ELSEVIER

Precambrian Research 102 (2000) 263–278

Precambrian Research

www.elsevier.com/locate/precamres

Nd and Pb isotopic evidence for provenance and post-depositional alteration of the Paleoproterozoic Huronian Supergroup, Canada

S.M. McLennan [a,b,*] , A. Simonetti [a] [,1], S.L. Goldstein [a,2]

[a] *Max-Planck-Institut für Chemie, Abteilung Geochemie, Postfach 3060, 55020 Mainz, Germany*
[b] *Department of Geosciences, ESS Building, State University of New York at Stony Brook, Stony Brook, NY 11794-2100, USA*

Received 24 August 1999; accepted 7 March 2000

Abstract

Neodymium model ages for fine-grained formations of the Paleoproterozoic Huronian Supergroup (McKim, Pecors, Gowganda, Gordon Lake) range from 3.00 to 2.55 Ga and indicate a provenance dominated by the Late Archean Superior Province to the north and west. The stratigraphically highest unit (Gordon Lake Formation) has a distinctive Nd-isotopic composition, with T_{DM} being 100-400 Ma younger than underlying mudstones. This suggests that the provenance changed, consistent with a previously documented change towards more negative Eu-anomalies, in the Gordon Lake. Lead isotopes are consistent with a Superior Province provenance and in addition provide evidence for two episodes of regional post-depositional disturbance of the U-Pb system. Lower Huronian (McKim, Pecors) samples align along ^{207}Pb/^{204}Pb–^{206}Pb/^{204}Pb slopes equivalent to 2170 ± 58 Ma (MSWD = 92, $n = 9$) and 2212 ± 92 Ma (MSWD = 9.1, $n = 5$), respectively. These ages are at the minimum age limit on sedimentation and within uncertainty of the Nipissing Diabase (2219 ± 4 Ma), a ubiquitous regional feature, parts of which may have intruded while much of the Huronian was unconsolidated. These Pb–Pb ages are interpreted to represent widespread diagenetic processes, possibly associated with an early phase of Nipissing intrusion. ^{206}Pb/^{204}Pb varies mostly from 19 to 34 (up to 59), whereas implied κ (^{232}Th/^{238}U) are mostly between 2 and 4, only slightly below the upper crustal value of 4. Changes in ^{206}Pb/^{204}Pb imply changes of μ (^{238}U/^{204}Pb) by factors of < 1–5 and thus resetting of the U–Pb system likely involved Pb loss, with or without U gain. The upper Huronian displays more complex Pb-isotope systematics. Data align along ^{207}Pb/^{204}Pb–^{206}Pb/^{204}Pb slopes of ca.1700 Ma, with regional variation in ^{207}Pb/^{204}Pb. For the Gowganda and Gordon Lake formations, ^{206}Pb/^{204}Pb ratios are 23–43 and 30–115, respectively, and imply changes in μ by factors commonly > 2 (and up to 12.5). Values for κ are also in the range 2–4 and, accordingly, Pb loss appears to dominate this disturbance. Elevated ^{206}Pb/^{204}Pb correlates with post-depositional addition of

---

* Corresponding author.

E-mail addresses: scott.mclennan@sunysb.edu (S.M. McLennan), simonetti.antonio.@uqam.ca (A. Simonetti), steveg@ldeo.columbia.edu (S.L. Goldstein)

[1] Present address: GEOTOP, Université du Québec à Montréal, Montréal, PQ, Canada H3C 3P8.

[2] Present address: Lamont-Doherty Earth Observatory and Department of Earth and Environmental Sciences, Columbia University, Palisades, NY 10964, USA.

PII: S0301-9268(00)00070-X

potassium in the Gordon Lake and possibly the Gowganda formations. K-metasomatism has been demonstrated previously in the underlying Serpent Formation and in paleosols developed at the unconformity beneath the Huronian Supergroup, the latter being dated at 1690–1730 Ma. Widespread metasomatism, resulting in K-addition and Pb-loss, may have been related to northerly directed basin wide fluid movement in response to post-tectonic intrusions and erosion of the ca. 1.85 Ga Penokean Orogen to the south. Since Pb isotope systematics in the lower Huronian mudstones appear unaffected, apart from natural conduits provided by unconformity surfaces and possibly lower Huronian sandstone aquifers (that also may have been affected by K-metasomatism), it appears that fluid movement was more pervasive in the upper levels of this sedimentary sequence.

Keywords: Huronian Supergroup; Lead–lead; Neodymium; Rare earths

1. Introduction

The Huronian Supergroup is a ca. 2.5–2.2 Ga succession of mainly terrigenous sedimentary rocks preserved on the north shore of Lake Huron, Canada (Figs. 1 and 2). The rocks were deformed and metamorphosed during the Penokean Orogeny that resulted in a major mountain range to the south, probably at about 1.85 Ga. The Huronian Supergroup has played a central role in understanding many aspects of Precambrian history, including climate, atmospheric compositions, Precambrian tectonic conditions and crustal evolution (e.g. Young, 1970; Roscoe,

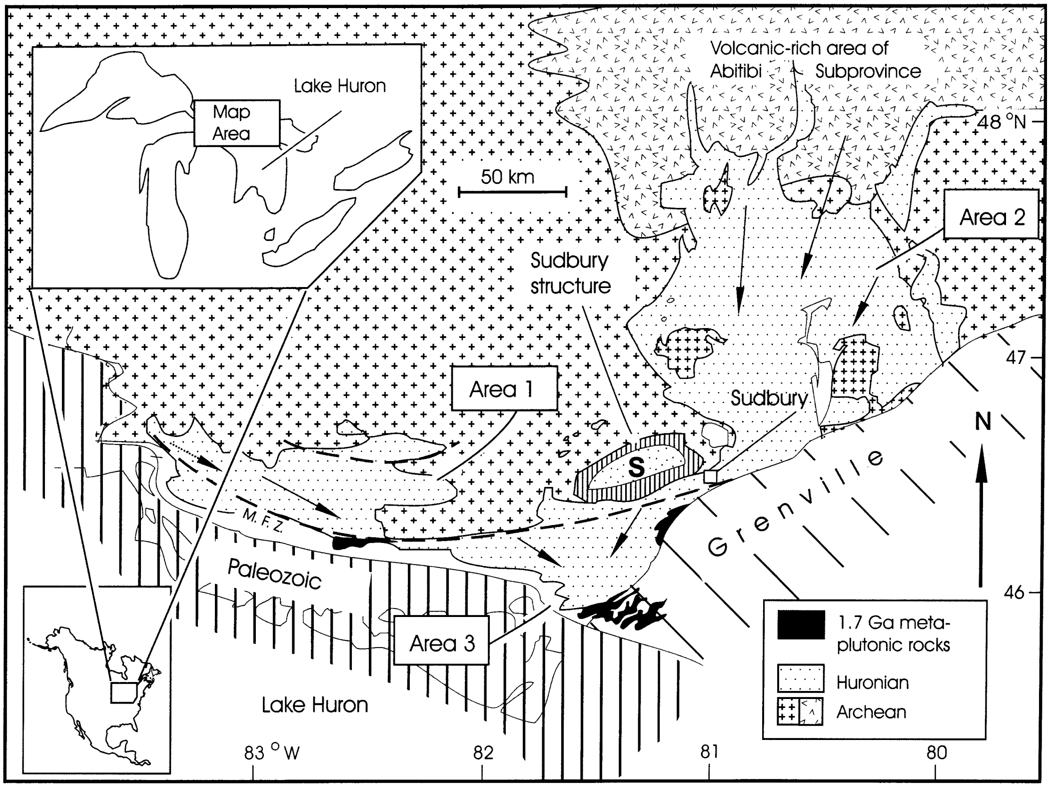

Fig. 1. Generalized geological map of the Huronian Supergroup (adapted from Fedo et al., 1997b). Arrows indicate regional paleocurrent directions for Huronian sedimentary rocks. Note the occurrence of ca. 1.7 Ga felsic metaplutonic rocks in the southern region of the Huronian outcrop belt and along the Grenville Front (ca. 1.0 Ga) M.F.Z. refers to the Murray Fault zone.

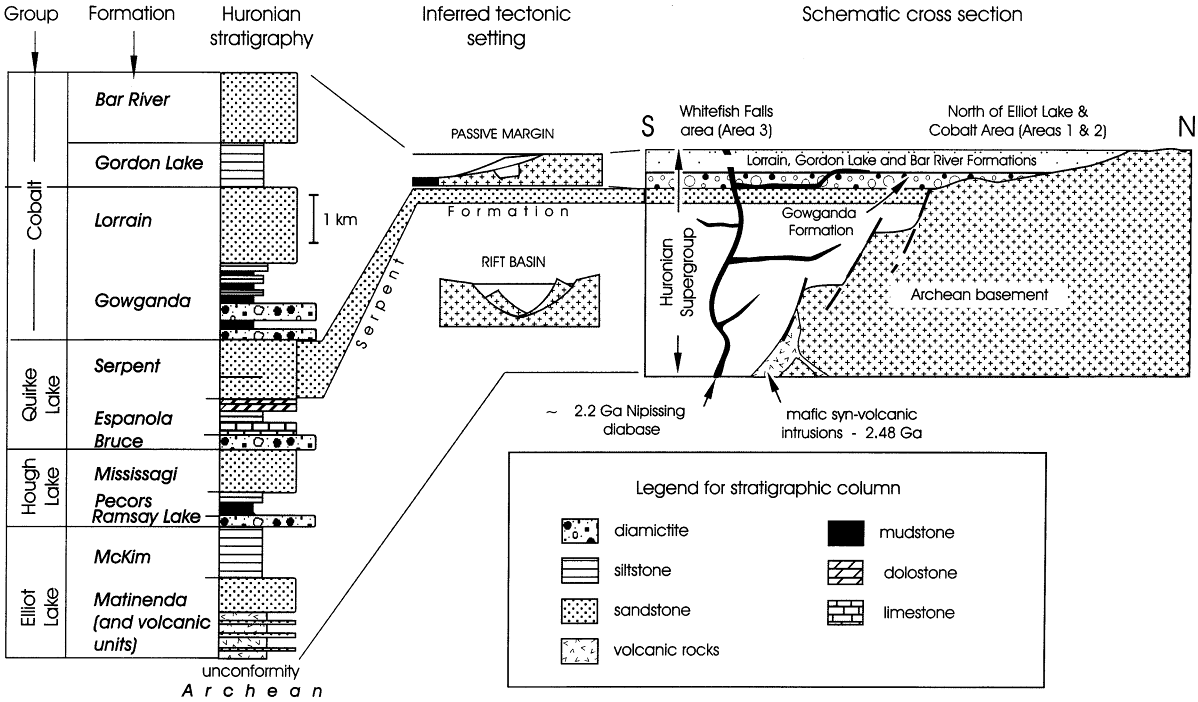

Fig. 2. Generalized stratigraphic and tectonic relationships of the Huronian Supergroup (adapted from Fedo et al., 1997b). Note that the transition from rift setting to passive margin setting takes place at about the time of deposition of the upper Quirke Lake Group.

1973; Young, 1983; McLennan et al., 1979; Fedo et al., 1997a).

McLennan et al. (1979) examined the rare earth element distributions of the fine grained sedimentary rocks of the Huronian Supergroup. They documented a clear stratigraphic evolution in REE patterns with more 'Archean-like' patterns having only minor depletion of Eu at the base (McKim and Pecors Formations) to 'post-Archean-like' patterns at the top of the succession with well developed negative Eu-anomalies (Gordon Lake Formation) (Fig. 3). These results were interpreted in terms of an evolving Late Archean continental crust where late- to post-tectonic intracrustally derived K-rich granitic rocks, possessing negative Eu-anomalies, increasingly were excavated, exposed and incorporated into Proterozoic sediments of the Huronian Supergoup. Thus, the Huronian was thought to record a major episode of Late Archean crustal growth and differentiation that, on a global scale, resulted in a fundamental change in crustal composition (e.g. Taylor and McLennan, 1985, 1995).

A variety of recent studies has also shown that parts of the Huronian Supergroup may have been affected by widespread alteration at about 1.7 Ga. For example, Rb–Sr studies of paleosols at the base of the Huronian record such ages (Roscoe et al., 1992) and are likely the result of alkali metasomatism. On the basis of detailed petrography and mineral chemistry, Fedo et al. (1997b) have shown that sedimentary rocks of the Serpent Formation also were affected pervasively by Na- and K-metasomatism, which they also inferred to have taken place at about 1.7 Ga although no direct age constraints are available. Although some ca. 1.7 Ga felsic plutons are present in the southern part of the Huronian belt (Fig. 1), metamorphism related to the Penokean Orogeny is generally thought to be older (1.85–1.80 Ga). In addition, hydrothermal monazite associated with albitization processes in Huronian sedimentary rocks yield U–Pb ages of 1700 ± 2 Ma (Schandl et al., 1994). Accordingly, Fedo et al. (1997b) concluded that K-metasomatism was related to groundwater circulation of deep basinal brines, with fluids being derived from the eroding Penokean Orogen to the south.

The use of Nd and Pb isotopes is now well established as an important tool for evaluating both the provenance and, in some cases, the post-depositional alteration history of terrigenous sedimentary rocks. In this paper, we report on whole rock Sm–Nd and Pb isotopic data for Huronian fine grained sedimentary rocks, originally studied by McLennan et al. (1979), and discuss their significance for understanding: (1) the provenance and post-depositional history of the Huronian Supergroup; and (2) crustal evolution in the southern part of the Superior Province.

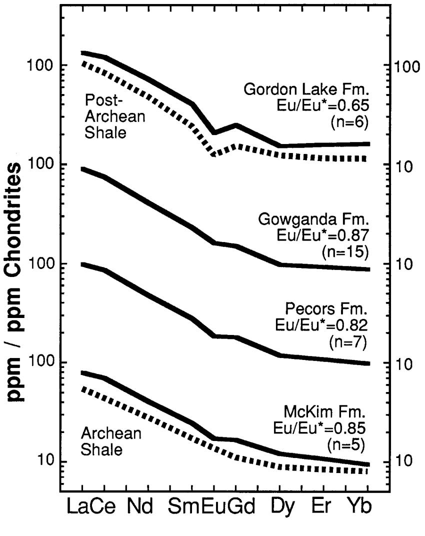

Fig. 3. Chondrite-normalized REE patterns of the average compositions of various Huronian fine-grained formations (data from McLennan et al., 1979). Shown for comparison are estimates of the average Post-Archean and average Archean shales (from Taylor and McLennan, 1985). Lower Huronian mudstones are characterized by REE patterns only slightly evolved to greater LREE-enrichment and negative Eu-anomalies from typical Archean shales whereas the upper Huronian Gordon Lake Formation is essentially identical to typical post-Archean shales. This evolution in REE patterns is interpreted as reflecting a change in the composition of the upper continental crust in this region during the Late Archean.

2. Geological background

The Huronian Supergroup crops out on the north shore of Lake Huron, Canada and forms the dominant element of the Southern Province. Huronian rocks consist of a 300 km arcuate east–west trending fold belt with intensity of deformation increasing southward. The Huronian succession reaches a maximum thickness of about 12 km near Lake Huron and rests unconformably on Archean basement that commonly exhibits a well developed paleosol. The entire succession thins to the north, primarily due to normal faulting (e.g. Murray Fault), that was active during lower Huronian sedimentation, and to wedging out of lower units.

The age of the Huronian Supergroup is not especially well established but is constrained to have been deposited sometime between about 2450 and 2219 Ma on the basis of U–Pb zircon and baddeleyite ages of lower Huronian mafic volcanic rocks and ubiquitous cross-cutting Nipissing Diabase dikes and sills (Krogh et al., 1984; Corfu and Andrews, 1986). The entire sequence was deformed and metamorphosed during the ca. 1.85–1.80 Ga Penokean Orogeny, with southerly regions being most severely affected (e.g. greenschist and local amphibolite grade) and more northerly regions being least affected (e.g. sub-greenschist grade) (Card, 1978). An earlier phase of ca. 2.4–2.2 Ga deformation (so-called Blezardian Orogeny) has long been suggested (e.g. Church, 1968; Riller et al., 1999) but there is no firm consensus on the exact nature or timing of this event, or indeed if it even exists (e.g. Long et al., 1999). In southern areas and along the current location of the Grenville Front, felsic to intermediate plutonic rocks were intruded at about 1.75–1.70 Ga (Davidson et al., 1992). This age is similar or slightly younger than post-tectonic plutons related to the Penokean Orogeny in Minnesota (Spencer, 1987; Holm et al., 1998) and the Mazatzal-Yavapi orogenies that affected much of the mid-continent of North America (e.g. Condie, 1992). Minor amounts of plutonic rocks intruded at various times through to the close of the Grenville Orogeny at ca. 1.0 Ga.

Huronian rocks were likely deposited in an evolving rift-passive margin setting (Young, 1983). The distribution of lower Huronian Elliot Lake (including McKim Formation), Hough Lake (including Pecors and Mississagi formations) and Quirke Lake Groups are relatively restricted and likely represent deposition in a continental rift basin. The upper Huronian Cobalt Group (including Gowganda and Gordon Lake formations) is far more extensive and represents deposition at a stable passive margin. Within the Huronian are three diamictite units (Ramsay Lake, Bruce, Gowganda) that have been interpreted as glaciogenic deposits with the Gowganda Formation being the most extensive and perhaps part of a continental scale glaciation (Young, 1970).

The Sudbury Basin, consisting of the Whitewater Group and Sudbury Igneous Complex (dated at 1850 ± 1 Ma; Krogh et al., 1984) formed after deposition and early deformation of the Huronian outcrop belt. The timing of major deformation of Huronian and Whitewater rocks during the Penokean Orogeny is not well constrained but further west in Minnesota, Wisconsin and Michigan appears to have taken place approximately during the interval of 1860–1835 Ma (e.g. Sims et al., 1989). In addition to development of felsic plutons at about 1.7 Ga, this time is also notable for widespread resetting of the Rb/Sr isotope system in paleosols at the base of the Huronian Supergroup (Roscoe et al., 1992) and in sedimentary rocks of the Gowganda Formation (Fairbairn et al., 1969).

3. Analytical methods

All analyses were conducted at the Max-Planck-Institut für Chemie. Sm–Nd isotopic data were determined by methods similar to those of White and Patchett (1984). Approximately 100 mg of sample powder were carefully weighed, spiked with a mixed ^{149}Sm–^{150}Nd spike, and dissolved with concentrated HF-HNO_3 in Krogh-type bombs for 48 h at 220°C. After removal from bombs, they were dried after addition of $HClO_4$ and re-dissolved in HCl. REE were separated using standard cation exchange methods and Sm and Nd were then separated using reverse phase chromatography. Sm and Nd isotopic compositions were determined on Finnigan MAT 261 multicollector mass spectrometers using a static mode of data acquisition. During the course of study, measured ^{143}Nd/^{144}Nd on ten analyses of the La Jolla standard (2σ) yielded 0.511847(24) and ^{143}Nd/^{144}Nd ratios for samples were accordingly corrected to be consistent with a La Jolla value of 0.511860. Uncertainties on ^{147}Sm/^{144}Nd are less than 1%.

Lead was separated in a 100 μl anionic exchange column using procedures similar to White and Dupré (1986). Procedural total Pb blanks ranged from 68 to 130 pg. To ensure uniform running conditions for mass spectrometric analysis, the chemical yield was measured for each sample by isotope dilution on a beaker aliquot. For each analysis, approximately 30 ng were loaded on a single Re filament using a silica gel-H_3PO_4 acid mixture (Cameron et al., 1969) and isotope ratios measured on a Finnigan Mat 261 mass spectrometer using static multicollection. Lead isotope ratios are corrected for mass fractionation by 0.04% amu^{-1} (average) based on repeated analyses of approximately 30 ng aliquots of NBS 982 standard solution ($\pm$0.02% amu^{-1}; 2σ; $n = 7$) run at the same temperature as the samples (1350–1400°C).

Duplicate Nd and Pb isotopic analyses for some samples were determined on separate powder dissolutions to ensure reproducibility and evaluate potential isotopic heterogeneity (representative duplicate analyses are included in Table 1).

4. Neodymium isotopes

The Sm–Nd isotopic composition of the McKim, Pecors and Gowganda formations are remarkably uniform (Table 1). The ^{147}Sm/^{144}Nd ratios vary from 0.1021 to 0.1123 and the ε_{Nd} calculated at the approximate time of sedimentation (2.3 Ga) vary from -2.47 to -4.97. The depleted mantle model ages (T_{DM}) are in the range 2.84–3.00 Ga (but note that model ages may be up to 0.2 Ga younger, depending on

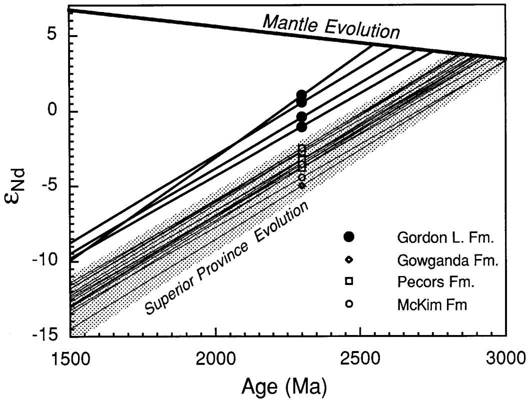

Fig. 4. Plot of ε_{Nd} versus age for Huronian sedimentary rocks. Solid lines represent evolution and data points are plotted at the approximate age of sedimentation (2.3 Ga). Also shown is a field representing Archean-aged Superior Province evolution (McCulloch and Wasserburg, 1978). Lower Huronian formations are consistent with a provenance exclusively from the Archean Superior Province. The Gordon Lake Formation is distinct with younger Nd-model ages and higher ε_{Nd} at the time of sedimentation. The possibility that the Gordon Lake Sm–Nd isotopic system was partially disturbed near the time of sedimentation cannot be excluded, however, such a process is unlikely to be entirely responsible for the high ε_{Nd} and a distinct provenance, with a younger component, is indicated.

which mantle evolution model is adopted). On Fig. 4 the Nd isotopic compositions are plotted as a function of age and also shown is a field representing the evolution of the Archean-aged Superior Province (McCulloch and Wasserburg, 1978). From this comparison, it is clear that a provenance entirely dominated by the Superior Province is likely. This is in complete agreement with previous paleocurrent, petrographic and geochemical data (e.g. Young, 1983).

The Sm–Nd isotopic characteristics of the overlying Gordon Lake Formation are distinctive from those of the other Huronian formations studied. Although the Sm/Nd ratios mostly overlap those from the McKim, Pecors and Gowganda, ε_{Nd} at the time of sedimentation is significantly higher, in the range -1.04 to $+1.06$, leading to younger T_{DM} values of 2.55–2.76 Ga.

There is growing evidence that under certain circumstances Sm–Nd isotopic systematics in sedimentary rocks may be disturbed by post depositional processes (Bock et al., 1994; McDaniel et al., 1994a; Lev et al., 1998, 1999). Is there any such evidence in the Gordon Lake Formation? A characteristic feature of Sm–Nd isotopic disturbance in sedimentary rocks appears to be a positive correlation between Sm/Nd ratio and T_{DM} (Bock et al., 1994). The Gordon Lake appears to show such a relationship but the range of Sm/Nd is small and with only four samples, it is not especially well constrained. However, ε_{Nd}(2.3 Ga) also correlates negatively with Rb/Sr, K/Na and $^{206}Pb/^{204}Pb$ (see Table 1), geochemical features that do appear to correlate with a metasomatic event at about 1.7 Ga (see below). Accordingly, the Sm–Nd isotopic systematics may have been partially disturbed, most likely either at the time of sedimentation or at about 1.7 Ga when the Pb isotopes were disturbed (see below).

It is unlikely that disturbance of the Sm–Nd isotope system can explain much of the differences in ε_{Nd} at about the time of sedimentation. The Sm/Nd ratios for the Gordon Lake are very similar to the other Huronian units studied and so any isotopic disturbance likely had only a minor effect on Sm/Nd ratios. Sm/Nd isotopic evolution lines for the Gordon Lake (Fig. 4) indicate that any reasonable upper crustal Sm/Nd prior to 1.7 Ga cannot shift the ε_{Nd} (2.3Ga) to values as low as the other Huronian units. Accordingly, the Nd isotopic data support a different provenance for the Gordon Lake including a significant component of younger mantle derived material.

5. Lead isotopes

Although there are not a large number of studies of Pb isotopes in clastic sedimentary rocks, it is clear that such data can provide information about provenance and/or post-depositional processes, depending on the exact geological history. Pb isotopic data for Huronian Supergroup mudstones fall into two stratigraphically distinct groups.

Fig. 5 is a plot of $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ for the mudstones of the lower Huronian Pecors and McKim formations. Also shown on this diagram are data for the McKim (1 sample) and Mississagi formations published by Dickin et al.

Table 1
Nd and Pb isotopic data and selected geochemical data for sedimentary rocks from the Huronian Supergroup[a]

Sample	Area	K_2O/Al_2O_3	Rb/Sr	Sm (ppm)	Nd (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	ε_{Nd}	ε_{Nd} (2.3 Ga)	T_{DM}	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
McKim Formation													
M1	3	0.136	0.35	6.431	36.05	0.1078	0.511167	−28.70	−2.47	2.84	25.417	16.649	41.428
M2	3	0.255	1.16								34.026	17.759	46.619
M3	3	0.149	0.56	7.357	40.74	0.1091	0.511132	−29.37	−3.54	2.93	22.499	16.349	41.367
M5	3	0.199	1.34	5.554	31.19	0.1076	0.511108	−29.84	−3.55	2.92	20.932	16.160	39.783
M6	3	0.168	0.54								18.567	15.832	38.259
M7	3	0.169	1.15	5.590	30.48	0.1109	0.511113	−29.75	−4.42	3.00	25.675	16.703	43.375
M7-Duplicate							(0.511115)				(25.676)	(16.705)	(43.393)
M8	3	0.255	6.53								59.087	21.314	72.303
Pecors Formation													
P10	1	0.169	3.55								22.889	16.545	40.210
P1	3	0.236	1.83	6.597	35.50	0.1123	0.511221	−27.64	−2.74	2.89	27.894	17.001	45.189
P5	3	0.168	1.09	4.694	27.78	0.1021	0.511040	−31.16	−3.25	2.87	29.993	17.317	46.282
P5-Duplicate							(0.511046)				(29.980)	(17.291)	(46.321)
P6	3	0.208	0.71								26.740	17.000	45.346
P7	3	0.219	0.89	8.392	47.71	0.1063	0.511076	−30.46	−3.79	2.93	23.012	16.333	40.550
P12	3	0.160	0.46	8.012	45.66	0.1060	0.511139	−29.24	−2.48	2.84	19.918	15.891	38.831
P13	3	0.178	0.52								20.681	16.039	41.469
Gowganda Formation													
G3	1	0.198	0.62	4.427	25.65	0.1043	0.511104	−29.93	−2.66	2.84	23.721	16.438	42.063
G3-Duplicate							(0.511097)				(23.694)	(16.438)	(42.052)
G5	1	0.175	0.55	4.290	24.75	0.1047	0.511065	−30.68	−3.54	2.90	25.530	16.646	43.687
G9	1	0.178	0.78	5.514	32.02	0.1041	0.511062	−30.75	−3.41	2.89	29.133	16.702	45.242
G11	2	0.209	1.61	7.471	43.42	0.1040	0.510981	−32.32	−4.97	3.00	43.049	18.199	54.457
G11-Duplicate							(0.510987)						
G16	2	0.136	0.37	4.887	27.34	0.1080	0.511133	−29.36	−3.19	2.90	26.988	16.512	44.770
G18	2	0.123	0.13	5.135	28.94	0.1072	0.511149	−29.04	−2.63	2.85	32.617	17.286	41.369
G21	3	0.193	0.45	4.760	28.16	0.1021	0.511015	−31.67	−3.76	2.91	28.441	17.024	40.668
G23	3	0.260	3.43	6.245	33.67	0.1121	0.511167	−28.70	−3.73	2.96	40.870	18.378	50.046
G23-Duplicate							(0.511174)						
G28	3	0.226	3.18	7.662	42.54	0.1088	0.511143	−29.17	−3.25	2.91	34.498	17.799	49.041
Gordon Lake Formation													
GL4	1	0.391	40.7	16.97	92.08	0.1114	0.511293	−26.24	−1.04	2.76	65.905	20.943	75.195
GL5	1	0.401	18.2								114.722	25.992	130.312
GL6	1	0.215	2.83								29.818	17.136	46.969
GL7	1	0.219	2.36	9.792	66.23	0.0894	0.511067	−30.65	+1.06	2.55	31.107	17.489	46.771
GL7-Duplicate*							(0.511105)						
GL1	3	0.355	13.7								60.691	19.686	67.431
GL2	3	0.248	3.74	10.22	58.64	0.1053	0.511285	−26.4	+0.59	2.62	48.419	18.693	60.114
GL2-Duplicate							(0.511287)				(49.033)	(18.712)	(60.497)
GL3	3	0.368	17.8	10.02	56.08	0.1080	0.511276	−26.56	−0.38	2.69	51.972	18.964	67.069

---

[a] K_2O/Al_2O_3 and Rb/Sr data from McLennan et al. (1979).

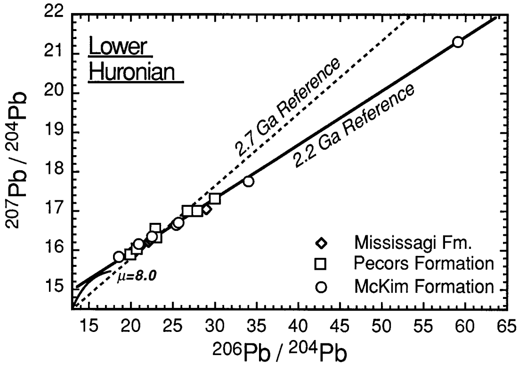

Fig. 5. Plot of $^{207}\mathrm{Pb}/^{204}\mathrm{Pb}$ versus $^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$ for sedimentary rocks from the lower Huronian formations including data for the Mississagi Formation from Dickin et al. (1996). Shown for reference are a $^{238}\mathrm{U}/^{204}\mathrm{Pb}$ $(\mu) = 8.0$ growth curve, a 2.7–0.0 Ga reference line designed to pass through unaltered igneous K-feldspars from the Archean Superior Province (data compiled in Hemming et al., 1996) and a 2.2–0.0 Ga reference line designed to pass through the majority of Huronian data. A regression of all lower Huronian data results in an age of 2169 ± 54 Ma. Regression results for individual formations are given in Table 2 and all fall in the range of about 2.0–2.2 Ga. These data indicate that the U–Pb isotope systems of lower Huronian sedimentary rocks were disturbed shortly after the time of sedimentation, which is constrained to sometime between 2450 and 2219 Ma (see text).

(1996). This and subsequent Pb isotope diagrams show a $\mu = 8.0$ growth curve and a 2.7–0.0 Ga reference line plotted to pass through the Pb isotope compositions of leached K-feldspars from Superior Province plutonic rocks and thus representative of undisturbed Superior Province evolution through to today. Pb isotopes in lower Huronian sedimentary rocks do not correspond to Superior Province evolution but rather have been disturbed at a younger time, in some cases leading to very high $^{206}\mathrm{Pb}/^{204}$ Pb ratios. Regression of the individual formations (Table 2) leads to ages in the range of about 2.0–2.2 Ga but with large uncertainties and considerable scatter (high M.S.W.D., mean square weighted deviations). Some scatter in $^{207}\mathrm{Pb}/^{204}$ Pb ratios is not unexpected in clastic sedimentary sequences since there are likely to have been variations in initial isotopic compositions among samples, related to slight variations in provenance. These ages compare to likely sedimentation ages, that lie somewhere in the range of 2.45–2.22 Ga (see above), and suggest a disturbance of the U–Pb isotope systematics at or shortly after the time of sedimentation.

Table 2
Summary of $^{207}\mathrm{Pb}/^{204}\mathrm{Pb}$-$^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$ regressions

Formation	Geographic area(s)	Number of samples	Age[a] (Ma)	M.S.W.D.[a]	μ_{Sup}[b]	Comments
McKim	3	9	2170 ± 58	92.1	23	Includes 1 sample from Dickin et al. (1996)
Pecors	3	5	2212 ± 92	9.1	22	Excludes Area 1 and 1 possible McKim
Mississagi	3	5	1996 ± 130	8.1	21	From Dickin et al. (1996)
Lower Huronian	1,3	21	2169 ± 54	120		
Gordon Lake	1	4	1679 ± 130	231	25	
Gordon Lake	1,3	7	1679 ± 250	2430		
Upper Huronian	1,2,3	16	1667 ± 120	1300		Gordon Lake and Gowganda formations

[a] Model 1 age regression (Ludwig, 1988); M.S.W.D. is mean square weighted deviation.

[b] $^{238}\mathrm{U}/^{204}\mathrm{Pb}$ ratio (μ) required to elevate $^{207}\mathrm{Pb}/^{204}\mathrm{Pb}$ and $^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$ ratios from a composition equivalent to the least radiogenic Superior Province igneous K-feldspar ($^{207}\mathrm{Pb}/^{204}\mathrm{Pb} = 14.50$; $^{206}\mathrm{Pb}/^{204}\mathrm{Pb} = 13.60$) to a point on the regressed line between 2700 Ma (t_1) and the regressed age (t_2).

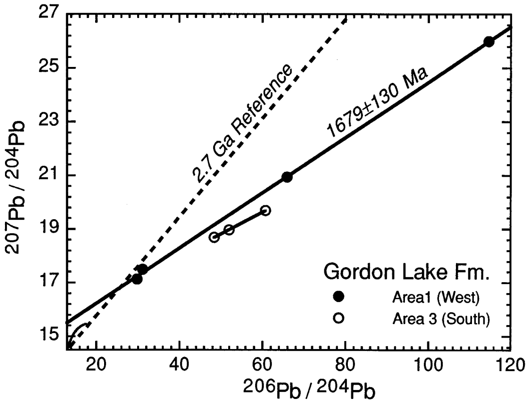

Fig. 6. Plot of ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb for sedimentary rocks from the Gordon Lake Formation. Shown for reference are a $\mu = 8.0$ growth curve and a 2.7–0.0 Ga reference line designed to pass through unaltered igneous K-feldspars from the Archean Superior Province. A regression for Gordon Lake Formation samples from Area 1 (west) correspond to an age of 1679 ± 130 Ma. Samples from Area 3 (south) have relatively little spread in ^{206}Pb/^{204}Pb ratios but the data are consistent with a similar age but differing initial Pb isotopic compositions. These ages suggest that the U–Pb isotope system was strongly disturbed in the Gordon Lake Formation at about 1.7 Ga.

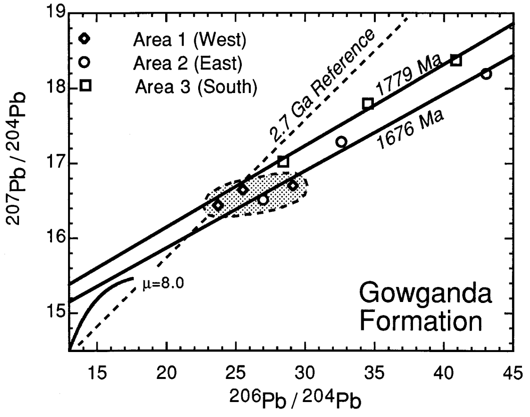

Fig. 7. Plot of ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb for fine-grained sedimentary rocks from the Gowganda Formation. Shown for reference are a $\mu = 8.0$ growth curve and a 2.7–0.0 Ga reference line designed to pass through unaltered igneous K-feldspars from the Archean Superior Province. Gowganda Formation samples show far greater scatter than other units, however, samples from Areas 2 (east) and 3 (south) correspond to linear arrays and regressions indicate ages of 1676 and 1779 Ma, respectively. These ages suggest that the U–Pb isotope system was strongly disturbed in at least some samples of the Gowganda Formation at about 1.7 Ga.

Lead isotopic systematics in upper Huronian sedimentary rocks indicate a second disturbance at about 1.7 Ga. This is best seen for the Gordon Lake Formation (Fig. 6) where ^{207}Pb/^{204} Pb versus ^{206}Pb/^{204} Pb is shown. The data are more scattered than lower Huronian samples and may suggest a regional control on variations in ^{207}Pb/^{204} Pb ratios. A regression of data from Area 1 (west) samples corresponds to an age of 1679 ± 130 Ma with a large MSWD (231). The three samples from Area 3 (south) fall along a similar or perhaps even shallower slope. Mudstones from the Gowganda Formation similarly show a great deal of scatter and the ^{207}Pb/^{204} Pb ratios also appear to be in part regionally controlled (Fig. 7). Only Areas 2 (east) and 3 (south) have sufficient variation in ^{206}Pb/^{204} Pb for calculating regressions and for these areas, these regressions lead to ages of about 1.7 Ga.

6. Discussion

6.1. Provenance and crustal evolution: Nd isotopes

The Nd isotopic evidence clearly points to a dominant role of the Archean Superior Province in the provenance of the Huronian Supergroup, as has been suggested by all previous studies. The Pb isotope data, although complex because of one or more episodes of resetting, are also consistent with a Superior Province provenance (see further discussion below). However, the Nd isotopic results for the Gordon Lake Formation stand out as suggesting a distinctive, apparently younger, component to the provenance compared to the underlying units. Within this general region, there are two possible origins of this younger component.

On the basis of the REE data (see Fig. 3), McLennan et al. (1979) suggested that the upper Huronian was derived largely from Late Archean K-rich granitic rocks that formed predominantly by intra-crustal melting of Late Archean crustal additions. The Nd isotopic data for the Gordon Lake are generally consistent with this model although they suggest that these K-rich granitic rocks totally dominated the source to the virtual exclusion of materials similar to those that provided detritus to the underlying Huronian sedimentary rocks.

Supracrustal rocks at the base of the Huronian are thought to be related to continental rifting (e.g. Young, 1983). Included in these successions are mafic to felsic volcanics and synvolcanic plutonic rocks. Incorporation of approximately 30–50% of such material into the Gordon Lake Formation might explain such a shift in Nd isotopic composition. A similar potential provenance component has also been described by Hemming et al. (1994) in a study of the Early Proterozoic Pokegama Formation in Minnesota. In that study, Pb isotopes were used to identify a minor quartz component of about 2345 ± 69 Ma age that was thought to be related to very early rifting in the southern Superior Province and suggests relatively large-scale transport of such material. A difficulty with this interpretation is that it is not clear how such rift-related igneous rocks could be largely excluded from lower Huronian sedimentary rocks and strongly concentrated in upper Huronian sedimentary rocks.

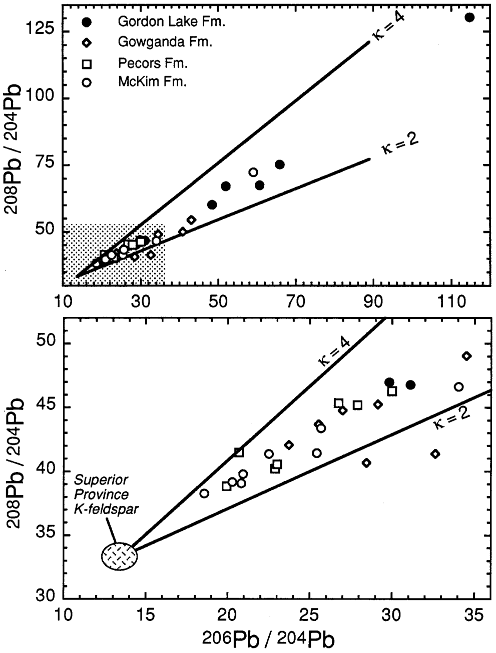

Fig. 8. Plot of $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ for Huronian sedimentary rocks. Stippled region in upper diagram is expanded and shown in lower diagram. Shown for reference are the field of least altered igneous K-feldspars from the Superior Province and lines corresponding to initial isotopic compositions equal to Superior Province K-feldspar and evolution with $^{232}Th/^{238}U$ $(\kappa) = 2$ and 4. Most data fall between $\kappa = 2$ and 4 which compares to typical upper crustal values of about 3.8 (Taylor and McLennan, 1985).

6.2. Re-equilibration of the Pb isotope system

The mechanism by which the Pb isotope system was reset in the Lower Huronian is not entirely clear but the age, which is close to or slightly younger than the age of sedimentation, suggests that diagenetic processes may be responsible. The 2219 Ma Nipissing Diabase complex, which is ubiquitous throughout the Huronian, is the minimum age constraint on the Huronian Supergroup. Intrusion of the Nipissing Diabase has been suggested as a possible cause of metal transport associated with Ag-vein deposits (e.g. Smyk and Watkinson, 1990). There is field evidence that an early phase of the diabase was intruded while much of the sedimentary sequence was still unconsolidated (Shaw et al., 1999) and this may have also played a role in providing conditions (e.g. temperature, fluids) for a significant increase in the U/Pb ratios of lower Huronian sedimentary rocks and thus leading to the effective resetting of the Pb isotope system.

The mechanism for changing U/Pb ratios in lower Huronian sediments was probably influenced by loss of lead with or without a significant gain in uranium. This can be seen in Fig. 8 which plots $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$. As will be discussed below, the likely $^{238}U/^{204}Pb$ ratio (μ) of Huronian sedimentary rocks when deposited was about 22. In order to achieve the highest $^{206}Pb/^{204}Pb$ ratios currently seen for the McKim and Pecors formations (in the range 30–60) an increase in μ from between a factor of 2–6 is required. However, the $^{232}Th/^{238}U$ ratios (κ) implied by the data are all between 2 and 4 which compares to the average upper crustal value of about 3.8 (Taylor and McLennan, 1985). Thus U gain can explain no more than a factor of about 2 change in μ. Accordingly, the McKim and Pecors formations samples with low $^{206}Pb/^{204}Pb$ (< 30)

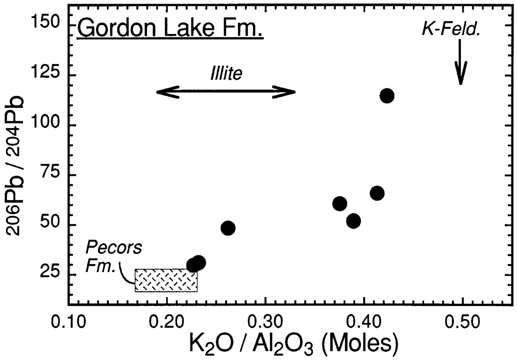

Fig. 9. Plot of $^{206}Pb/^{204}Pb$ versus mole ratio K_2O/Al_2O_3 for the Gordon Lake Formation. For reference, the hatched region encompasses all data for the Pecors Formation. Typical K_2O/Al_2O_3 ratios for the minerals K-feldspar and illite are also shown for reference. The Gordon Lake Formation has much higher K_2O/Al_2O_3 than typical shales and these high values correlate with $^{206}Pb/^{204}Pb$ suggesting that resetting of the U/Pb isotope system was related to addition of potassium to these rocks.

can be explained entirely by U gain but the higher $^{206}Pb/^{204}Pb$ samples require significant Pb loss.

The resetting of the Pb isotope system in the upper Huronian sedimentary rocks appears to correspond to changing conditions at about 1.7 Ga. There are a variety of well documented events within North America, including the Huronian region, at about this time:

1. Felsic plutons, of limited aerial extent but with ages of about 1.70–1.75 Ga, occur in the southern regions of the Huronian outcrop belt and in the Southern Province along the Grenville Front (e.g. Davidson et al., 1992, see Fig. 1). Similar rocks of 1.77–1.76 Ga age are found in the Penokean Orogen of Minnesota where they are associated with staurolite-grade metamorphism (Holm et al., 1998);
2. The 1.79–1.70 Ga Yavapi and Mazatzal orogenies affected a broad region of southwestern North America at about this time (Condie, 1992).
3. $^{40}Ar/^{39}Ar$ whole rock ages of Huronian sedimentary rocks (including McKim, Gowganda and Gordon Lake formations in Areas 1 and 3) show clear evidence of disturbance at 1.76–1.70 Ga, in addition to 1.85–1.80 Ga Penokean ages, but without any ages indicative of the Late Archean provenance (Hu et al., 1998). The 1.76–1.70 Ga ages were interpreted to represent a period of rapid post-Penokean uplift.
4. Late Archean-early Proterozoic paleosols at the base of the Huronian Supergroup have had the Rb/Sr isotopic system reset at about 1.7 Ga (Roscoe et al., 1992), thought to be related to late potassium enrichment (Rainbird et al., 1990; Prasad, 1995);
5. In Area 3, the Rb/Sr isotopic system of the Gowganda and Espanola formations was reset at ≈1.7–1.8 Ga (Fairbairn et al., 1969). Further to the north, in Area 2, the Gowganda Formation shows a Rb/Sr age of about 2.12 Ga.
6. Hydrothermal monazite, associated with albitization in Huronian sedimentary rocks, Nipissing Diabase and Sudbury breccia yield near concordant U–Pb ages of 1700 ± 2 Ma (Schandl et al., 1994).
7. On the basis of detailed petrography and geochemistry, Fedo et al. (1997b) concluded that K- and Na-metasomatism pervasively affected sedimentary rocks within the Serpent Formation and inferred from indirect evidence that this process occurred at about 1.70–1.75 Ga.
8. Sandstone and shale of the 1.85 Ga Chelmsford Formation exhibit REE mobility occurring sometime near the age of deposition (McDaniel et al., 1994a). During post-depositional albitization there is also evidence of Pb addition to diagenetically altered detrital feldspars (Hemming et al., 1996). It is not clear if the two features are themselves related, nor are the ages of these disturbances well established except to be generally in the range 1.85–1.7 Ga.

6.3. Alkali metasomatism in upper Huronian mudstones

Fine-grained sedimentary rocks from both the Gowganda and Gordon Lake formations exhibit evidence for post-depositional alteration coinciding with resetting of the Pb isotope system at about 1.7 Ga. In Fig. 9 $^{206}Pb/^{204}Pb$ is plotted against K_2O/Al_2O_3 for the Gordon Lake Formation. Shown for reference are the values and ranges of K_2O/Al_2O_3 for K-feldspar and illite and the field for the Pecors Formation from the lower Huronian. There is a strong positive relationship and Gordon Lake samples with highest $^{206}Pb/^{204}Pb$ are those with K_2O/Al_2O_3 ratios unrealistically high for typical mudstones, suggesting post-depositional addition of potassium.

$^{206}Pb/^{204}Pb$ ratios for the Gowganda Formation are not especially high and no clear relationship is seen when plotted against K_2O/Al_2O_3. Nevertheless, the Gowganda Formation also shows evidence for post-depositional alteration, for example from resetting of the Rb–Sr system at about 1.7 Ga (see discussion above). Fig. 10 shows ternary plots of mole fraction of Al_2O_3-($CaO + Na_2O$)-K_2O with various minerals and rock compositions plotted for reference (data from McLennan et al., 1979). On the left, it can be seen that samples from the Pecors and McKim formations cluster around the value for average shale, suggesting a rather typical sedimentary history. However, samples from the Gowganda and Gordon Lake Formations exhibit quite different features. Gordon Lake samples fall on a trend from compositions more K-rich than muscovite and extending on a line that would intersect the Al_2O_3-($CaO + Na_2O$) tie line at about 50–55. Such relationships cannot be developed from typical weathering reactions and are generally regarded as clear evidence for post-depositional addition of potassium (Nesbitt and Young, 1989; Fedo et al., 1995).

Gowganda Formation samples also define a shallow trend that intersects the Al_2O_3-($CaO + Na_2O$) tie line at about 40–45. This shallow trend is consistent with that found for Gowganda mudstones and diamictites by Young and Nesbitt (1999). If variation among major elements was dominated by simple weathering processes, a trend that is parallel to the Al_2O_3-($CaO + Na_2O$) tie line would be expected (Nesbitt and Young, 1984; Fedo et al., 1995). Young and Nesbitt (1999) interpreted this trend to represent mixing between unweathered glacial rock flour and more severely weathered recycled shale. However, such shallow trends are also consistent with post-depositional addition of potassium (e.g. Fedo et al., 1995) and it is possible that both processes are taking place.

Rubidium behaves in a manner similar to potassium and Rb/Sr generally correlates with $^{206}Pb/^{204}Pb$ in all Huronian mudstones again with the Gordon Lake and some Gowganda Formation samples being most severely affected (Fig. 11). This is especially significant given the evi-

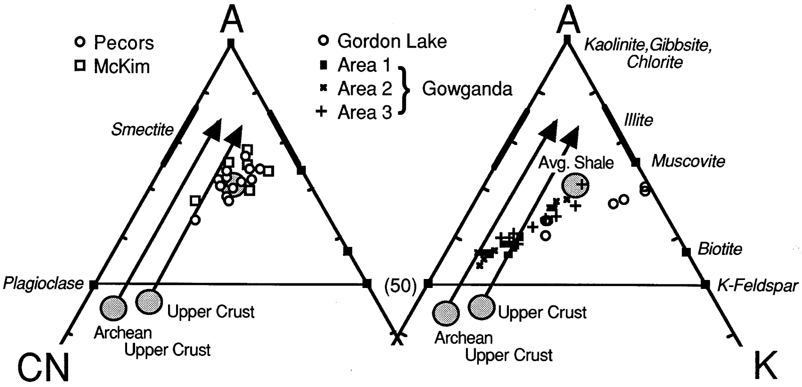

Fig. 10. Ternary plots of mole fractions Al_2O_3-($CaO + Na_2O$)-K_2O (A-CN-K) for Huronian sedimentary rocks. Shown for reference are typical sedimentary minerals, average post-Archean shale, and average Archean and post-Archean upper crust with predicted weathering trends for such compositions (see Nesbitt and Young, 1984). Lower Huronian sedimentary rocks tend to plot in the vicinity of average shale and are consistent with a normal weathering history influencing the major element composition of these sedimentary rocks. Data for the Gowganda Formation tend to plot below average shale, consistent with the lesser weathering history expected for such glacial related sediments. In contrast to lower Huronian samples, sedimentary rocks from the Gowganda and Gordon Lake formations define a shallow slope that intersects the A-CN tie line.

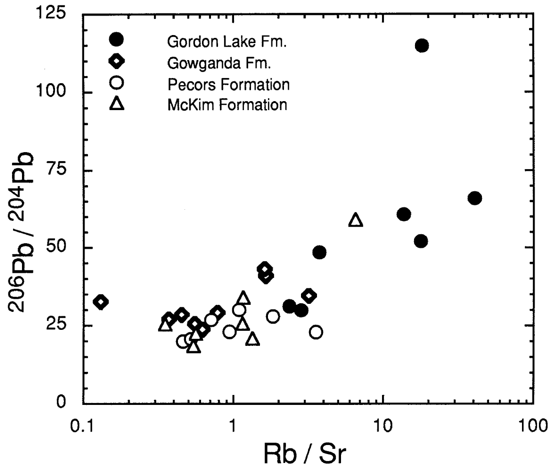

Fig. 11. Plot of $^{206}Pb/^{204}Pb$ versus Rb/Sr ratio for Huronian sedimentary rocks. There is a strong correlation for the Gordon Lake Formation and possible correlation for the Gowganda and McKim Formations.

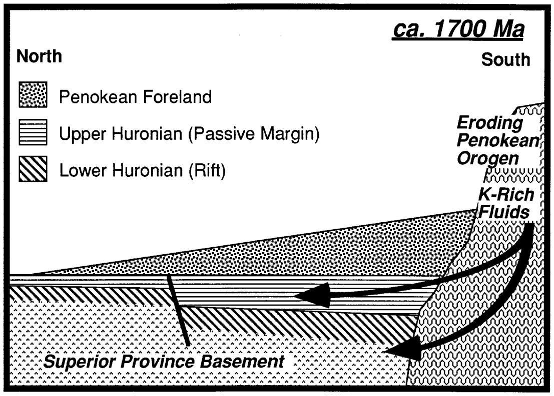

Fig. 12. Schematic model of alkali metasomatism in the Huronian Supergroup at about 1.7 Ga. At about 1.7 Ga, a northerly flowing groundwater system is likely to have existed throughout the Huronian outcrop belt in response to erosion of the mountain belt formed during the ca. 1.85 Ga Penokean Orogeny. It is suggested that this system was enriched in alkali elements (K, Rb, possibly Na) and preferentially invaded upper Huronian sedimentary rocks and other localized permeable regions such as the pre-Huronian unconformity surface, and possibly some lower Huronian sandstones (but not mudstones). These fluids resulted in the disturbance of the Rb/Sr and U/Pb through addition of Rb and possibly U and loss of Pb.

dence that the Rb–Sr isotopic systematics records post-depositional ages in a variety of Huronian sedimentary rocks (Fairbairn et al., 1969).

Fedo et al. (1997b) suggested that one likely explanation for K-metasomatism in the Serpent Formation was a gravity driven groundwater system derived from the high standing Penokean Orogen to the south, and possibly influenced by the post-tectonic 1.70–1.75 Ga felsic plutonism, resulting in brines flushing through the Huronian rocks to the north (Fig. 12). Currently available data suggest that the effects of such a system were most effective in upper Huronian sedimentary rocks (Serpent, Gowganda, Gordon Lake formations), possibly sandstones of the overlying Whitewater Group (McDaniel et al., 1994a,b; Hemming et al., 1996), and along the natural conduit that likely was provided by the unconformity surface at the base of the Huronian Supergroup. In the lower Huronian mudstones (McKim and Pecors formations) there is no evidence of either post-depositional potassium addition or 1.7 Ga Pb isotope disturbance. On the other hand, lower Huronian sandstone units (e.g. Matinenda and Mississagi formations) do show evidence for post-depositional K-addition (e.g. Pienaar, 1963; Pukovsky, 1975; McLennan, 1976) but the Mississagi Formation does not display evidence for Pb disturbance at 1.7 Ga (Dickin et al., 1996; also see Fig. 5, Table 2). Accordingly, any 1.7 Ga fluids may have affected relatively permeable lower Huronian sandstones but not the less permeable compacted mudstones.

6.4. History of the U/Pb isotope system in the Huronian Supergroup

A model for the overall history of the U/Pb isotope system in Huronian mudstones from 2.7 Ga is summarized in Fig. 13. Shown for reference is a $\mu = 8.0$ Pb isotope evolution curve and the locations of the least radiogenic igneous K-feldspar data for the Abitibi Subprovince of the Superior Province (Gariépy and Allègre, 1985; Vervoort et al., 1994) and the Penokean Orogen (Spencer, 1987). For the various Pb-Pb isochrons listed in Table 2, it is possible to calculate μ_{Sup} which is the value of $^{238}U/^{204}Pb$ required to elevate $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ from the least radiogenic Superior Province value to a point on the regressed isochron between 2700 Ma and the regressed age (values listed on Table 2). In the lower Huronian, μ_{Sup} is interpreted to reflect the average U/Pb ratio of Huronian sediments when deposited.

From several lines of evidence, including the Nd isotopic data discussed above, the provenance of the Huronian sedimentary sequence was dominantly from the Archean-aged Superior Province. At about 2700 Ma such a provenance, on average, would have had Pb isotopic characteristics approximating the igneous K-feldspar data of the Superior Province field plotted in Fig. 13 and a ^{238}U/^{204}Pb ratio (μ) of about 10–15, values typical of upper continental crust (e.g. Taylor and McLennan, 1985). Between 2.7 Ga and about 2.2 Ga (the minimum age of sedimentation), a variety of processes were in effect, including erosion, weathering and transportation, to form Huronian sediments. During these processes, μ was raised to an average value of about 22 over this time interval (heavy black line marked $\mu_{\text{Sup}} = 22$ in Fig. 13). At about the time of sedimentation (given as 2.2 Ga in Fig. 13) there was a disturbance possibly resulting from diagenetic processes, resulting in a resetting of the U/Pb isotope system. The disturbance resulted in samples from the lower Huronian (McKim, Mississagi, Pecors formations) having increases in U/Pb ratios by factors ranging from about 1 to 5. The low degree of scatter in Pb isotopic compositions of lower Huronian samples both on a stratigraphic and regional scale (e.g. Fig. 5) suggests that the provenance was quite homogeneous with respect to its Pb isotopic characteristics.

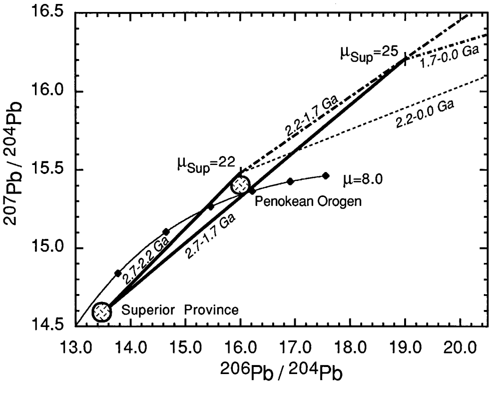

Fig. 13. Plot of ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb schematically showing possible Pb isotopic evolutionary history of Huronian sedimentary rocks. Shown for reference are values for igneous K-feldspars from the Archean Superior Province and Early Proterozoic Penokean Orogen, and a $\mu = 8.0$ growth curve (ticks at 500 Ma intervals). The 2.2–0.0 and 1.7–0.0 Ga lines are representative of regressions for lower and upper Huronian sedimentary rocks, respectively. See text for further discussion.

The U/Pb isotope system of upper Huronian rocks was disturbed at 1.7 Ga, and two models may explain this. The first is that during sedimentary processes forming the upper Huronian sediments, the μ was elevated to an average of about 25 over the interval 2.7–1.7 Ga (heavy black line $\mu_{\text{Sup}} = 25$ in Fig. 13), rather than 22 as was the case in the lower Huronian. In this model, the 2.2 Ga disturbance may not have significantly affected the upper Huronian. Nd isotope evidence indicates that the Gordon Lake Formation had a distinctive provenance and so it is also possible that a significant difference in the initial Pb isotopic composition of the Gordon Lake existed. On the other hand, the Gowganda Formation has identical Nd isotopic characteristics to the lower Huronian formations but is similar to the Gordon Lake in terms of Pb isotopes.

The alternative, and favored, model is that the U/Pb isotope system of upper Huronian sedimentary rocks was disturbed both at about 2.2 and again at 1.7 Ga. The major evidence considered to support this model is the considerable scatter observed in the age regressions of the Upper Huronian on both a stratigraphic and geographic scale. Thus, in this model, the upper Huronian sedimentary rocks had an increase in μ to a fairly uniform value of about 22 during weathering and transport. At about 2.2 Ga, a disturbance generated a further increase and in this case, a substantial spread in μ. Upper Huronian sedimentary rocks then evolved from 2.2 to 1.7 Ga (illustrated schematically by heavy dashed line marked 2.2–1.7 Ga in Fig. 13) with variable μ that in part was stratigraphically and geographically controlled. At 1.7 Ga, the U/Pb isotope system was again disturbed, this time by alkali metasomatism primarily affecting the upper part of the Huronian section, resulting a further increase in μ and highly scattered 1.7 Ga age regressions.

Acknowledgements

Much of this research was carried out while S.M.M. was a Visiting Scientist at the Max-Planck Institut für Chemie and he thanks Al Hoffman for his hospitality and generous support during this visit. We are also grateful to Sieglinde Raczek for her technical assistance and to Grant Young for providing Figures 1 and 2 and much useful information and advice. We are also grateful to Grant Young and Clément Gariépy for commenting on an earlier draft of the manuscript and to F. Corfu and G.M. Ross for journal reviews. Part of this research was supported by an NSF grant (EAR8957784) and a DAAD Study Visit Research Grant to S.M.M. A. Simonetti acknowledges financial support of a NSERC postdoctoral fellowship.

References

Bock, B., McLennan, S.M., Hanson, G.N., 1994. Rare earth element redistribution and its effects on the neodymium isotope system in the Austin Glen Member of the Normanskill Formation, New York, USA. Geochim. Cosmochim. Acta 58, 5245–5253.

Cameron, A.E., Smith, D.H., Walker, R.L., 1969. Mass spectrometry of nanogram-size samples of lead. Anal. Chem. 1, 525–526.

Card, K.D., 1978. Metamorphism of the Middle Precambrian (Aphebian) rocks of the eastern Southern Province. Geol. Surv. Canada Paper 78-10, 269–282.

Church, W.R., 1968. The Penokean and Hudsonian orogenies in the Great Lakes region, and the age of the Grenville Front. Abst. 14th Ann. Inst. on Lake Superior Geology, Superior, Wisconsin, pp. 16–18.

Condie, K.C., 1992. Proterozoic terranes and continental accretion in southwestern North America. In: Condie, K.C. (Ed.), Proterozoic Crustal Evolution. Elsevier, pp. 447–480.

Corfu, F., Andrews, A.J., 1986. A U–Pb age for mineralized Nipissing diabase, Gowganda, Ont., Canada. J. Earth Sci. 23, 107–109.

Davidson, A., van Breemen, O., Sullivan, R.W., 1992. Circa 1.75 Ga ages for plutonic rocks from the Southern Province and adjacent Grenville Province: what is the expression of the Penokean Orogeny. Geol. Surv. Canada Paper 92-2, 107–118.

Dickin, A.P., Artan, M.A., Crocket, J.H., 1996. Isotopic evidence for distinct crustal sources of North and South Range ores, Sudbury Igneous Complex. Geochim. Cosmochim. Acta 60, 1605–1613.

Fairbairn, H.W., Hurley, P.M., Card, K.D., et al., 1969. Correlation of radiometric ages of Nipissing diabase and Huronian metasediments with Proterozoic orogenic events in Ontario. Can. J. Earth Sci. 6, 489–497.

Fedo, C.M., Nesbitt, H.W., Young, G.M., 1995. Unraveling the effects of potassium metasomatism in sedimentary rocks and paleosols, with implications for paleoweathering conditions and provenance. Geology 23, 921–924.

Fedo, C.M., Young, G.M., Nesbitt, H.W., 1997a. Paleoclimatic control on the composition of the Paleoproterozoic Serpent Formation, Huronian Supergroup, Canada: a greenhouse to icehouse transition. Precambrian Res. 86, 201–223.

Fedo, C.M., Young, G.M., Nesbitt, H.W., et al., 1997b. Potassic and sodic metasomatism in the Southern Province of the Canadian Shield: evidence from the Paleoproterozoic Serpent Formation, Huronian Supergroup, Canada. Precambrian Res. 84, 17–36.

Gariépy, C., Allègre, C.J., 1985. The lead isotope geochemistry and geochronology of late-kinematic intrusives from the Abitibi greenstone belt, and the implications for late Archean crustal evolution. Geochim. Cosmochim. Acta 49, 2371–2383.

Hemming, S.R., McLennan, S.M., Hanson, G.N., 1994. Pb isotopes as a provenance tool for quartz: examples from plutons and quartzite, northeastern Minnesota. Geochim. Cosmochim. Acta 58, 4455–4464.

Hemming, S.R., McDaniel, D.K., McLennan, S.M., et al., 1996. Pb isotope constraints on the provenance and diagenesis of detrital feldspars from the Sudbury Basin, Canada. Earth Planet Sci. Lett. 142, 501–512.

Holm, D.K., Darrah, K.S., Lux, D.R., 1998. Evidence for widespread ≈ 1760 Ma metamorphism and rapid crustal stabilization of the Early Proterozoic (1870–1820 Ma) Penokean Orogen, Minnesota. Am. J. Sci. 298, 60–81.

Hu, Q., Evenson, N.M., Smith, P.E., et al., 1998. A world in a grain of sand: regional metamorphic history from 40Ar/39Ar laser probe analyses of Proterozoic sediments from the Canadian Shield. Precambrian Res. 91, 287–294.

Krogh, T.W., Davis, D.W., Corfu, G., 1984. Precise U–Pb zircon and baddeleyite ages for the Sudbury area. In: Pye E.G. et al. (Eds.), The Geology and Ore Deposits of the Sudbury Structure. Ontario Geol. Surv. Special Volume 1, 431–446.

Lev, S.M., McLennan, S.M., Meyers, W.J., et al., 1998. A petrographic approach for evaluating trace element mobility in a black shale. J. Sed. Res. 68, 970–980.

Lev, S.M., McLennan, S.M., Hanson, G.N., 1999. Mineralogic controls on REE mobility during black-shale diagenesis. J. Sed. Res. 69, 1071–1082.

Long, D.G.F., Young, G.M., Rainbird, R., Fedo, C., 1999. Actualistic and nonactualistic Precambrian sedimentary styles: examples from the Proterozoic north of Lake Huron. GAC-MAC Joint Ann. Meeting 1999 (Sudbury), Field Trip B5 Guidebook, 50 pp.

Ludwig, K.R., 1988. ISOPLOT for MS-DOS. A plotting and regression program for radiogenic-isotope data, for IBM-

PC compatible computers, version 1.00. U.S.G. Open-File Report 88-577.

McCulloch, M.T., Wasserburg, G.J., 1978. Sm–Nd and Rb–Sr chronology of continental crust formation. Science 200, 1003–1011.

McDaniel, D.K., Hemming, S.R., McLennan, S.M., et al., 1994a. Resetting of neodymium isotope and redistribution of REEs during sedimentary processes: the Early Proterozoic Chelmsford Formation, Sudbury Basin, Ont., Canada. Geochim. Cosmochim. Acta 58, 931–941.

McDaniel, D.K., Hemming, S.R., McLennan, S.M., et al., 1994b. Petrographic, geochemical, and isotopic constraints on the provenance of the Early Proterozoic Chelmsford Formation, Sudbury Basin, Ontario. J. Sed. Res. A64, 362–372.

McLennan, S.M., 1976. Geochemistry of the Kinga Formation and the problem of lower Proterozoic sandstones (abst.). Geol. Assoc. Canada, Edmonton, Prog. Abst., 1, p. 62.

McLennan, S.M., Fryer, B.J., Young, G.M., 1979. Rare earth elements in Huronian (Lower Proterozoic) sedimentary rocks: composition and evolution of the post-Kenoran upper crust. Geochim. Cosmochim. Acta 43, 375–388.

Nesbitt, H.W., Young, G.M., 1984. Prediction of some weathering trends of plutonic and volcanic rocks based on thermodynamic and kinetic considerations. Geochim. Cosmochim. Acta 48, 1523–1534.

Nesbitt, H.W., Young, G.M., 1989. Formation and diagenesis of weathering profiles. J. Geol. 97, 129–147.

Pienaar, P.J., 1963. Stratigraphy, petrology, and genesis of the Elliot Group, Blind River, Ontario, including the uraniferous conglomerate. Geol. Surv. Canada Bull. 83, 140.

Prasad, N., 1995. The concentration trends of alkalis and alkaline earths and timing of potash-enrichments in 2.45–2.22 Ga sub-Huronian paleosols, Canada (ext. abst.). Inter. Assoc. Sediment. Sedimentological Congress, Recifé, Brazil.

Pukovsky, G.M., 1975. The petrology and geochemistry of the Mississagi quartzite at Quirke Lake. B.Sc.(Hon.) Thesis, University of Western Ontario, London, Canada. 50 pp.

Rainbird, R.H., Nesbitt, H.W., Donaldson, J.A., 1990. Formation and diagenesis of a sub-Huronian saprolith: comparison with a modern weathering profile. J. Geol. 98, 801–822.

Riller, U., Schwerdtner, W.M., Hall, H.C., et al., 1999. Transpressive tectonism in the eastern Penokean orogen, Canada. Consequences for Proterozoic crustal kinematics and continental fragmentation. Precambrian Res. 93, 51–70.

Roscoe, S.M., 1973. The Huronian Supergroup, a Paleoaphebian succession showing evidence of atmospheric evolution. In: Young, G.M. (Ed.), Huronian Stratigraphy and Sedimentation. Geol. Assoc. Canada Special Paper 12, 31–47.

Roscoe, S.M., Thériault, R.J., Prasad, N., 1992. Circa 1.7 Ga Rb–Sr re-setting of two Huronian paleosols, Elliot Lake, Ontario and Ville Marie, Quebec. Geol. Surv. Canada Paper 92-2, 119–124.

Schandl, E.S., Gorton, M.P., Davis, D.W., 1994. Albitization at 1700 ± 2 Ma in the Sudbury-Wanapitei Lake area, Ontario: implications for deep-seated alkalic magmatism in the Southern province. Can. J. Earth Sci. 31, 597–607.

Shaw, C.S.J., Young, G.M., Fedo, C.M., 1999. Sudbury-type breccias in the Huronian Gowganda Formation near Whitefish Falls, Ontario: products of diabase intrusion into incompletely consolidated sediments? Can. J. Earth Sci. 36, 1435–1448.

Sims, P.K., van Schmus, W.R., Schultz, K.J., et al., 1989. Tectono-stratigraphic evolution of the Early Proterozoic Wisconsin magmatic terranes of the Penokean orogen. Can. J. Earth Sci. 26, 432–445.

Smyk, M.C., Watkinson, D.H., 1990. Sulphide remobilization in Archean volcano-sedimentary rocks and its significance in Proterozoic silver vein genesis, Cobalt, Ontario. Can. J. Earth Sci. 27, 1170–1181.

Spencer, K.J., 1987. Isotopic, major and trace element constraints on the sources of granites in an 1800 Ma old igneous complex near St. Cloud, Minnesota. Ph.D. dissertation, State University of New York at Stony Brook.

Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: its Composition and Evolution. Blackwells, Oxford, p. 312.

Taylor, S.R., McLennan, S.M., 1995. The geochemical evolution of the continental crust. Rev. Geophys. 33, 241–265.

Vervoort, J.D., White, W.M., Thorpe, R.I., 1994. Nd and Pb isotope ratios of the Abitibi greenstone belt: New evidence for very early differentiation of the Earth. Earth Planet Sci. Lett. 128, 215–229.

White, W.M., Dupré, B., 1986. Sediment subduction and magma genesis in the Lesser Antilles: isotopic and trace element constraints. J. Geophys. Res. 91, 5927–5941.

White, W.M., Patchett, P.J., 1984. Hf–Nd–Sr isotopes and incompatible element abundances in island arcs: Implications for magma origins and crust-mantle evolution. Earth Planet Sci. Lett. 67, 167–185.

Young, G.M., 1970. An extensive Early Proterozoic glaciation in North America? Palaeogeog. Palaeoclim. Palaeoecol. 7, 85–101.

Young, G.M., 1983. Tectono-sedimentary history of early Proterozoic rocks of the northern Great Lakes region. Geol. Soc. America Mem. 160, 15–32.

Young, G.M., Nesbitt, H.W., 1999. Paleoclimatology and provenance of the glaciogenic Gowganda Formation (Paleoproterozoic), Ontario, Canada: a chemostratigraphic approach. Geol. Soc. Amer. Bull. 111, 264–274.