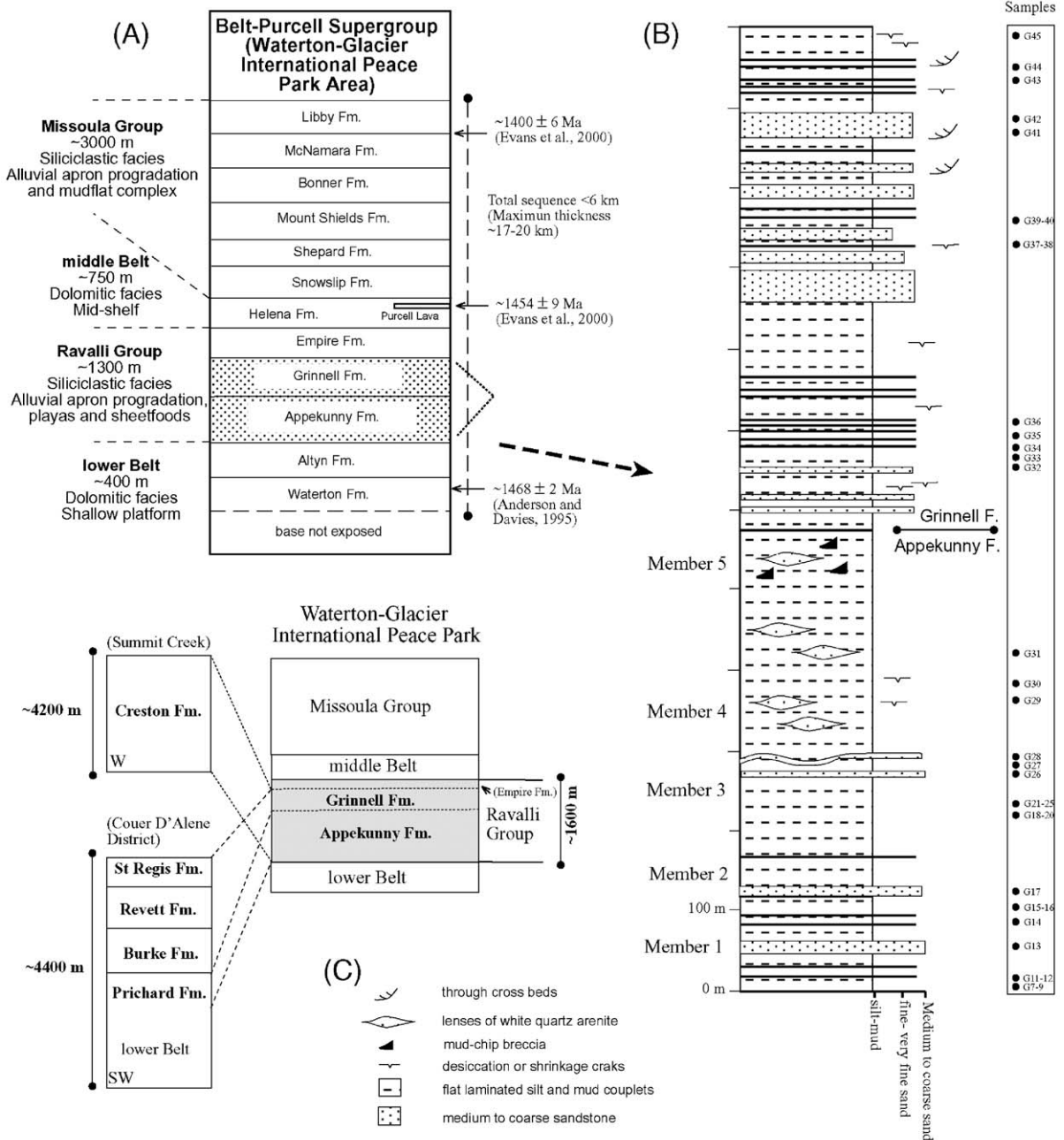


Fig. 2. (A) General stratigraphic sequence of the Belt-Purcell Supergroup at Wateron-Glacier International Peace Park (based on Whipple et al., 1997). (B) Lateral correlation of the Appekunny and Grinnell formations (McMechan, 1981; Whipple et al., 1984; Winston, 1990). (C) Stratigraphic situation of samples used in the present study (Whipple et al., 1984; Link, 1997).

Supergroup (Fig. 1). It outcrops in an anticlinal structure of the Purcell Anticlinorium (Yoos et al., 1991). This Supergroup overlies igneous and metamorphic basement rocks of Archean to Paleoproterozoic age, which are only locally exposed (Kleinkopf, 1997), as well as Cretaceous sedimentary rocks (Yin and Kelly, 1991).

The Belt-Purcell Supergroup has been divided into four main stratigraphic divisions: the lower Belt, Ravalli Group, middle Belt, and Missoula Group (Fig. 2A; e.g., Whiple et al., 1984; Earhart et al., 1984; Winston, 1986). The lower Belt is interpreted as platform carbonate and subtidal turbidites (McMechan, 1981; Whiple et al., 1984). These rocks grade upwards into the Ravalli Group, which includes the Appekunny, Grinnell, and Empire formations, composed dominantly of argillites with interbedded crossbedded medium-coarse-grained sandstone viewed as subaerial and shallow water facies (McMechan, 1981; Winston, 1990; Whiple et al., 1997). In turn, the Ravalli Group grades into the middle Belt carbonate, the Helena Formation, interpreted as mid-shelf limestones (Pratt, 2001). The stratigraphically highest Missoula Group comprises a wide variety of siliciclastic facies that have been interpreted as the result of progradational alluvial aprons and mudflat complex (e.g., Winston, 1984; Whiple et al., 1997).

From trace element systematics of tholeiitic gabbros and diorites of the Moyie sills intruded into the lower Belt, Anderson and Goodfellow (2000) suggested their origin as the result of intraplate magmatism. Ross and Villeneuve (2003) documented predominant sediment input from the west, rapid rates of subsidence, and large-scale facies distributions, which they interpreted as evidence for an extensional basin to the west, comparable to a Black Sea-type setting. Sears et al. (2004) interpreted the large volume of siliciclastic detritus to reflect fluvial transport from a low relief, continent-scale catchment. Lower units were deposited during active rifting, whereas the upper Belt is considered to represent basinal subsidence from thermal contraction of the lithosphere (Sears and Price, 2000; Lydon, 2000).

Previous studies constrained the duration of sedimentation for the Belt-Purcell Supergroup to be ≤ 75 Ma. The lower-middle Belt spans ≤ 25 Ma, with a minimum age of sedimentation constrained at 1468 ± 2 Ma and 1469 ± 3 Ma by U-Pb dating of zircons in a sill situated near the base of the Supergroup (Anderson and Davis, 1995; Sears et al., 1998), whereas a maximum age of 1454 ± 9 Ma is determined from zircons in a tuff horizon at the upper part of the middle Belt carbonate (Fig. 2A; Evans et al., 2000).

The Belt-Purcell Supergroup records a range of metamorphism from subgreenschist in the upper

sequence, through greenschist facies in the northeast, to amphibolite facies in the southwest (Maxwell and Hower, 1967; Harrison, 1972). In the Jurassic-Paleocene (160 to 60 Ma), during the Laramide event of the North American Cordillera, the Belt-Purcell Supergroup was displaced eastward by thrusting, being completely detached and emplaced onto the basement and Cretaceous strata.

There are several key characteristics of the Belt-Purcell Supergroup: (1) an enormous amount of subsidence over 75 Ma; (2) large volumes of detrital input; (3) and a consistency of sediment contribution for almost 75 Ma indicating long semi-continuous deposition interrupted by hiatuses but not major unconformities (Harrison, 1972).

3. Sample design

The Appekunny and Grinnell formations were selected for this study given that they are mainly argillites interbedded with sandstones. Both formations are thick and are well exposed throughout the Belt basin. These formations are differentiated based on color and abundance of sandstone-argillite interbedding. In Waterton-Glacier International Peace Park and the Whitefish Range they are 670 m and 800 m thick respectively (Whiple et al., 1984). These siliciclastic rocks are dominantly argillites with white sandstones interbedded more developed at the top of the upper Grinnell Formation (which include quartzarenites, subarkoses, and sublitharenites; terminology of Folk, 1968; Fig. 2B; e.g., Whiple et al., 1984, 1997; Winston, 1990). Their metamorphic grade is lower greenschist facies. The presence of interbedded argillites and sandstones in these two formations allows testing of hypotheses for distinct or common provenance of these two facies for the lower Belt-Purcell sequence, both by whole rock compositions and monazite chemical age populations.

Winston (1989, 1990) interpreted the whole Ravalli Group, which includes the Appekunny and Grinnell formations, as the result of prograding alluvial aprons, playa-lakes and sheetfloods, whereas McMechan (1981) viewed the laterally equivalent Creston Formation to the northwest as subtidal to tidal deposits (Fig. 2C; Table 1). Paleocurrents from the Grinnell sandstones indicate northwestward and northeastward trends (Table 1; Link, 1997 and references therein).

Mineralogically, argillites have an assemblage of quartz with minor plagioclase and microcline, in a matrix of chlorite and illite-micas (Maxwell and Hower, 1967; Harrison, 1972; Frost and Winston, 1987; Lydon,

Table 1
Principal stratigraphic features of the Appekunny and Grinnell formations

Formation	Thickness (west-east)	Lithology	Sedimentary structures	Paleocurrents	Lateral correlation	Depositional environment	References
Grinnell	~ 800 m	Mainly red argillite with interbedding of white quartz arenite mainly at the top of the sequence	Parallel and non-parallel lamination, mud-breccias, fluid escape structures, subaqueous shrinkage cracks, cross laminated	Northeast and northwest trends (quartz arenites)	St Regis-Revelt-Burke to the southwest in Mission Range, Montana, and Creston to the north in Alberta and B.C.	Alluvial aprons, playas and sheetfloods or intertidal-subtidal	(1) McMechan (1981), (2) Höy (1993), (3) Whiple et al. (1984), (4) Winston (1990), (5) Link (1997)
Appekunny	~ 700–100 m	Predominant green argillite, with sparse layers of quartz arenite	Parallel and non-parallel lamination, low angle cross laminae, mud-breccias, fluid escape structures, subaqueous shrinkage cracks and fining-upward couplets		Pritchard to the southwest in Mission Range, Montana and Creston to the north in Alberta and B.C.	Alluvial aprons, playas and sheetfloods or intertidal-subtidal	(1) McMechan (1981), (2) Höy (1993), (3) Whiple et al. (1984), (4) Winston (1990)

2000). Sandstones have an assemblage of quartz, plagioclase, with <5 modal percent K-feldspar, muscovite, monazite, and chlorite. Most monazite grains in argillites are <~5 µm, whereas counterparts in sandstones are typically <~12 µm. Rarely monazites have diameters of >15 µm. Monazites occur in three textural varieties in both facies: (1) as separate elements of a detrital skeleton; (2) as crystals within rock fragments, or (3) as euhedral grains. Based on texture, the former two are interpreted as detrital whereas the third is diagenetic. Many of the detrital grains that were not included in rock fragments display overgrowths.

Various studies have established that REE in sedimentary rocks are concentrated mainly in the clay-size and silt-size (<20 µm) fractions, but are not associated with any particular clay mineral species, such that fine-grained sedimentary rocks best preserve the geochemical characteristics of the source area (Cullers et al., 1979; Chaudhuri and Cullers, 1979; Taylor and McLennan, 1985; Condie, 1991; Gao and Wedepohl, 1995; Nesbitt et al., 1996; Faupl et al., 1998). Sandstone facies may display geochemical effects due to heavy mineral sorting as a significant fraction of their trace element budget may reside in heavy minerals (e.g., Roaldset, 1979; Taylor and McLennan, 1985; Condie, 1991; Roser, 1996).

Accordingly, taking into account these geochemical effects the Appekunny and Grinnell formations from Waterton-Glacier International Peace Park, northern Montana, and southwestern Alberta were comprehensively sampled (Figs. 1 and 2B). A subset of 33 samples, selected to be representative of argillites and sandstones over the stratigraphic extent of the two formations, were analysed for major and trace elements (Fig. 2B).

Monazite is a common detrital mineral in siliciclastic deposits, and in this study has been identified as relatively abundant in some units in the Appekunny and Grinnell formations. Monazite contains a high concentration of rare earth elements (e.g., Ni et al., 1995; Cressey et al., 1999). Accordingly, six samples of argillites and five of sandstones with high total REE abundances were selected for monazite chemical Th–U total Pb dating.

4. Analytical methods

4.1. Elemental compositions

Major elements were determined using X-ray fluorescence spectrometry (XRF) at the Société Générale de Surveillance (SGS) Laboratories, Ontario,

Canada. Precision is ± 0.01 wt.%. Trace elements, including the REE and high field strength elements (HFSE), were analysed using inductively coupled plasma mass spectrometry (ICP-MS; model Perkin Elmer Elan 5000) at the University of Saskatchewan. To address potential problems stemming from incomplete dissolution of refractory minerals, the procedure of Jenner et al. (1990) was followed, whereby a sodium peroxide sinter was used for Th, Nb, Ta, Zr, Hf, Y, Sc and REE, and an HF–HNO₃ digestion on a separate aliquot was used for the remaining trace elements. Detailed analytical methodology is presented in Fan and Kerrich (1997). The protocol includes standard additions, pure elemental standards for external calibration, and reference materials. Modern Canadian Shield lake sediment (LKSD-1) was used as a reference material, inasmuch as the REE and HFSE contents are comparable to those in the argillite analysed, and reference material basalt (BCR-2). Long-term reproducibility in this laboratory for the low-level reference material basalt (BCR-1) is given in Table 2, abstracted from Xie et al. (1994).

Detection limits (in ppm) defined as 3σ of the calibration blank for some critical elements are as follows: Nb (0.016), Hf (0.042), Zr (0.103), La (0.018), Ce (0.014), Nd (0.086) and Sm (0.065). Wet chemistry operations were conducted under clean laboratory conditions. Analyses of acids, distilled deionized water and procedural blanks give levels of <1 ppb for REE, Nb, Zr, and Hf, relative to their concentration in the rocks (Xie et al., 1994).

Values of Ce/Ce* and Eu/Eu* were calculated relative to the post-Archean upper continental crust

Table 2
ICP-MS multi-element analysis of international reference material basalt BCR-1 for selected trace elements for the University of Saskatchewan ICP-MS laboratory excerpted from Xie et al. (1994)

Elements	x	1 σ	C%	CV
Zr	201	12	6	190
Nb	14.6	0.7	4.8	14
La	26	0.8	3.1	24.9
Pr	6.95	0.33	4.7	6.8
Eu	1.95	0.11	5.6	1.95
Ho	1.26	0.05	4	1.26
Tm	0.54	0.02	3.7	0.56
Lu	0.502	0.02	4	0.51
Hf	5.87	1.49	8.3	4.95
Ta	1.03	0.16	15.5	0.81
Th	6.7	0.52	7.8	5.98
U	1.75	0.1	5.7	1.75

(x) Average; (1 σ) standard deviation; (C%) relative standard deviation; (CV) compiled values from Potts et al. (1990).

(PA-UCC) average of Taylor and McLennan (1995), following Taylor and McLennan (1985).

4.2. Monazite chemical Th–U total Pb dating

The chemical Th–U total Pb method has been developed on the basis of precise electron probe microanalyses and described by Suzuki and Adachi (1991) and has been widely used with monazite for geochronology (e.g., Suzuki and Adachi, 1994; Rhede et al., 1996; Mougeot et al., 1997; Finger and Helmy, 1998). Monazite does not become metamict from radiation (Nasdala et al., 1999) and behaves as a geochemically closed system without loss of parent or daughter nuclides below ~ 725 °C (Copeland et al., 1988). Belt-Purcell rocks did not exceed ~ 400 °C in the study area during metamorphism (e.g., Harrison, 1972).

The chemical Th–U total Pb dating method is based on the premise that initial lead in monazite does not exceed 1 ppm (Parrish, 1990), and monazite does not incorporate appreciable external lead during its crystallization (Scherrer et al., 2000). Standard assumptions are that monazites remained as a closed system, such that measured U/Pb and Th/Pb ratios are due only to radioactive decay (e.g., Faure, 1986; Montel et al., 1996; Harrison et al., 2002; Hodges, 2004; Dahl et al., 2005). These appear to be robust assumptions, and the monazite chemical dating method has been used in numerous studies of metamorphism and detrital age populations (e.g., Suzuki and Adachi, 1991; Ayers et al., 1999; Montel et al., 2000; Rasmussen et al., 2001).

The Th–U total lead chemical dating method is a relatively quick and low-cost method to obtain ages for detrital monazites using the electron microprobe, but less accurate than isotopes methods (e.g., Cocherie et al., 2005; Pyle et al., 2005). In this study, all monazite grains of ~ 5 μm or larger were analysed in situ on polished thin sections. Monazites in Appekunny argillites were large enough to be analysed, but not in Grinnell counterparts. Due to the generally small grain sizes (5–10 μm) most monazites were analysed for one spot, thereby not permitting construction of an isochron to determine possible Pb loss (Suzuki and Adachi, 1991).

In the chemical Th–U total Pb dating method age (t) is calculated by solving the following equation (e.g., Suzuki and Adachi, 1991; 1994):

$$\frac{\text{PbO}}{W_{\text{Pb}}} = \frac{\text{ThO}_2}{W_{\text{Th}}} \{ \exp(\lambda_{232}\tau) - 1 \} + \frac{\text{UO}_2}{W_{\text{U}}} \left\{ \frac{\exp(\lambda_{235}\tau) + 137.88\exp(\lambda_{238}\tau)}{138.88} - 1 \right\}$$

where W is the gram-molecular weight of each oxide ($W_{\text{Pb}}=224$, $W_{\text{Th}}=264$ and $W_{\text{U}}=270$ for monazite), and λ_{232} , λ_{235} and λ_{238} are the radioactive decay constants for ^{232}Th , ^{235}U and ^{238}U respectively.

Analyses were conducted on a Cameca SX-100 electron microprobe equipped with three wavelength-dispersive spectrometers (WDS) at the Warsaw University, Faculty of Geology, Poland. The accelerating voltage was 20 kV, probe current 50 nA, and beam diameter 3 μm . Pentaerythritol (PET) crystals were used to analyse ThM_{α} , UM_{β} , PbM_{β} , thallium acid phthalate (TAP) for YL_{α} . Standards were synthesized glasses of Th and U from P&H Developments Ltd., Derbyshire, UK; and PbCrO_4 for Pb; a Y–Al garnet standard was used to measure the Y content of monazite. Spectral interferences of YL_{γ} and ThM_{ξ} on PbM_{α} and ThM_{γ} on UM_{β} were corrected. X-ray counting uncertainties for ThO_2 and UO_2 values are ~ 2 – 3% at 0.5 wt.%, and below 2% for higher concentrations. For PbO , relative error is $\sim 6\%$ at 0.1 wt.% concentration. Only analyses that met the criteria of >97 wt.% to 102 wt.% of total oxides, and ≥ 0.01 wt.% ThO_2 , UO_2 and PbO , were used to calculate 79 chemical Th–U total Pb ages, on 73 grains, yielding 38 ages for sandstones and 41 for argillites (Tables 3–5) covering the three textural

varieties. Chemical ages were plotted using Isoplot (Ludwig, 1999).

5. Analytical results

From sample grain-size characteristics, petrographic observations, and SiO_2 –loss on ignition (LOI) relationships, there are two distinct populations of rocks: 15 sandstones and 18 argillites (Fig. 3).

5.1. Geochemistry of argillites

Argillites comprise a compositionally uniform population. They possess contents of most major elements close to post-Archean upper continental crust (PA-UCC) of Taylor and McLennan (1995), but with systematically greater abundances of MgO and K_2O , and pronounced depletions of MnO , CaO , and Na_2O (Fig. 4C; see appendix). Potassium is correlated with Al_2O_3 , potentially indicative of primary smectite, and is also highly correlated with Rb, Cs and Tl. Na_2O covaries with Al_2O_3 . From major element composition the primary mineralogy is estimated to be quartz–feldspar–smectite clays. This inferred primary mineralogy is in keeping with the conclusions of Lydon et al. (2000) for compositionally similar argillites of the lower Belt

Table 3
Selected examples of monazite analyses of argillites in the Appekunny Formation presenting examples of the main detrital and post-depositional ages

Sample	Detrital USO3 (2)	Detrital USO12 (4)	Detrital USO1 (26)	Detrital USO1 (30)	Detrital USO1 (18)	Detrital USO13 (6)	Detrital USO13 (4F)	Detrital USO13 (5F)	Diagenetic USO3(3)	Diagenetic USO3(12)	Diagenetic USO1(22)
La_2O_3 (wt.%)	13.43	12.46	14.57	13.48	14.81	14.58	14.24	13.9	16.61	14.17	17.69
Ce_2O_3	26.84	27.57	28.23	27.57	28.79	28.06	27.91	27.95	31.21	30.44	30.00
Pr_2O_3	3.10	3.50	3.08	3.06	3.00	3.11	2.98	3.18	3.20	3.54	3.17
Nd_2O_3	11.75	16.00	10.74	12.06	10.39	11.91	11.67	11.78	11.79	14.10	12.05
Sm_2O_3	2.09	3.13	1.73	2.12	1.89	2.13	2.06	2.12	1.46	2.6	2.05
Gd_2O_3	1.72	1.87	1.08	1.49	1.24	1.51	1.58	1.68	0.65	1.32	1.19
Tb_2O_3	0.27	0.06	0.10	0.15	0.19	0.19	0.20	0.11	0.09	0.09	0.01
Dy_2O_3	0.80	0.26	0.26	0.48	0.39	0.52	0.56	0.61	0.08	0.10	0.18
Ho_2O_3	0.04	0.03	0.06	0.02	0.08	0.06	0.11	0.07	0.11	u.d.	0.00
Er_2O_3	0.17	0.06	0.11	0.10	0.09	0.04	0.15	0.20	0.01	0.06	u.d.
Yb_2O_3	0.02	u.d.	u.d.	u.d.	u.d.	u.d.	u.d.	u.d.	u.d.	u.d.	u.d.
P_2O_5	30.32	29.43	30.03	29.92	29.36	29.51	29.69	29.23	29.34	29.55	30.55
PbO	0.44	0.24	0.52	0.44	0.50	0.33	0.43	0.44	0.20	0.03	0.06
UO_2	0.60	0.36	0.24	0.45	0.13	0.16	0.80	0.83	0.07	0.02	0.02
ThO_2	3.18	2.06	6.48	4.47	6.03	4.05	2.91	2.71	3.31	0.76	1.10
CaO	0.91	0.50	1.10	1.15	0.78	0.77	0.90	0.88	0.43	0.28	0.31
Y_2O_3	3.19	0.77	1.44	1.59	1.33	1.02	2.37	2.49	0.23	0.19	0.26
SiO_2	0.75	0.27	0.61	0.42	0.78	0.43	0.11	0.09	0.61	0.56	0.44
Total	99.69	98.63	100.45	99.04	99.84	98.46	98.76	98.35	99.47	97.88	99.14
Age (Ma)	1859 \pm 9	1668 \pm 43	1614 \pm 18	1663 \pm 21	1743 \pm 29	1641 \pm 37	1704 \pm 32	1747 \pm 17	1307 \pm 32	852 \pm 26	1200 \pm 43

(u.d.) Under detection limit; (App) Appekunny Formation.

Table 4

Selected monazite analyses of sandstones in the Appekunny and Grinnell formations, displaying some examples of detrital and post-depositional ages

Sample	Detrital 2AP(19)	Detrital 2AP(6)	Detrital 2AP(3)	Detrital 2AP(4)	Detrital 1AP(3)	Detrital MGR(25)	Diagenetic MGR6(10)	Diagenetic 2AP	Diagenetic 2AP(11)	Diagenetic 2AP(20)	Diagenetic 2AP(8)	Diagenetic 2AP(5)
La ₂ O ₃ (wt.%)	23.71	13.80	14.49	14.58	16.69	14.62	14.13	15.82	28.31	18.20	16.16	14.42
Ce ₂ O ₃	27.62	27.40	27.71	27.97	30.10	29.36	29.18	27.42	28.07	29.77	27.44	28.10
Pr ₂ O ₃	3.08	2.95	2.97	2.96	3.05	3.27	3.12	3.74	2.29	3.61	3.85	2.89
Nd ₂ O ₃	9.66	10.25	10.32	10.401	10.47	11.94	12.37	14.95	6.94	13.26	14.13	10.41
Sm ₂ O ₃	1.42	1.90	1.70	1.66	1.20	2.06	2.26	2.60	0.98	1.86	2.51	1.93
Gd ₂ O ₃	0.68	1.43	1.32	1.40	0.53	1.45	1.57	1.41	0.53	0.69	1.25	1.32
Tb ₂ O ₃	0.03	0.13	0.16	0.07	0.01	0.20	0.21	0.12	0.10	u.d.	0.14	0.23
Dy ₂ O ₃	0.11	0.58	0.44	0.42	0.05	0.59	0.47	0.11	0.06	u.d.	0.04	0.46
Ho ₂ O ₃	u.d.	0.05	0.05	0.02	0.01	0.10	0.14	0.03	u.d.	u.d.	u.d.	0.12
Er ₂ O ₃	u.d.	0.15	0.11	0.12	0.01	0.11	0.12	0.01	u.d.	0.02	0.03	0.11
Yb ₂ O ₃	u.d.	0.02	0.02	0.04	0.04	0.00	0.01	u.d.	u.d.	u.d.	u.d.	u.d.
P ₂ O ₅	29.70	29.05	28.18	28.51	30.30	30.22	30.57	30.73	30.39	29.47	29.59	28.95
PbO	0.04	0.61	0.58	0.58	0.42	0.26	0.18	0.07	0.03	0.01	0.04	0.42
UO ₂	0.01	0.39	0.34	0.37	0.23	0.23	0.15	0.01	0.02	0.01	0.01	0.32
ThO ₂	0.55	7.04	6.72	6.60	5.42	2.77	3.49	1.86	0.68	0.45	1.21	6.18
CaO	0.37	0.84	0.65	0.66	0.76	0.63	0.72	0.20	0.31	0.25	0.18	0.75
Y ₂ O ₃	0.17	2.45	1.97	2.05	0.56	1.88	1.11	0.26	0.18	0.07	0.26	2.11
SiO ₂	0.54	1.08	1.20	1.15	0.86	0.41	0.41	0.49	0.09	0.35	0.83	1.00
Total	97.78	100.22	99.01	99.62	100.77	100.17	100.25	99.90	99.04	98.08	97.73	99.80
Age (Ma)	1585±46	1648±18	1668±22	1682±29	1546±37	1659±25	1059±37	870±38	941±44	492±28	753±18	1334±32

(u.d.) Under detection limit; (App) Appekunny Formation; (Gr) Grinnell Formation.

Table 5
Summary of monazite chemical age data

Stratigraphic location (Fig. 2B)	Sample	Formation	Location at Waterton-Glacier International Peace Park	Analyses/grains (total 79/73)	Age range (Ma) (a) Archean source (b) Proterozoic source (c) Post-Belt deposition	Facies
G7	USO 13	Appekunny	Poia Lake/Apekuni Mountain	7/6	1747–1641 1347–907	Green laminated argillite
G18	USO 1	Appekunny	Dead Horse	16/13	1743–1614 1074–445	Green laminated argillite
G20	USO 3	Appekunny	Dead Horse	11/11	1859–1551 1339–628	Green laminated argillite
G29	USO 12	Appekunny	Dead Horse	8/8	3074 1859–1551 1298–907	Green laminated argillite
G13	App1	Appekunny	Poia Lake/Apekuni Mountain	2/2	1546 562	Medium to coarse white sandstone
G14	2App	Appekunny	Poia Lake/Apekuni Mountain	14/14	2285–1640 1126–602	Medium to coarse white sandstone
G17	3App	Appekunny	Poia Lake/Apekuni Mountain	3/3	1723 870–506	Medium to coarse white sandstone
G37	MGR	Grinnell	Red Rock Canyon	18/16	2654 1877–1693 1069–264	Medium to coarse white sandstone

based on major element compositions; he compared that mineral assemblage to counterparts in the Gulf basin, southeastern USA. Thorium, light rare earth elements (LREE), total REE (Σ REE), Sc, V, and Co also correlate with Al_2O_3 ($r^2 > 0.64$).

Two types of REE patterns are evident in the Appekunny and Grinnell formations. (1) Flat relative to PA-UCC at 1.3 to 1.5 times PA-UCC, where normalized HFSE and transition metals broadly follow REE. Light REE and middle REE covary with Al_2O_3 . (2) Patterns characterized by flat LREE relative to PA-UCC at 1 to 1.5 times PA-UCC, in conjunction with more abundant HREE than LREE relative to PA-UCC (Fig. 4A and B).

5.2. Geochemistry of sandstones

Two compositional groups of sandstones cluster at values ≥ 4 wt.% Al_2O_3 and < 4 wt.% Al_2O_3 . Both groups are present in the Appekunny and Grinnell formations. There is no correlation between Al_2O_3 and Eu/Eu^* , interpreted as an insignificant contribution from plagioclase to the whole-rock Al budget. Consequently, the Al budget is controlled by the clay sized fraction.

The former population shows covariation of Th, U, Nb, K_2O , Zr, La, Yb, Σ REE, V and Sc with Al_2O_3 , as in the argillite. The latter population has similar covariant trends for Th, Zr, K_2O , V, and Sc, whereas Nb, REE, and U are scattered. From these relationships, combined with petrographic observations, the sandstones compositionally are argillites highly diluted by detrital quartz.

Rare earth element abundances are controlled by quartz content. There are two REE patterns referenced to PA-UCC, as for argillites: type 1 is flat at 0.1 to 0.9 PA-UCC, whereas type 2 features flat LREE at 0.1 to 0.9 PA-UCC and more abundant HREE than LREE. In some samples there are variably negative Ce anomalies and variable upturns at Yb–Lu. Positive peaks at Eu in a few type 2 samples likely reflect detrital plagioclase (Fig. 4F). On PA-UCC normalized diagram peaks at K could be explained by detrital smectite or secondary illite.

5.3. Monazite chemical Th–U total Pb ages

Monazites in argillite of the Appekunny Formation display peaks at ~ 1860 , ~ 1740 and ~ 1680 Ma with one date at ~ 3080 Ma; sandstones have a main peak at ~ 1960 ,

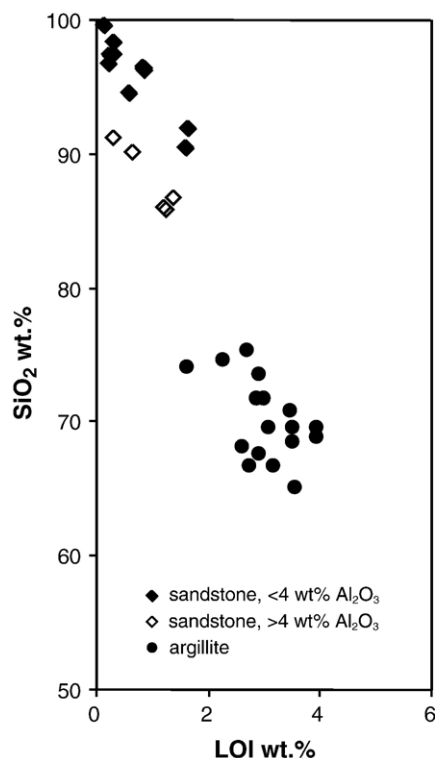


Fig. 3. Sample grouping based on SiO₂–LOI (loss-in-ignition) relationship. Two main groups are delineated: sandstones (>75 wt.% SiO₂ to <2 wt.% LOI and argillites <75–60 wt.% SiO₂ to <5 wt.% LOI).

at ~1690 Ma and a single point date at ~2290 Ma; both facies display a wide range of ages <~1400 Ma. Counterparts from the Grinnell Formation show peaks at ~1890, ~1780, ~1720 Ma, one date at ~2660 Ma, as well as scattered ages <~1400 Ma (Fig. 5).

Monazite grains and their counterparts >~1400 Ma show more rounded features and some grains display syntaxial cement (Fig. 6B and C; texture 1) coupled with other euhedral grains as inclusions in quartz and feldspars (texture 2), whereas grains <~1400 Ma are more euhedral (texture 3; Fig. 6D). Compositional differences between monazites >~1400 Ma and <~1400 Ma are plotted in Fig. 5. Images of monazites are shown in Fig. 7. All chemical analyses not listed in Tables 3 and 4 are in the journal data depository.

6. Discussion

6.1. Provenance

Taylor and McLennan (1985) considered that REE profiles from Proterozoic shales are distinct from

Archean counterparts. This compositional transition is due to a major period of growth and differentiation of continental crust at the end of the Archean. Archean UCC is characterized by high (La/Yb)_{cn}, with no Eu anomalies, combined with low Y, Th/Sc and LREE/HREE, whereas PA-UCC has opposite geochemical features including systematic negative Eu anomalies. This general compositional switch was interpreted to reflect a transition from first-cycle detritus shed off juvenile terranes dominated by bimodal basalt and dacite/tonalite arcs, to a period of growth and differentiation of continents caused by intracrustal melting that gave rise to K-rich granites. In shales, the Th/Sc ratio is an indicator of crustal differentiation, given that it is an index of felsic versus mafic lithologies. Thorium is enriched in felsic rocks whereas Sc is depleted, and the inverse is true for mafic lithologies (Taylor and McLennan, 1985; Young, 1999).

The majority of argillites of the Appekunny and Grinnell formation have type 1 REE, and multi-element PA-UCC normalized patterns close to 1, consistent with a dominantly post-Archean source area for the sediments. The same samples normalized to Archean upper continental crust values display a pronounced Eu depletion (Fig. 4A and B). Similarly, Th/Sc ratios, Cr–Ni contents and Eu/Eu* versus (Gd/Yb)_{cn} plot in the post-Archean field (Fig. 8A, C and D). These results are in keeping with dominantly Paleoproterozoic ages of detrital zircons and monazites for the Ravalli Group at Waterton-Glacier International Peace Park area (Ross et al., 1992; Ross and Villeneuve, 2003; this study: see below).

Total LREE versus total HREE plot mostly in the Archean field (Fig. 8B). This last, apparently contradictory, feature is interpreted as a diagenetic overprint of secondary HREE enrichment in some samples (type 2 REE pattern), as discussed in Section 6.5.

Slack and Höy (2000) suggested four distinct source terranes for the Aldridge and the Fort Steele formations of the equivalent lower Belt in southeastern British Columbia, determined largely on the basis of REE–Th–Sc systematics. They equate these with the following terranes: (1) dominant in all stratigraphic units are sediments derived from a fractionated calc-alkaline igneous and (or) meta-igneous terrane; (2) an unfractionated counterpart; (3) a terrane dominated by fractionated granites and (or) rhyolites, including alkalic granites; and (4) a terrane comparable to the third example, but with contributions from Fe-rich chemical sediments (see also Schandl et al., 2000). They suggested the possibility of the Mazatzal and

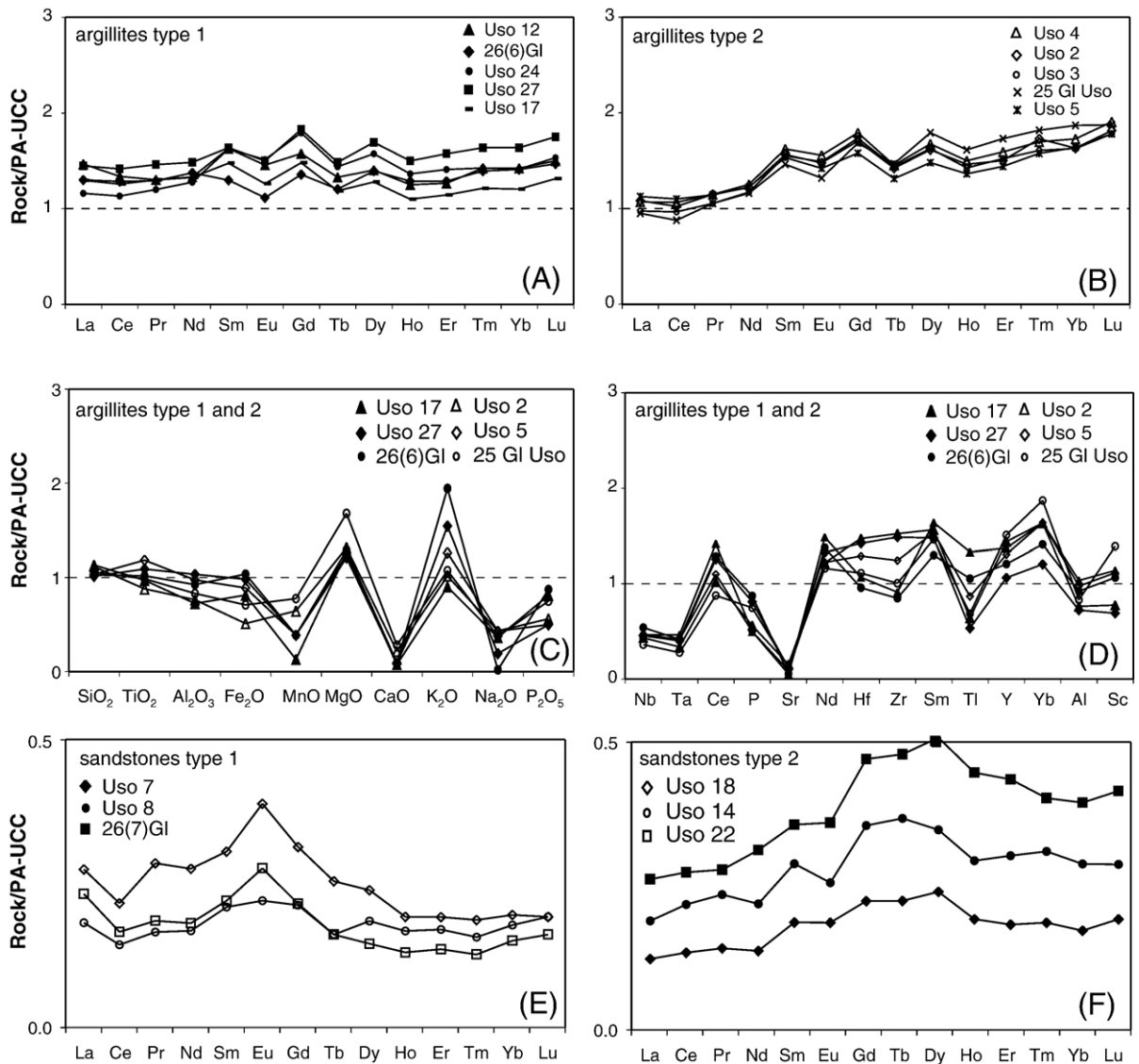


Fig. 4. Plots for argillites and sandstones; (A) rare earth elements (REE) for argillites type 1, displaying flat REE pattern reference to PA-UCC; (B) REE for argillites type 2, representing an enrichment of HREE relative to LREE; (C) variation diagram of major elements for each of the argillite types; (D) multi-element plot for argillite types 1 and 2; (E) REE pattern for sandstones with Al_2O_3 content lower than 4 wt.%; (F) REE plot for sandstones with $\text{Al}_2\text{O}_3 > 4$ wt.%. All plots are on linear scales and values are normalized to post-Archean upper continental crust values from Taylor and McLennan (1995).

Yavapai Provinces as possible minor sources for the Aldridge Formation in the lower Belt.

Argillites of the stratigraphically higher Appekunny and Grinnell formations are geochemically more uniform than Aldridge and Fort Steele counterparts. Compositional uniformity is interpreted as reflecting progressive growth of the river-catchment system as the Belt-Purcell basin was filled. The compositional uniformity of argillites is in keeping with uniform Nd-isotope systematics (Frost and Winston, 1987).

6.2. Chemical Th–U total Pb dates

Ross and Villeneuve (2003) conducted an extensive study of SHRIMP U–Pb ages on zircons collected from sandstones of the Belt-Purcell Supergroup. Their results for the Ravalli Group (Fig. 2C) are summarized in Table 6. They interpreted the data in terms of the Grinnell Formation having a Paleoproterozoic provenance from the Canadian Shield, but with an Archean source in Laurentia for the Creston Formation. The Revett

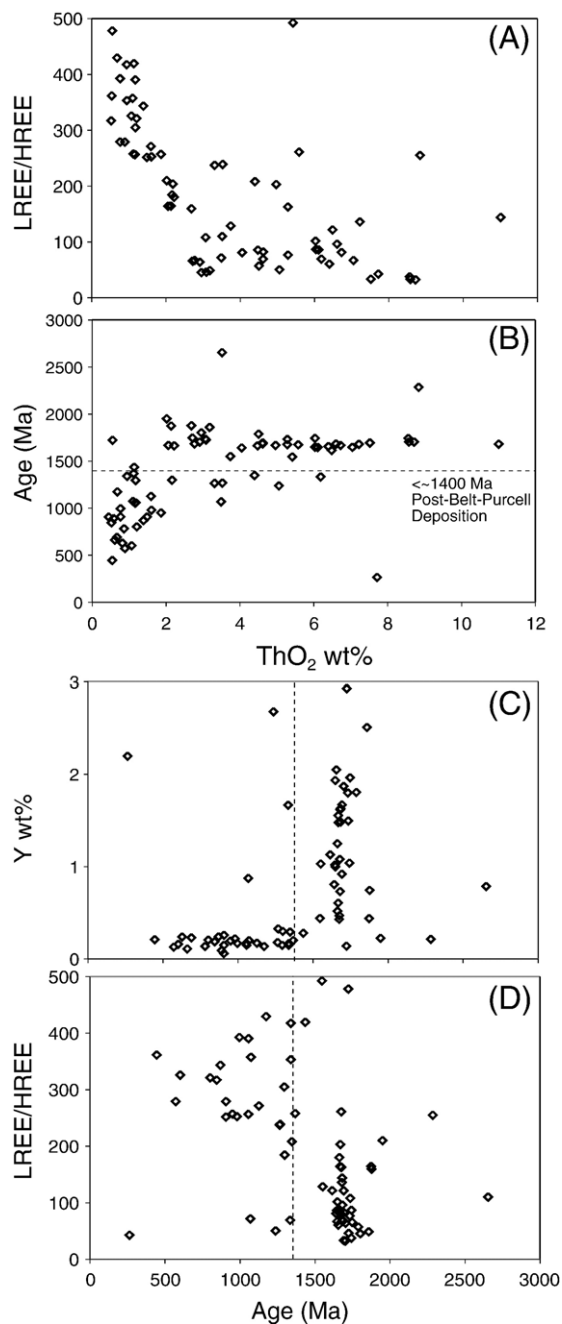


Fig. 5. Plots for monazite compositions; (A, B) variation of light rare earth elements/heavy rare earth elements ratio (LREE/HREE) and age versus ThO₂ content, respectively; (C, D) Y and LREE/HREE content versus age. There is a systematic trend in composition which indicates two monazite populations with post-depositional ages: diagenetic <~1400 Ma and detrital >~1400 Ma.

Formation and the turbiditic facies of the Prichard Formation in the east of the Belt-Purcell Basin were interpreted as fed from a western terrane. Two lines of evidence were used to argue for a western catchment: (1)

paleocurrents, and (2) detrital zircon ages of 1620 to 1505 Ma are within the so-called “North American gap” (1610–1490 Ma) when there are no known magmatic provinces in Laurentia (Fig. 9B; Ross and Villeneuve, 2003). In addition, Ross et al. (1992) suggested that at least part of the Revett Formation sediment could have been contributed from the ~1570 Ma Priest River Complex in the west (Fig. 9C).

For the Grinnell sandstones, three older peaks of this study are in agreement with the results of Ross and Villeneuve (2003), consistent with Paleoproterozoic and Archean terranes of Laurentia. However, the main peaks at ~1700 Ma and the <~1400 Ma ages are not recorded in their zircon study. The distribution of monazite ages in sandstones of the Appekunny Formation is similar, with a younger peak at ~1700 Ma for sandstones.

For the Grinnell Formation, paleocurrents from the southeast and southwest, coupled with general thinning of sandstones to the west and thickening of the argillites to the southwest for the Appekunny and Grinnell formations, could be consistent with a source terrane (s) in Laurentia.

The 1850 Ma Andean type calc-alkaline of the Wathaman batholith in the Trans-Hudson Orogen (e.g., Clowes et al., 1998) could be a possible source for the upper range of the monazite ages found in the Grinnell sandstones, or the southern Wyoming Province of the mid-continent region (Frost and Winston, 1987).

Detrital monazites having ages in the range 1780–1680 Ma could be sourced in Laurentia. Included are the Yavapai, Mazatzal Provinces and the Central Plains of the southwest USA and Mexico (~1800–1600 Ma; e.g., Hoffman, 1988; Clowes et al., 1998; Fig. 9C), which fits the paleocurrent data. The absence of an ~1700 Ma peak in the zircon data set for the Grinnell Formation of Ross and Villeneuve (2003) could be due to an artifact of sampling. According to Vermeesch (2004), data sets of less than 117 grains do not have a 95% probability of reflecting the complete age spectrum of a sediment’s provenance. Alternatively, the absence of that peak could stem from igneous zircons but metamorphic monazites (see Section 6.5).

Archean monazite chemical ages are present sparsely in the Appekunny Formation argillite and the Grinnell Formation sandstone (Fig. 6A and C). Proximal Archean terranes are present in the Hearne, Sask, and Wyoming cratons, and the Black Hills of South Dakota in Western Laurentia. More distal are the Superior and Slave Provinces, the 2400–2200 Ma terrane of Nevada and Utah, or the Paleoproterozoic Huronian Supergroup sourced in the Superior Province, the former contiguous with the Paleoproterozoic Snowy Pass Supergroup,

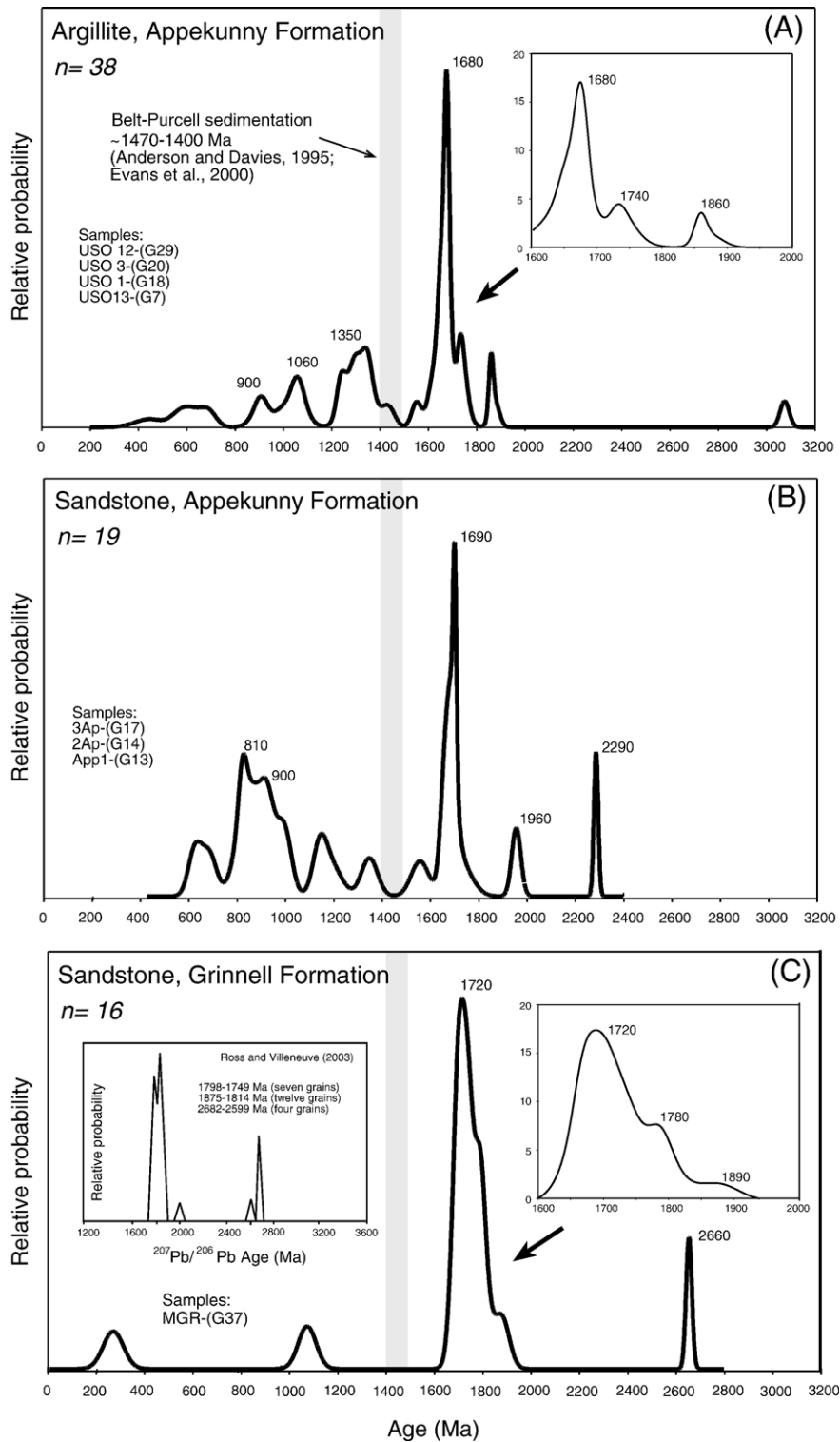


Fig. 6. Probability plots of monazite chemical ages from this study and from zircons dated by Ross and Villeneuve (2003) for the Grinnell Formation; (A) argillites from the Appekunny Formation display a main peak at ~1700 Ma; (B) medium-coarse-grained sandstones of the same formation peak at ~1700 Ma and display an important post-Belt-Purcell deposition population; (C) medium-coarse-grained sandstones from the Grinnell Formation present peaks at ~1880 Ma, ~1780 Ma and 1700 Ma; and an inset of Ross and Villeneuve (2003) data shows main peaks at 2680–2600 Ma, ~1875–1815 Ma and ~1800–1750 Ma for sandstones from the Grinnell Formation.

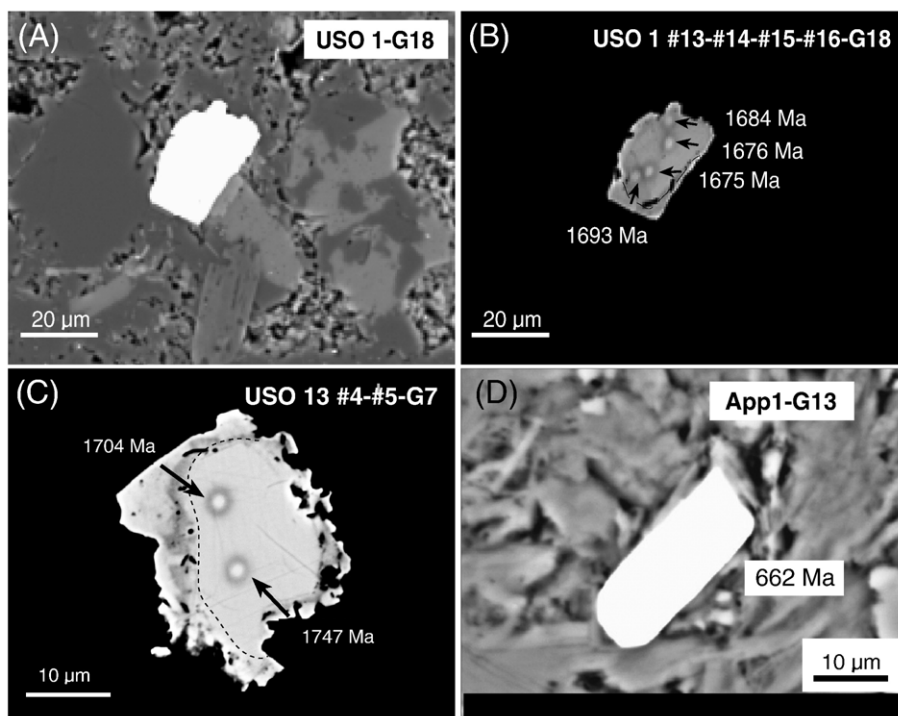


Fig. 7. Backscattered electron images of monazite detrital grains. (A–C) Argillite samples USO 1 and USO 13 from the Appekunny Formation displaying detrital grains presenting syntaxial cement surrounding part of the core with ages ~ 1700 Ma; and (D) euhedral monazite grain from medium-coarse-grained sandstone in the Appekunny Formation with post-Belt-Purcell deposition age.

Wyoming (Frost and Winston, 1987; Bekker and Ericksson, 2003).

In summary, with the actual data available, we find that Laurentia could have been the main source for the Appekunny and Grinnell formations in the lower Belt-Purcell sequence inasmuch as both Archean and Paleoproterozoic terranes, or metamorphic belts, of requisite age are present.

6.3. Thermochronology

There are two possible explanations for the younger monazite peaks at ~ 1700 Ma. One possibility is that the data set of this study records another Paleoproterozoic terrane ~ 200 to 35 Ma younger than the Laurentian terrane recorded in other studies (Ross et al., 1991; Ross and Villeneuve, 2003). The upper end of this range exceeds errors in monazite ages (Table 5). Paleoproterozoic terranes of this age in Laurentia are presented in Fig. 9C.

Given that all monazites $> \sim 1400$ Ma are detrital, an alternative explanation may lie in a two stage process. The common older peaks for both zircons and monazites are magmatic ages. In contrast the younger ages reflect cooling of metamorphic monazites through the blocking

temperature of $725^{\circ} \pm 25$ °C (Copeland et al., 1988), or as low as $530^{\circ} \pm 25$ °C according to Black et al. (1984), following regional metamorphism and unroofing. Zircon behaves as a closed system at temperatures up to 900 °C (Cherniak et al., 2004). Studies of the thermochronology of deeply buried metamorphic rocks in orogenic belts constrains the duration from magmatism, through burial and peak metamorphism, to cooling through ~ 700 °C from ~ 30 to 100 Ma (Eglington and Armstrong, 2004; Hodges, 2004 and references therein). A metamorphic origin for the younger monazites could concurrently explain the lack of zircon ages of this range (~ 1700 Ma) in the data set of Ross and Villeneuve (2003). The Wyoming province has metamorphic monazites of ~ 1800 – 1600 Ma (Dahl et al., 2005).

6.4. One or more cratonic provenance catchments?

The provenance of the Belt-Purcell Supergroup is controversial. Sources in the Australia, Siberia, and Laurentia have variously been suggested, or combinations. Frost and Winston (1987) reported Nd-isotope data for argillites of the Belt-Purcell Supergroup. Crustal residence ages range from 2100 to 1600 Ma,

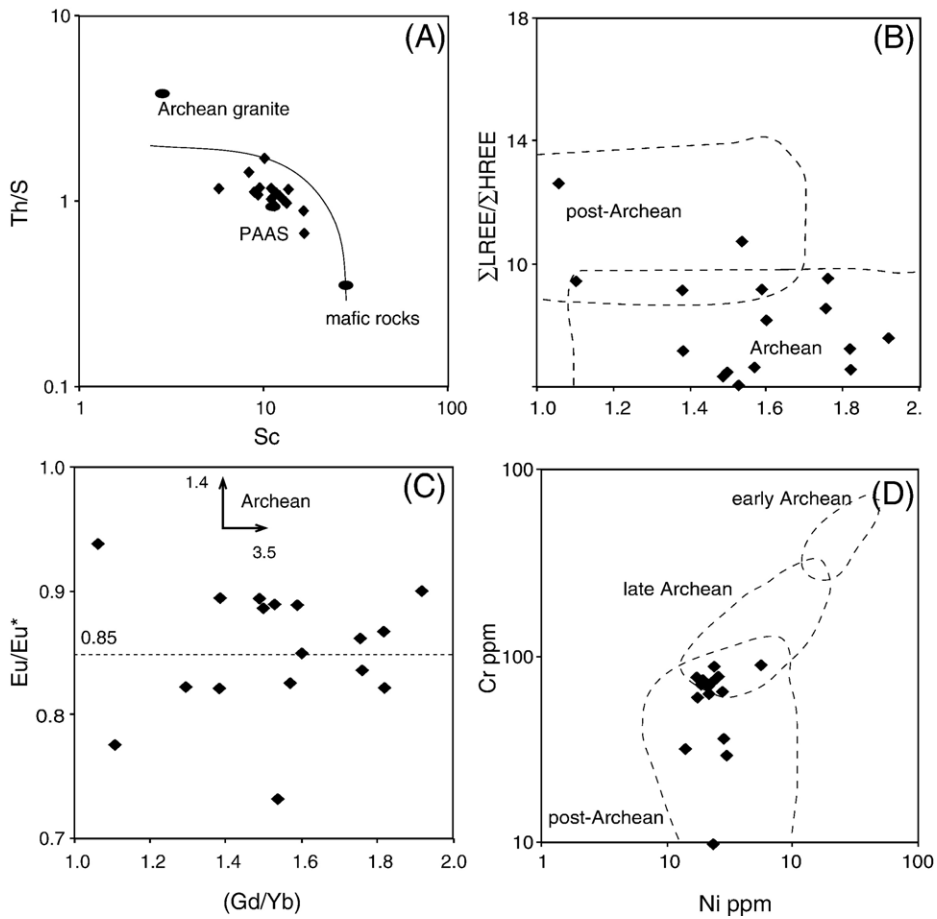


Fig. 8. (A) Plots of Th/Sc versus Sc; (B) $\Sigma\text{LREE}/\Sigma\text{HREE}$ versus $(\text{Gd}/\text{Yb})_{\text{cn}}$; (C) Eu/Eu^* versus $(\text{Gd}/\text{Yb})_{\text{cn}}$; (D) Cr versus Ni. In (A) Archean granite and the mixing line from Archean granite to mafic rocks are from Bhat and Ghost (2001). Post-Archean fields in (B) and (C) are from Taylor and McLennan (1985), and McLennan et al. (1990) respectively. The inset in (D) is from Wronkiewicz and Condie (1989, Fig. 4). Argillites from the Apekunny and Grinnell formations plot in post-Archean fields except for (B) which is interpreted as a probable effect of HREE mobility during diagenesis. See Section 6.

averaging 2000 Ma. They concluded that argillites could have been derived from a variety of provinces in Laurentia, but on sedimentologic grounds preferred a western terrane, Siberia or Australia. Sandstones have similar Nd-isotopic compositions as argillites, exempting one sample from the LaHood Formation

Table 6
Principal zircon age clusters from Ross and Villeneuve (2003)

Revelt F.	Grinnell F.	Prichard F.	Creston F.
1590–1505	1798–1749 (7)	1452 (1)	Discordant array at 1900
1682	1875–1814 (12)	1489 (1)	2678–2502 (14)
1893–1793	2682–2599 (4)	1611–1540 (16)	
		1818–1740 (6)	
		2551–2509 (2)	

Age is in Ma and number of grains in brackets.

(lower Belt) with a 3800–2900 Ma crustal residence age that they ascribed to a proximal catchment in the Wyoming Province.

Ross et al. (1992) determined U–Pb detrital zircon ages, from quartzarenites of the lower Belt–Purcell sequence collected from the west of the basin, which gave concordant ages of 1600–1590 Ma and a discordant age of 1780 Ma. The 1600–1590 Ma age range has no possible source known in North America and therefore they concluded that this was the age of the source terrane from the west. Given detrital zircon ages of the Revelt Formation at ~1600–1500 Ma and the Grinnell Formation at ~1875–1750 Ma, Ross and Villeneuve (2003) concluded that the former sandstones were fed from the Laurentian craton whereas the latter formation was derived from a western source.

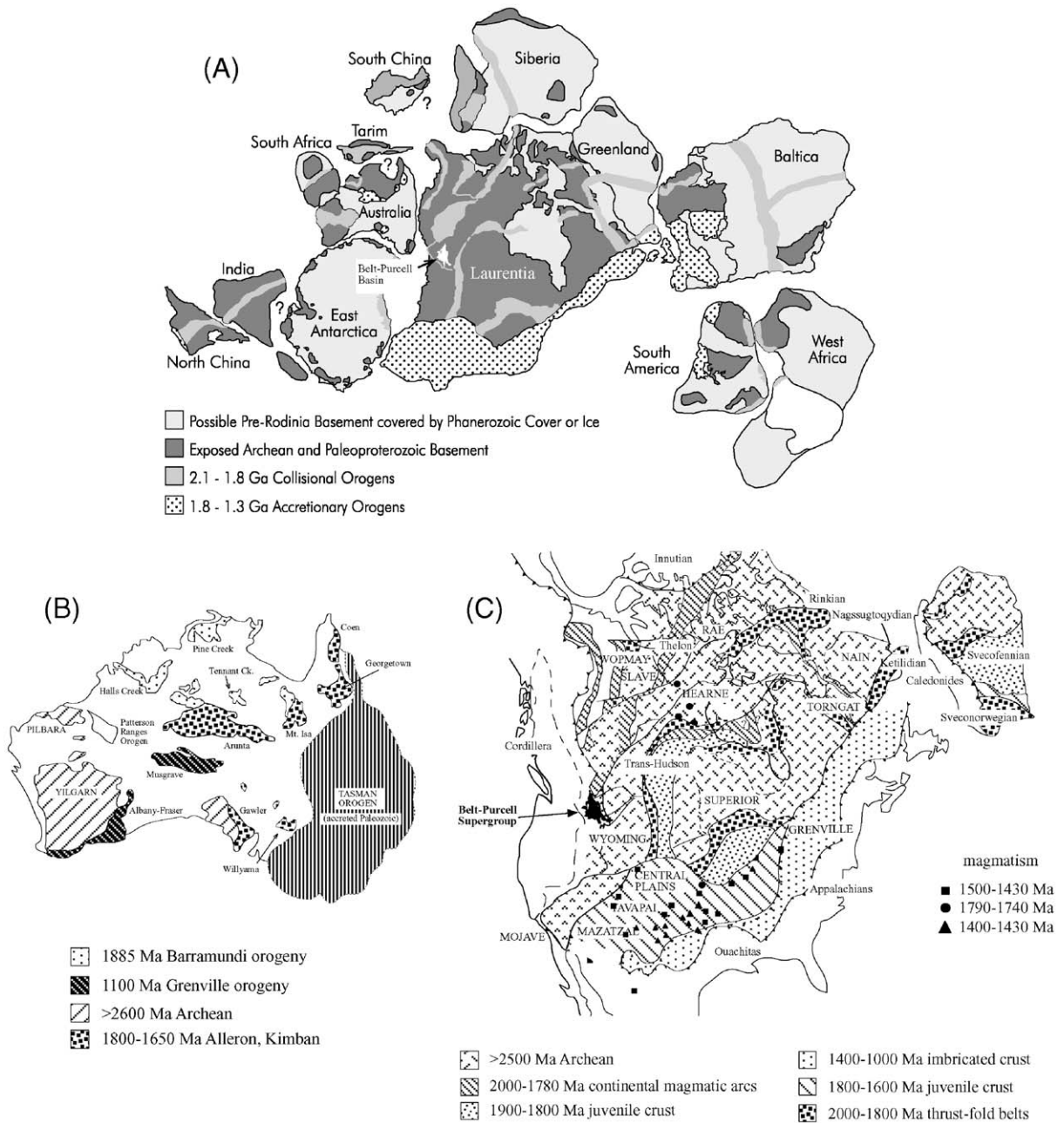


Fig. 9. (A) Reconstruction of Columbia Supercontinent based on Zhao et al. (2004) showing collisional and accretionary orogens and the relative position of the Belt-Purcell basin; (B) basement terranes of Australia (Ross et al., 1992); (C) basement of Laurentia showing potential sources for the lower Belt-Purcell Supergroup sequence (extracted from Ross and Villeneuve, 2003).

Sears et al. (2004) place Siberia to the west of Laurentia at the time of the Belt-Purcell sedimentation channeling sediment from a cratonic source through the Udzha rift. The Siberian craton presents Proterozoic ages at ~2000 Ma and ~1850 Ma (Poller et al., 2005) that could match some of the Grinnell detrital zircons (Ross and Villeneuve, 2003), but paleocurrents from

southeast of the Grinnell formation are not consistent with a western provenance (Winston, 1990; Link, 1997 and references therein).

The most recent reconstruction of the supercontinent Columbia places Australia adjacent to western Laurentia in the Mesoproterozoic (Fig. 9A; Zhao et al., 2004). If the Appekunny and Grinnell formations,

in whole or in part, have a catchment in Australia the following terranes are possible source areas: Arunta (~1700 Ma), Gawler (~2000–1600 Ma); Willyama (~1800–1600 Ma); Mt. Isa (~1800–1600 Ma); Georgetown (~1700–1600 Ma) and Musgrave (1900–1700 Ma) (Fig. 9B; cf. Ross et al., 1992 and references therein; Kyser et al., 2000).

There has also been the more specific controversy as to whether sandstones and argillites were derived from different provenances. Sandstones trend to thin to the west and argillites thicken to the southwest (Table 1; Winston, 1990; Link, 1997 and references therein). Rounded detrital grains in the Grinnell and Appekunny formations are common. In sandstones, the presence of hummocky cross-stratification, current-ripples, normal grading, and sharp contacts are evidence for high-energy depositional environment events (e.g., Whipple et al., 1997). Pronounced sorting of heavy mineral titanite and zircon occurred which is reflected in deep troughs at Nb–Ta, Ti, and variable Zr–Hf (Fig. 4D).

Given that the REE, Th, Sc, and Co budget of the quartzite is dominated by the admixed clay fraction, these data could be interpreted as inconclusive as to a common or separate source. However, the most straightforward explanation of the common monazite age populations of the Appekunny and Grinnell sandstones is a common provenance, and the presence of similar older and younger peaks in the Appekunny sandstones and argillites is consistent with the same source too. A common source for the majority of the argillites and sandstones is also in keeping with the Nd-isotope data (Frost and Winston, 1987).

From this discussion, we consider that the sandstones and argillites of the Appekunny and Grinnell formations had a common main provenance in Laurentia, likely to the south; the two facies had geographically separate high- and low-energy depositional environments respectively, and became interbedded during storms.

6.5. Diagenetic effects

Monazite chemical ages in argillite and sandstone display an age range <~1400 Ma, up to 900 Ma post-Belt-Purcell deposition (Fig. 6). Grains that present these ages are euhedral, and are compositionally distinct, supporting their interpretation as secondary (see Fig. 7). Various studies show that REE can be redistributed locally in sedimentary environments, and that growth of diagenetic monazite may play a part in this process (e.g., Milodowski and Zalasiewicz, 1991; McDaniel et al., 1994; Lev et al., 1999; Evans et al., 2002). Several studies describe secondary monazite formation in shales

(e.g., Evans and Zalasiewicz, 1996; Rasmussen et al., 2001). Studies by Burnotte et al. (1989), and Schandl and Gorton (2004) show that low ThO₂ contents of ~<0.1 wt.% is a criterion for identifying hydrothermal monazite, whereas igneous monazites typically have 2–12 wt.% ThO₂. The low ThO₂ content is attributed to a slow growth and low mobility of Th in the environment of crystallization (Fig 5B; Milodowski and Zalasiewicz, 1991; Schandl and Gorton, 2004).

Monazites of the Appekunny and Grinnell formations that range <~1400 Ma have higher values of LREE/HREE, <2 wt.% ThO₂, and lower Y contents than their counterparts at >~1400 Ma (Fig. 5). Based on their compositional features, textural characteristics, and chemical ages, most of these monazites are interpreted as the result of diagenetic processes.

Monazite chemical age populations from sandstones of the Appekunny Formation display a striking major age range at <~1400 Ma. These results are interpreted to reflect a more intense diagenetic stage than in the Grinnell Formation, possibly controlled by differential permeability (Fig. 6B).

Normalized enrichment of HREE over LREE relative to PA-UCC in some samples of sandstones and argillites could be a provenance signature, or result from weathering, sorting or diagenesis. Boninites and low-Ti tholeiites are the only rock types known to have primary normalized HREE>LREE. However, these igneous rocks are rare, and possess high contents of Cr, Co, and Ni, unlike Belt-Purcell sediments (e.g., Brown and Jenner, 1989). The compositional and Nd-isotopic homogeneity also rule out such singular rock types (Frost and Winston, 1987; Table 7).

Studies of soil-protolith profiles have identified fractionation of REE in regolith relative to the parent rock. Overall, saprolite is generally enriched in total REE (Duddy, 1980). In detail, there is enrichment of LREE but depletion in HREE due to preferential removal of HREE by complexation reactions (e.g., Braun et al., 1993). The top horizon of the saprolite

Table 7
Crustal residence ages (T_{cr}) and ϵ_{Nd}^{**} of fine- and coarse-grained facies of the Belt-Purcell Supergroup rocks from Frost and Winston (1987)

	Fine-grained facies	Coarse-grained facies*	Appekunny Formation	Grinnell Formation
T_{cr}	2100–1600 Ma	2240–1980 Ma	1950 Ma	2240–2060 Ma
ϵ_{Nd}	-8.1–(-20.0)	-6.6–(-20.2)	-15.6	-6.61–(-15.8)

*LaHood Formation results are not included.

** $\epsilon_{Nd} = \{[(^{143}Nd/^{144}Nd)_{sample}/(^{143}Nd/^{144}Nd)_{bulk\ earth}] - 1\} \times 10^4$.

develops a positive Ce anomaly due to crystallization of cerianite (Braun et al., 1990; Marsh, 1991). Such effects are not present in the argillites or sandstones of this study, nor in the North American Shale Composite (NASC), or post-Archean Australian Shale (PAAS) composite (e.g., Taylor and McLennan, 1985).

Sedimentary sorting with accumulation of minerals enriched in HREE could generate the observed patterns. Zircon is the most likely candidate. However, sandstones and argillites have variably negative normalized troughs at Zr–Hf relative to MREE, and there is no covariation of the magnitude of the anomaly with Gd/Yb_{cn}. The presence of the Zr troughs in both sandstones and argillites signifies that sedimentary sorting processes are an unlikely cause of the observed HREE fractionations.

Normalized enrichments of HREE over LREE have been documented in alkaline brines discharging into lakes of the East African Rift where Magadi-type cherts, which have similar REE patterns, are precipitating (Kerrich et al., 2002). High contents of Y have been documented in diagenetic U deposits of the Paleoproterozoic Athabasca silticlastic sequence Saskatchewan (Fayek and Kyser, 1997). We interpret the <~1400 Ma monazite ages, restricted to euhedral low-ThO₂ monazites, and the HREE-enriched patterns relative to LREE when normalized to PA-UCC, as due to protracted flow of basinal brines, preferentially through permeable units, of the Appekunny and Grinnell formations. Protracted, episodic flow of diagenetic brines has been recorded in several Proterozoic siliciclastic sequences (Kyser et al., 2000).

7. Conclusions

- (1) Coarse-grained sandstones have the same geochemical fingerprint as argillite for both the Appekunny and Grinnell Formations of the lower Belt-Purcell Supergroup sequence. Sandstone developed in a separate high-energy environment, generating efficient transport winnowing of fine from coarse-grained quartz and feldspar. Argillite and sandstone become interbedded during storms. Geochemical data are consistent with a dominantly post-Archean source area for the lower Belt sediments: specifically, compliance of rare earth element and multi-element patterns to PA-UCC, Cr–Ni and Th/Sc–Sc systematics.
- (2) Detrital monazite chemical Th–U total Pb ages from the Appekunny and Grinnell sandstones, and argillites of the former at ~1700 Ma supports a main Paleoproterozoic source for this sediments.

This area could have been from a Laurentian source at ~1700 Ma or at ~1875–1750 Ma that cooled through the blocking temperature of monazite ~1700 Ma. The Yavapai, Mazatzal and Central plains in Laurentia are potential sources. Rare >2500 Ma monazite ages in argillite and sandstone represent marginal contributions from Archean terrane(s) from the southeast and southwest of the Belt-Purcell Basin.

- (3) Diagenetic overprint in the Belt-Purcell rocks is widespread and is displayed as HREE enrichment relative to LREE when normalized to PA-UCC, and texturally and compositionally distinct of secondary monazites with chemical ages <~1400 Ma, lower ThO₂ and Y, and higher LREE/HREE content than >~1400 Ma monazites.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.chemgeo.2005.12.004](https://doi.org/10.1016/j.chemgeo.2005.12.004).

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