



The ~1100 Ma Sturgeon Falls paleosol revisited: Implications for Mesoproterozoic weathering environments and atmospheric CO₂ levels

Ria L. Mitchell^a, Nathan D. Sheldon^{b,*}

^a Dept. of Earth Sciences, Royal Holloway, University of London, Egham TW20 0EX, UK

^b Dept. of Geological Sciences, 2534 CC Little Building, 1100 North Univ. Avenue, Ann Arbor, MI 48109-1005, USA

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ABSTRACT

During the active rifting stage of the ~1100 Ma Midcontinental Rift in North America, alluvial sediments were deposited intermittently between basalt flows on the north and south shores of present day Lake Superior. At times of depositional quiescence, paleosols developed in both areas on the alluvial sediments and on the antecedent basalt. New results from the Sturgeon Falls paleosol in Michigan characterizing the weathering processes at the time of its formation indicate moderate maturity, high degrees of hydrolysis and leaching, and a low degree of salinization. Geochemical provenance indices indicate a homogeneous source for the paleosols, and in contrast to earlier work, there is little evidence for K metasomatism. As a result, atmospheric CO₂ levels of 4–6× pre-industrial atmospheric levels were calculated using a mass-balance model. This result is consistent with previous calculations from nearly contemporaneous paleosols from the other side of the Keweenawan Rift and from the ~100 Ma younger Sheigra paleosol in Scotland. The calculated CO₂ values are also consistent with the calculated weathering environment proxies that indicate weak to moderate weathering at this time frame and suggest that the higher greenhouse gas loads indicated by Paleoproterozoic paleosols had dissipated by the mid-late Mesoproterozoic.

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1. Introduction

Precambrian paleosols have long been studied for information regarding ancient atmospheric compositions (e.g., Retallack, 1986; Zbinden et al., 1988; Sheldon, 2006b), weathering regimes (e.g., Maynard, 1992; Driese et al., 2007; Mitchell and Sheldon, 2009), and paleoenvironmental reconstructions (e.g., Kalliokoski, 1986). Precambrian paleosols are preserved all over the world, many of which were parented by basaltic rocks (e.g., the Waterval Onder Clay Paleosol (Retallack, 1986) and the Mount Roe #2 paleosol (Rye and Holland, 2000)), and many of which have proven useful for understanding the Precambrian atmospheric composition (Holland et al., 1989) and Precambrian life (e.g., Watanabe et al., 2000). However, the majority of Precambrian paleosols have been affected by K metasomatism (e.g., Maynard, 1992), which complicates reconstructions of past paleoenvironments and of paleocommunities.

The failed MCR contains both sedimentary and igneous rocks that outcrop on the north and south shore of Lake Superior (Fig. 1). Paleosols are not common in the syn-rift sedimentary rocks of the MCR, and only a few have been documented on the south shore (Kalliokoski and Welch, 1985; Kalliokoski, 1986; Zbinden

et al., 1988). Furthermore, only a handful of paleosols of this age are known from other localities (Retallack and Mindszenty, 1994; Mitchell and Sheldon, 2009).

Here we study the Sturgeon Falls paleosol, which was formed on volcanic material belonging to the Siemens Creek Formation of the Powder Mill Group (Fig. 2) in Michigan, USA. In contrast to many Precambrian and Phanerozoic paleosols that have wide distributions, the Sturgeon Falls paleosol is known only from one locality, so understanding the weathering environment in which it formed is crucial to understanding weathering processes at this time. In addition to this, previous work (Zbinden et al., 1988) that suggested that the Sturgeon Falls paleosol has undergone significant K metasomatism is addressed, and the new results are compared to results from the nearly contemporaneous Good Harbor Bay Paleosols of Mitchell and Sheldon (2009) from the other side of the rift. The new data indicate that this paleosol is not as altered by K metasomatism as previously thought. This enables the Sturgeon Falls data to be used confidently to reconstruct CO₂ levels ~1100 Ma ago.

2. Geological setting

2.1. Midcontinental Rift (MCR)

The failed ~1100 Ma North American MCR extends 1400 km in length from the Great Lakes region of the USA/Canada as far south

* Corresponding author. Tel.: +1 734 647 7569; fax: +1 734 763 4690.
E-mail address: nsheldon@umich.edu (N.D. Sheldon).

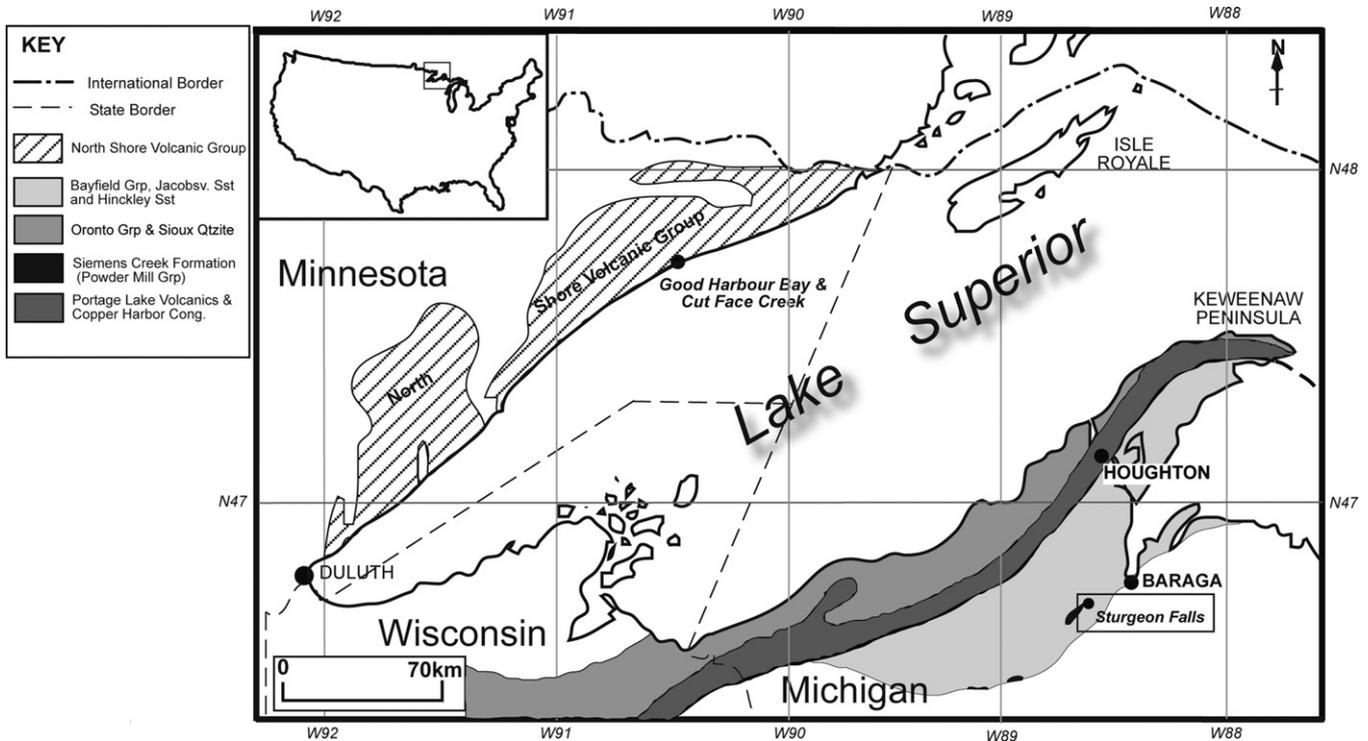


Fig. 1. Simplified geologic map of the Lake Superior region. The main formations studied on the south shore include the Jacobsville Sandstone, Oronto Group, Siemens Creek Formation, Portage Lake Volcanics, and the Copper Harbor Conglomerate. The location of Sturgeon Falls is shown, some 20 km south of Baraga. Scale shown. Modified from Mitchell and Sheldon (2009), USGS (1974) and Finley-Blasi (2006).

as Kansas (Davis and Green, 1997). Rifting initiated from activity associated with a mantle plume beneath the North American Craton (Green, 1983; Cannon and Hinze, 1992; Davis and Green, 1997) and subsequently failed because of compression at the Grenville Front to the east (Cannon and Hinze, 1992; Davis and Green, 1997). Volcanism associated with rifting lasted between 1108 and 1086 Ma (Davis and Green, 1997), with two main phases of volcanism occurring at 1109–1105 and 1100–1094 (Paces and Miller, 1993). Intermittent sedimentary deposition occurred between and during these phases, but it was not until compression occurred and rifting ceased that sediments were exclusively deposited and basin infill occurred. Throughout the period of rift formation and post-rift sedimentation, Laurentia was drifting from mid-latitudes (~50°N) to low latitudes (~20°N) (Swanson-Hysell et al., 2009). Grenville compression to the east resulted in the reactivation of normal faults

to thrusts at 1060 ± 20 Ma, meaning the central graben of Lake Superior became uplifted (Bornhorst et al., 1988; Cannon et al., 1993; Davis and Green, 1997). This resulted in deposition of vast and thick packages of terrestrial fluvial and alluvial sediments, such as the Jacobsville Sandstone and Bayfield Group (Davis and Green, 1997; Fig. 2). The south shore of Lake Superior in Wisconsin and the Upper Peninsula of Michigan has a variety of formations associated with the rift that do not necessarily correlate with nomenclature used on the North Shore (see Ojakangas et al., 2001). A simplified correlative stratigraphic section on the south and north shore is given in Fig. 2.

2.2. Powder Mill Group – Siemens Creek Formation

The Powder Mill Group is a ~6100 m thick succession (Zbinden et al., 1988) and is only represented in Wisconsin and Michigan. It correlates with the lower part of the North Shore Volcanic Group (NSVG) in Minnesota (Fig. 2). The Siemens Creek Formation forms the lower part of the Powder Mill Group (Zbinden et al., 1988; Fig. 2) and is dominated by a series of olivine tholeiite flows together with minor amounts of andesite (Jolly and Smith, 1972; Zbinden et al., 1988). Some of the flows have undergone low-grade metamorphism to lower greenschist facies (Kalliokoski, 1974), which contrasts with pencontemporaneous basalt flows from the present-day Minnesota side of the MCR where the basalt flows are only rarely altered (Ojakangas et al., 2001), and where the Good Harbor Bay Paleosols are derived from unaltered basalt (Mitchell and Sheldon, 2009).

2.3. Sturgeon Falls

The modern day Sturgeon River Falls is situated south of the Keweenaw Peninsula in the Upper Peninsula of Michigan, USA (Fig. 1). The Sturgeon Falls paleosol formed between underlying parent metabasalt (belonging to the Siemens Creek Formation) and

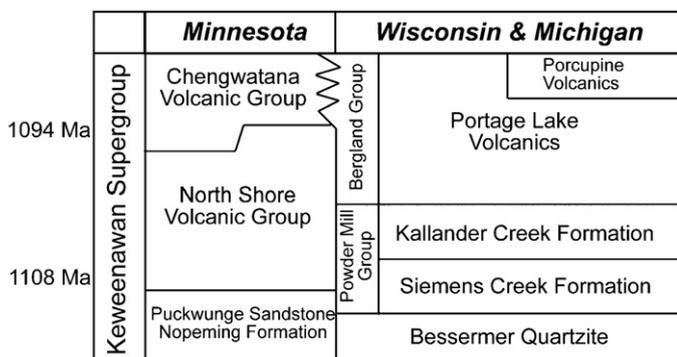


Fig. 2. Simplified stratigraphic log of the relevant formations in the Keweenaw Supergroup. The correlation of units on the north and south shore are shown, with ages. The Siemens Creek Formation forms the bottom part of the Powder Mill Group in Wisconsin and Michigan, and correlates with the bottom of the North Shore Volcanic Group in Minnesota. Modified from Ojakangas et al. (2001).

Table 1
Sample numbers and lithologies for the Sturgeon Falls paleosol.

Sample number	Depth (m)	Category	Lithology	Features
SF1	1.5	Paleosol	Siltstone	Horizontal laminations
SF2	2.4	Paleosol	f. sandstone	Horizontal laminations
SF3	3.5	Paleosol	f. sandstone	
SF4	4.4	Paleosol	f. sandstone	
SF5	4.9	Paleosol	Siltstone	Colour mottling
SF6	4.9	Paleosol	Siltstone	Colour mottling
SF7	6.6	Paleosol	Siltstone	Colour mottling
SF8	7.4	Paleosol	Siltstone	Colour mottling
SF9	7.9	Paleosol	Siltstone	Colour mottling
SF10	8.8	Paleosol	Siltstone	Colour mottling
SF11	9.6	Paleosol	Siltstone	
SF12	11.4	Parent	Metabasalt	Veining
SF13	overlying	Jacobsville Sandstone	m. sandstone	Bleached, quartz-rich

f. sandstone, fine-grained sandstone; m. sandstone, medium-grained sandstone.

the unconformably overlying Jacobsville Sandstone. Other silt- to sandstone grade sedimentary rocks outcrop on the opposite bend of the river, and are part of the Jacobsville Sandstone.

3. Methods

The outcrop of the Sturgeon Falls paleosol is reached by wading through the Sturgeon River to the opposite shore to the north (Fig. 3A). Following removal of ~10 cm of surficial material, eleven fresh rock samples were taken from the paleosol, along with one each of the Jacobsville Sandstone and underlying metabasalt (sample numbers are prefixed and labelled SF-XX; Table 1). Photographs were taken of the samples, the outcrop as a whole, and of noteworthy structures. Colours were determined from dried samples using a Munsell Soil Colour chart at Royal Holloway. Whole rock geochemical data was obtained using a Perkin Elmer Optima 3300RL ICP-AES and an Agilent Technologies 7500 Series ICP-MS for major and trace elements respectively. Samples were crushed to powders and fusions were produced by melting rocks in a muffle furnace at 900 °C with lithium metaborate flux, and then added to a 10% nitric acid solution. Samples for trace element analyses were digested with a combination of hydrofluoric and perchloric acid in a fume hood for 2 h and diluted using purified water. Two analyses were made of each sample, and multiple samples were collected and analyzed of sample SF9 to test reproducibility ($n = 5$). The standard deviation between the multiple analyses of a given sample was 0.1 wt.%, except for SiO₂, where it was 0.4 wt.%. Loss on ignition data was obtained from heating samples in a furnace at 900 °C for approximately 2 h. Point counts were collected on a James Smith Model F point counter from thirteen thin section slides. All of the analyses were performed at Royal Holloway, University of London (RHUL). While modern-day soil taxonomic nomenclature is not strictly applicable to Precambrian paleosols, it can be useful as a descriptive tool (Retallack and Mindszenty, 1994; Mitchell and Sheldon, 2009) and will be used at times herein where appropriate. The data discussed herein are compiled in Data Repository item #xxxxxx.

4. Results

4.1. Physical sedimentology

4.1.1. Sturgeon Falls paleosol and metabasalt outcrop

The Sturgeon Falls paleosol forms a paleohill (Zbinden et al., 1988) and overlies an altered metabasalt flow belonging to the Siemens Creek Formation, near the modern day banks of the Sturgeon River (see Figs. 1 and 3A). The paleosol is composed only

of finer grained (fine sand and silt) clastic material to a depth of ~450–490 cm, below which metabasalt corestones are common. The entire paleosol is ~12 m thick including a 6.5 m eroded metabasalt unit similar to a “C” horizon in modern soil taxonomy (Soil Survey Staff, 1999; Figs. 3 and 4). This is logged as a conglomerate in Fig. 4, and consists of red, finer grained weathered material intercalated with weathered and eroded boulders on the surface of the metabasalt (Fig. 3B–D). The boulders range from 20 to 70 cm in diameter and are sub-angular to rounded. Zbinden et al. (1988) did not include this conglomeratic “C” horizon, which accounts for the discrepancy in our measured thicknesses (Fig. 3C). Munsell Soil Colours range between 10R 5/3 and 10R 6/6.

Grains making up the red paleosol range in size from mudstone to medium-grained sandstone and are dominated by quartz and muscovite, with small amounts of iron oxides and plagioclase feldspar (Supplemental data). Grains are generally well-rounded and sorted, but there are some larger mm-scale flakes of muscovite present. Some parts of the paleosol are clay-rich (Fig. 5C and E and Section 4.2). There is however a lack of pedogenic structure preserved (e.g., peds). Munsell Soil colours are typical of heavily oxidized paleosols.

Horizontal laminations are abundant (particularly in the top half of the paleosol), as are green mottles (Fig. 3B–C) that become more abundant with depth. Relict sedimentary structures observed in the penecontemporaneous Good Harbor Bay paleosols (cross bedding, dessication cracks, and thin, black, carbon-bearing laminations; Mitchell and Sheldon, 2009), are absent.

The metabasalt outcrop is grey and is dominated by an aphyric texture. There are numerous calcite veins that cut through the metabasalt, but not the paleosol (Fig. 3), which indicates that the veining event was pre-pedogenesis.

4.1.2. Jacobsville Sandstone

The paleosol is overlain unconformably by the Jacobsville Sandstone (Fig. 3a and d), which is a quartz-rich sandstone that is considered the last stage of deposition associated with the MCR (Ojakangas et al., 2001). The Jacobsville Sandstone is well-sorted and -rounded, and is composed of fine- to coarse-grained sandstones interpreted to have been deposited by fluvial systems (Kalliokoski, 1982; Ojakangas and Dickas, 2002). Zbinden et al. (1988) described the base of the Jacobsville Sandstone as being lenticular due to fluvial processes, and containing channel structures and cross stratification, indicating that the Sturgeon Falls paleosol was still soft when the Jacobsville sands were deposited. The lenticular base was not observed, but this may be due to recent erosion of the site.

4.2. Petrography

4.2.1. Sturgeon Falls paleosol

Point count data indicates that the Sturgeon Falls paleosol is dominated by quartz (up to 70%; Fig. 5C–E), but also that it is has a significant matrix component of clays (>20% and up to 30%). In contrast to the penecontemporaneous Good Harbor Bay paleosols (Mitchell and Sheldon, 2009), there is a lack of plagioclase feldspar preserved (up to 14% at Sturgeon Falls in comparison to as high as 78% in Good Harbor Bay paleosols; Mitchell and Sheldon, 2009). Feldspar grains have been altered and in most cases removed. Grains are for the most part well sorted and rounded, often aligned to show micro-laminations. Other minor constituents include iron oxides (Fig. 5C), muscovite, lithic clasts (Fig. 5E), dolomite and microcline. Lithic clasts are a mixture of mafic volcanic and sedimentary rocks; these are thought to have originated from the metabasalt and local sedimentary rocks respectively. Red hematite-staining of grains is also common (Fig. 5C), as well as in the matrix (Fig. 4E). The percentage of calcite cement reaches up to 25%. Cal-

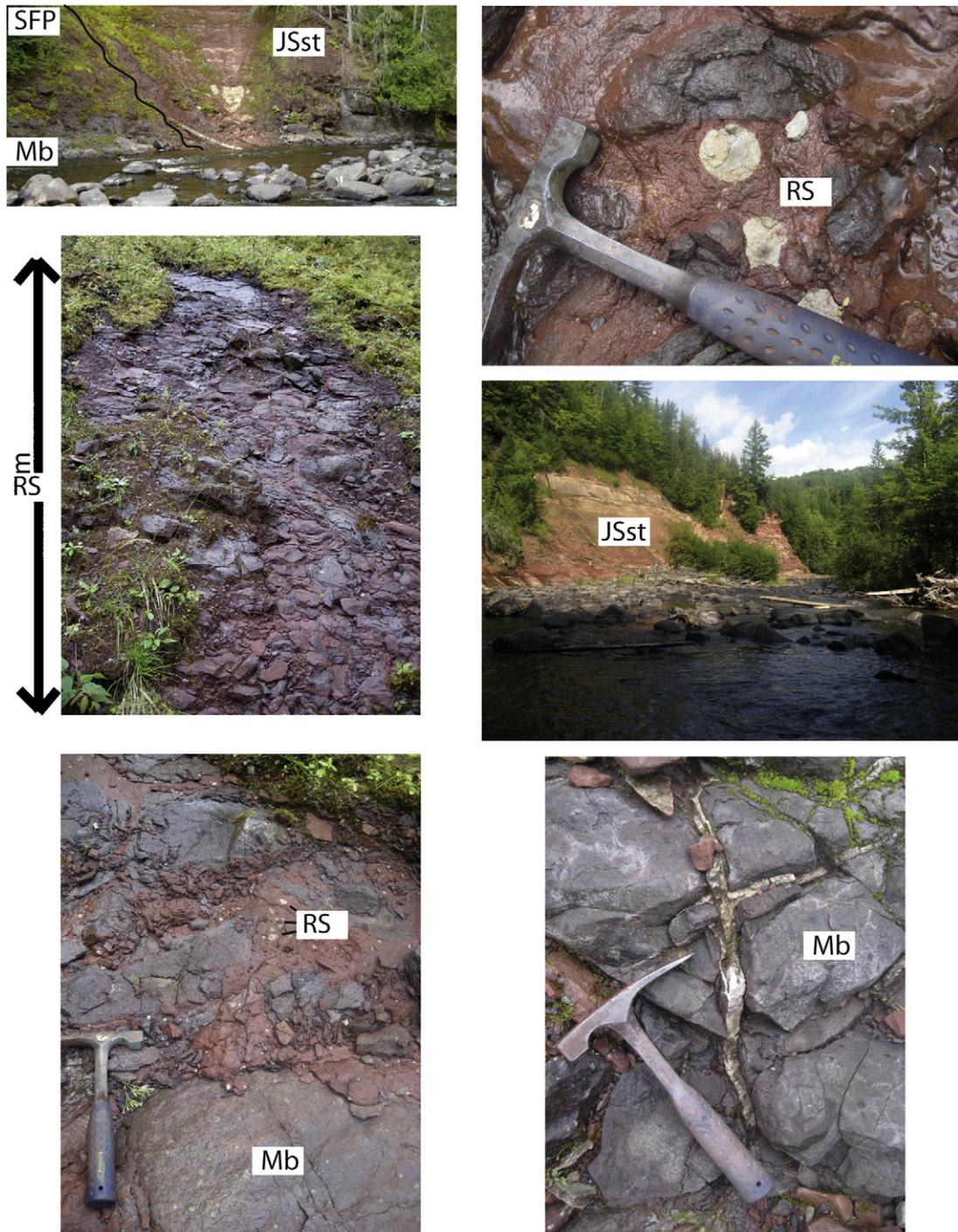


Fig. 3. Outcrop photographs of the Sturgeon Falls paleosol. (A): Outcrop photograph of the Sturgeon Falls paleosol, underlying metabasalt, and adjacent Jacobsville Sandstone (b) partial outcrop photo of the Sturgeon Falls paleosol; the outcrop fines up from intermixed sediment and basaltic corestones at the base to finer grained clastic sediments at the top; (c): Weathered metabasalt boulders at the bottom of the paleosol (grey) and surrounding siltstone/paleosol (red). Photo taken at 6.6m depth; (d): reduction (mottle) spots in silt- and sandstones. Weathered metabasalt boulders are also shown. Photo taken at 8.8m depth; (e) outcrop photo showing the extent of the Jacobsville Sandstone locally, which filled in the Sturgeon Falls era paleotopography): Large calcite veins in the parent metabasalt. Scales shown (hammer = 35 cm length). Labels are: SFP, Sturgeon Falls paleosol; JSst, Jacobsville Sandstone; Mb, metabasalt; RS, reduction spot.

citic cement is post-depositional with some micro-veining (Fig. 5F). The high percentage of matrix means the majority of the Sturgeon Falls paleosol is classifiable as a wacke, rather than an arenite in the conventional classification of Pettijohn (1975) (Fig. 6). In contrast, the pencontemporaneous Good Harbor Bay paleosols were typically arkosic arenites with only rare lithic arenites (Fig. 6 of Mitchell and Sheldon, 2009). Black carbon-bearing matrix observed

in the pencontemporaneous Good Harbor Bay paleosols (Fig. 5 of Mitchell and Sheldon, 2009) is absent in the Sturgeon Falls paleosol.

4.2.2. Parent metabasalt

The underlying metabasalt (sample SF12; Fig. 4) is nearly aphyric, with just 3% plagioclase, 1% olivine, 1% pyroxene, and 82% groundmass (Data Repository). The remaining counts were all of

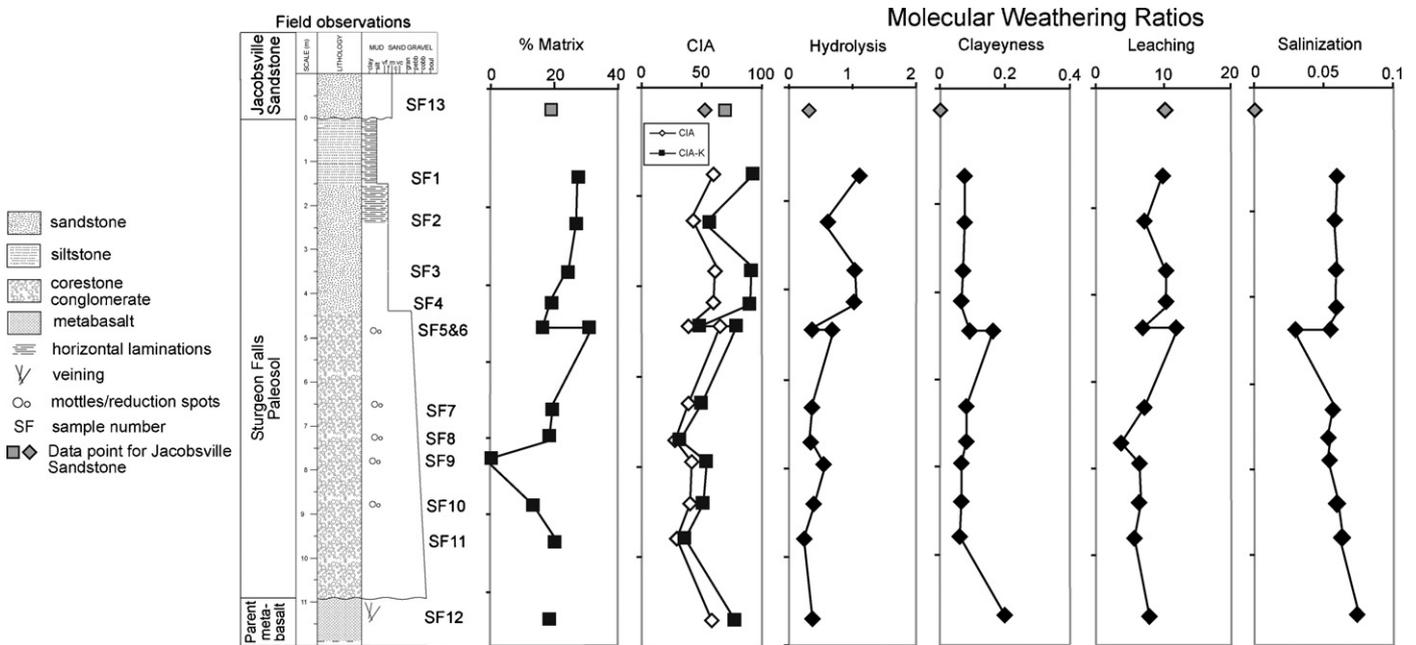


Fig. 4. Sedimentary log and representative trends of molecular weathering ratios in the Sturgeon Falls paleosol. Sample numbers are shown. All indices fluctuate throughout the profile with the largest changes occurring in the top half of the paleosol, which is consistent with *in situ* weathering (summarized in Sheldon and Tabor, 2009). Data for the overlying Jacobsville Sandstone are also plotted.

calcite (13%), a product of post-emplacement alteration common to the Siemens Creek Formation (Kalliokoski, 1974).

4.2.3. Jacobsville Sandstone

At Sturgeon Falls, the overlying Jacobsville Sandstone is composed of 81% quartz and matrix material, 14% calcite cement, with just 3% plagioclase feldspar (*Data Repository*). There is also no evidence of adularia (metamorphic K-feldspar) overgrowths in the Jacobsville Sandstone, a feature that has previously been used to identify K metasomatism (e.g., Driese et al., 2007). The sample falls near the wacke-arenite boundary in Pettijohn (1975) classification, which is consistent with the Jacobsville Sandstone at other Keweenaw Peninsula localities (Kalliokoski, 1982).

4.3. Geochemistry

4.3.1. Molecular weathering ratios

Five molecular weathering ratios were calculated based on the Sturgeon Falls paleosol (Fig. 4). These ratios were obtained by converting the weight percentages of elements to moles. The molecular weathering ratios calculated include (1) hydrolysis; (2) clayeyness; (3) leaching; (4) salinization and (5) the chemical index of alteration (CIA). The results can be seen in Fig. 4. These ratios have been applied to younger paleosols formed on basalt in the Columbia River Basalt (Sheldon, 2003) and in Hawaii (Sheldon, 2006b) to characterize the weathering environment.

4.3.1.1. Hydrolysis. Hydrolysis (*H*) is calculated as follows:

$$H = \frac{\text{Al}}{\text{Ca} + \text{Mg} + \text{K} + \text{Na}} \quad (1)$$

The hydrolysis ratio measures the loss of base cations (denominator in Eq. (1)) which is based on the idea that these elements are lost during weathering in comparison to Al, resulting in the formation of clay (Sheldon and Tabor, 2009). Base cations are common in high temperature minerals such as olivine and pyroxene, however from petrological studies, these minerals are generally absent from the Sturgeon Falls paleosol because of removal through hydrolysis. Fig. 4 shows some variability through the top half of the paleosol

profile but becomes more consistent in the bottom half. The parent metabasalt has a value of 0.7 ± 0.1 (analytical uncertainty). Values in the Sturgeon Falls paleosol reach up to 1.1 in the upper portions of the profile, but are similar to in the metabasalt parent material below 490 cm, indicating less hydrolysis deep in the profile. The higher values in the top half indicate that the paleosol is more well-developed than the penecontemporaneous Good Harbor Bay paleosols studied by Mitchell and Sheldon (2009) on the other side of the rift.

4.3.1.2. Clayeyness. “Clayeyness” (*C*) is calculated as follows:

$$C = \frac{\text{Al}}{\text{Si}} \quad (2)$$

“Clayeyness” is an indication of the amount of clay formation, due to the removal of base cations by hydrolysis and the subsequent accumulation of Al relative to Si (Sheldon and Tabor, 2009). Higher values are a crude indication of the amount of clay formation from the dissolution of feldspars and other easily weathered minerals. “Clayeyness” is consistently below 0.1 throughout the Sturgeon Falls profile, indicating limited clay formation. The parent metabasalt value of “clayeyness” is $0.2 \pm <0.1$ (analytical uncertainty). However, there is a small peak in the central part of the profile (samples SF6) which corresponds with matrix point count data (up to 30% total sample; see Fig. 6) and petrographic thin sections (Fig. 5). The parent metabasalt has an elevated “clayeyness” value in comparison to the paleosol, probably due to pre-pedogenic metamorphic alteration to form the metabasalt from basalt.

4.3.1.3. Leaching. Leaching (*L*) is calculated by the following equation:

$$L = \frac{\text{Ba}}{\text{Sr}} \quad (3)$$

High values are an indication of leaching, free drainage, and time of development because Sr is the more soluble of the two elements (Retallack, 2001; Sheldon and Tabor, 2009). Generally, there is a consistent trend down profile but the values higher than in the paleosols of Mitchell and Sheldon (2009). The parent metabasalt value is 8.09 ± 0.4 (analytical uncertainty), and paleosol values are

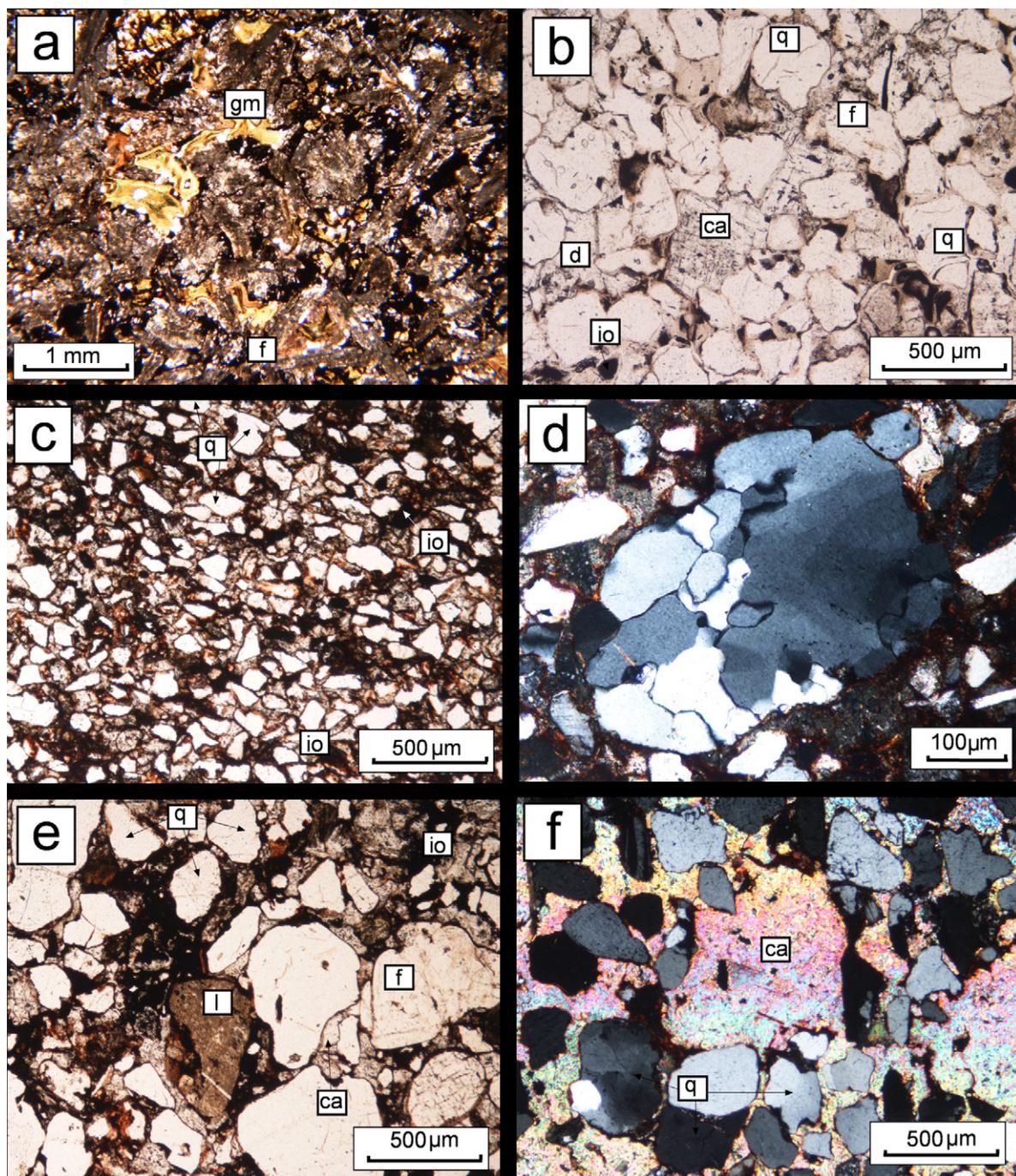


Fig. 5. Petrological photographs of samples through the Sturgeon Falls paleosol profile. (A) Altered metabasalt (sample SF12) in PPL; (B) Jacobsville Sandstone (sample SF13) showing calcitic cement; (C) Well sorted quartz sandstone (sample SF6); (D) Strained quartz in the paleosol (sample SF5); (E) Poorly sorted sandstone with a greater variety of components in comparison to (C) (sample SF8); (F) Calcitic cement between sub-rounded quartz grains (sample SF11). Labels are: ca, calcite cement; f, feldspar; q, quartz; d, dolomite; io, Fe/Ti oxide; l, lithic clast; gm, groundmass. Scales shown.

variable (3.7–12), with a mean of 10.04 ± 1.7 (1σ) for the uppermost 490 cm. Values near 10 are indicative of acidic, sandy soils (Retallack, 2001) indicating a well leached, highly drained paleosol with a long time of development. This is also consistent with the degree of clay formation and thickness of the profile, which both indicate moderate development.

4.3.1.4. Salinization. Salinization (S) is calculated by the following equation:

$$S = \frac{\text{Na} + \text{K}}{\text{Al}} \quad (4)$$

Values for the Sturgeon Falls paleosol are very similar down profile (mean 0.57 ± 0.03 (1σ)) and the parent metabasalt yields a salinization of 0.44 ± 0.05 (analytical uncertainty). The paleosols values are well below the threshold of 1 set by Retallack (2001) for significant salinization, and therefore indicating limited synformational evaporation (Fig. 6). This contrasts with the penecontemporaneous Good Harbor Bay paleosols of Mitchell and Sheldon (2009) where six of the seven paleosols had salinization values in excess of 1, including three in excess of 2.3. This may indicate that the Sturgeon Falls paleosol received a higher level of precipitation (Sheldon and Tabor, 2009) than the Good Har-

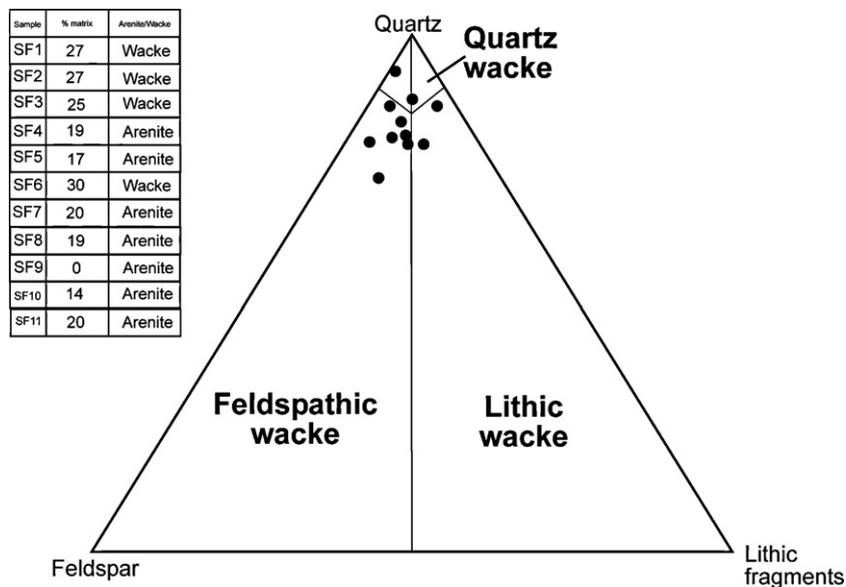


Fig. 6. A quartz-feldspar-lithic (QFL) plot for the Sturgeon Falls paleosol. All samples contain >60% quartz. This is different from the QFL plot by Mitchell and Sheldon (2009) from the North Shore in Minnesota and is presumably due to the difference and change of source and parent material in the local vicinity.

bor Bay paleosols, or that there was a lower rate of evaporation locally.

4.3.1.5. Chemical Index of Alteration (CIA). The Chemical Index of Alteration (CIA) of Nesbitt and Young (1982) is another indicator of the degree of weathering in paleosol samples. It is a measurement of the breakdown of feldspars and other minerals by the removal of base cations to produce clays (Nesbitt and Young, 1982). With increased clay content, Al will also increase, and Ca, Na, and K will be lost. The CIA is calculated as follows:

$$\text{CIA} = 100 \times \frac{\text{Al}}{\text{Al} + \text{Ca} + \text{Na} + \text{K}} \quad (5)$$

Values increase with a higher degree of weathering (up to 100), while unweathered samples are low (nearer to 0). The CIA of paleosols varies depending on the amount of weathering but also on the composition of parent material. For example, basalts have a value <45 (Sheldon, 2003) and shales have a value 70–75 (Maynard, 1992), therefore, the initial value will have a strong effect on the value of paleosols formed from the weathering of different lithologies. In Paleozoic and modern soil profiles, the most weathered parts of a paleosol profile, typically the “B” horizon will have the highest values (Sheldon and Tabor, 2009). This however is not the case in the Sturgeon Falls paleosol (Fig. 6). The “B” horizon is difficult to determine based on physical characteristics, as there is no obvious lithological grain size or colour change, and so it has been decided best not to rely on this type of horizon nomenclature in this paper. The average CIA for the profile to a depth of 490 cm is ~58 (range 43–65), though samples collected by Zbinden et al. (1988) indicate values in excess of 70 (see [Data Repository Supplemental Fig. 1](#)) for samples collected higher in the profile than the new samples compiled here. The parent metabasalt is somewhat variable as well with different values for corestone samples (SF 5) and unweathered metabasalt (SF12) of ~38 and 58, respectively, which suggests some pre-pedogenesis compositional heterogeneity. The large range of CIA values through the profile in comparison to the Good Harbor Bay paleosols is supported by petrographic evidence; there is a distinct lack of feldspars in the most weathered samples (i.e., higher CIA), and feldspars, micas and rare olivine/pyroxenes are present in the least weathered samples (i.e., lower CIA). The CIA values are highest in the top half of the profile, which is consistent

with the greatest degree of weathering chemical weathering having occurred near the paleosurface, and limited pedogenesis occurring deeper in the profile. The similarity of many of the paleosol values to the underlying basalt is consistent with an overall weak to moderate degree of pedogenesis.

4.3.2. Provenance ratios

Numerous geochemical ratios can be applied to paleosols to determine the provenance of material within them (Fig. 8). The most commonly used ratio is Ti/Al, which is an excellent indicator of whether paleosols are derived from uniform parent material (Sheldon, 2006a; Hamer et al., 2007; Mitchell and Sheldon, 2009).

Ti/Al values for the Sturgeon Falls paleosol are consistent down profile, except for an area in the centre of the profile displaying elevated values. These samples (SF 5, 6 and 7) are between metabasalt boulders, therefore suggesting physical addition of Ti-bearing minerals since Ti is otherwise generally immobile during weathering (Sheldon and Tabor, 2009). The rest of the profile has values around 0.05, which suggests a uniform source of material. Other ratios of immobile elements including Ti/Zr and Sm/Nd that have previously been used as provenance indicators for paleosols (Sheldon, 2006b) are also constant with depth in the profile and consistent with the parent metabasalt value (Fig. 8).

4.3.3. Loss on Ignitions (LOI)

Loss on Ignition (LOI) data from the Sturgeon Falls paleosol reveals a range of values from ~2.5% up to >10%, which is consistent with the presence of hydroxylated and hydrous minerals (i.e., weathering products). The highest values correspond to samples that also have some inherited calcite from the weathering of the parental metabasalt, which had pre-pedogenic calcite veins.

5. Discussion

5.1. Formation of the Sturgeon Falls paleosol

Based upon the combined geochemical and petrographical data compiled herein, the following sequence of events is proposed for the formation of the Sturgeon Falls paleosol:

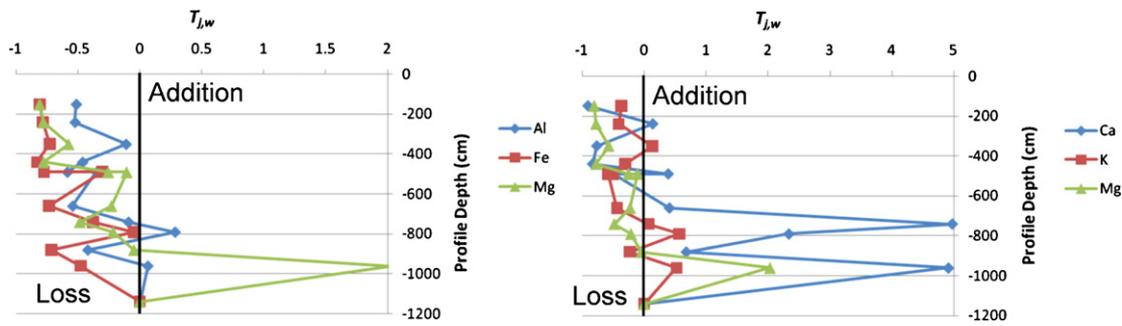


Fig. 7. Mass balance graph showing the gain/loss of selected major elements through the paleosol profile. The majority of elements were heavily leached from the paleosol, whereas Na and Ca were partly lost and partly redistributed down the profile. The heavy black line represents a $\tau_{j,w}$ value of 0.

1. Emplacement of the underlying basalt as part of the Siemens Creek Formation (Fig. 2; ~1108 Ma) and alteration to lower greenschist facies (Zbinden et al., 1988). Because the calcite veins in the metabasalt do not penetrate the overlying Sturgeon Falls paleosol, the alteration was pre-pedogenic.
2. First stage *in situ* weathering of the metabasalt, resulting in deep fractures and metabasaltic corestones with weathering rinds.
3. Deposition of sediment derived from local weathering of basalt and of either granite or rhyolite by fluvial processes, which infilled cracks in the top of the metabasalt flow. This explains the presence of quartz throughout the paleosol profile and of the weakly developed laminar structure near the top of the paleosol. A mixed clastic source is necessary because clay formation, and clayeyness and hydrolysis geochemical ratios are consistent with mafic source material, whereas the presence of quartz is not.
4. Second stage *in situ* weathering of the mixed metabasalt and clastic sediments to form the Sturgeon Falls paleosol. This explains the consistent provenance geochemical ratios throughout the paleosol profile (Fig. 8), while at the same time providing

a reasonable explanation for the strong chemical discrepancies between the Sturgeon Falls paleosol and the overlying Jacobsville Sandstone, which was derived from a mixture of metamorphic and volcanic sources areas (Kalliokoski, 1982). The second stage of *in situ* weathering is also indicated by the higher proportion of weathered, fine-grained material at the top of the profile and of the up profile increase in hydrolysis and CIA ratios, which is consistent with Phanerozoic soil formation and the weathering of mafic or dominantly mafic source materials (Sheldon, 2003; Sheldon and Tabor, 2009).

5. Erosion of the paleosurface of which the Sturgeon Falls paleosol was a part, to create the paleohill (Zbinden et al., 1988) and paleo-valley topography that was subsequently filled in by and then buried by the Jacobsville Sandstone (~1060 Ma ago).

Thus, the age of formation of the Sturgeon Falls paleosol can be bracketed to between 1108 and 1060 Ma ago, and given that the metabasalt had to be exposed at the surface for stages 2–5, it is probably much closer in age to the younger constraint.

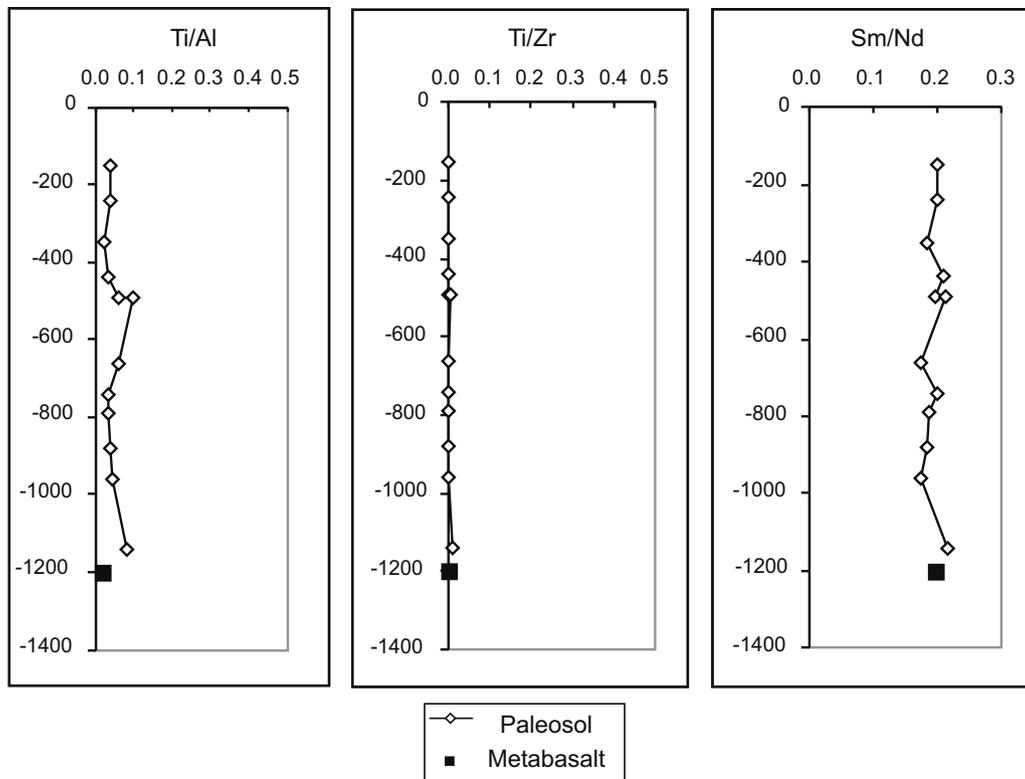


Fig. 8. Provenance ratios (Ti/Al and Ti/Zr) and REE indicators of provenance (U/Th, La/Lu and Sm/Nd). Parent metabasalt values are also plotted for comparison. There is general consistency down-profile, with only considerable differences amongst metabasalt boulders. This indicates homogeneity in the source of the paleosol.

5.2. Comparison of geochemical data with previous work

Previous analytical work on samples from the Sturgeon Falls paleosol used a somewhat unusual analytical technique. Zbinden et al. (1988) ground up their samples and made fused glasses with a 1:1 sample:flux ratio. The glasses were reground and remelted a second time to homogenize the samples, and then the disks were spot-analyzed using an electron microprobe. As a result of the sample preparation, their results are volatile-free. However, as discussed in Section 4.3.3, the LOI totals for our samples were moderate, so some of the discrepancies between the new analyses and the previous work can be explained by this difference. Calculated CIA values (Eq. (5)) are consistent (Supplemental Fig. 1) between our results and those of Zbinden et al. (1988) for samples collected from approximately the same depth within the Sturgeon Falls paleosol, and both sets of data support the conclusion that the top of the profile was more heavily weathered than deeper in the profile, which is consistent with a surface-only biosphere (Mitchell and Sheldon, 2009). In detail, however, there are some significant differences between the two sets of results. For example, Zbinden et al. (1988) found significantly lower SiO₂ values than we did. While this discrepancy could be due in part to the relatively larger analytical uncertainty for SiO₂ when using an ICP-OES than for other elements, the analytical uncertainty is not likely to have approached the discrepancy. Instead, the difference is probably a function of collection bias. As an example, at –490 cm within the paleosol, two samples were collected, one “pure” paleosol sample and one with both paleosol and fragmentary metabasalt. The “pure” paleosol sample contained 61% SiO₂ whereas the sample from the metabasalt contained 53.5% SiO₂ and was significantly closer to the Zbinden et al. (1988) values for this stratigraphic level. Our results for the “pure” paleosol sample correspond much better to the point count results (Fig. 6), which indicate a significant proportion of quartz. Taken together, these results suggest both that there is some lateral heterogeneity within the paleosol and that there may have been some fragmentary metabasalt in many of the samples analyzed by Zbinden et al. (1988), either from slope wash, or *in situ* in the section line that they chose.

5.3. Mass balance calculations

Following the approach of Brimhall and Dietrich (1987), mass balance equations have been used to measure the gains and losses of various elements through the paleosol relative to the metabasalt parent material. This is achieved by comparing element values to an immobile index element, such as Ti, Zr, Al or Nd (Sheldon and Tabor, 2009). Normalizing the data in this way means this widely accepted approach is more reliable than simply using raw data as Zbinden et al. (1988) have used. Mass balance calculations are useful because they are not constrained by the age of paleosols as other techniques might be, and can yield successful results in a range of ages; Precambrian (e.g., Driese, 2004; Mitchell and Sheldon, 2009), Paleozoic (e.g., Sheldon, 2005; Kahmann et al., 2008), Mesozoic (Cleveland et al., 2008), and Cenozoic (e.g., Sheldon, 2003; Sheldon, 2006c; Hamer et al., 2007) paleosols.

Mixed metabasalt and sandstone (see Section 5.4 below) was used as the parent material and Zr as the immobile element instead of Ti just as in Mitchell and Sheldon (2009). Generally, there is a loss in every element from the profile (Fig. 7). This is consistent with data showing the Sturgeon Falls paleosol is well leached and drained (Eq. (3) and Fig. 6). Loss occurs in every element (except Na) until 660 cm depth (sample SF7), where the sedimentary rocks are in contact with boulders of parent metabasalt. The inclusion of the C horizon in this way enables the geochemistry of the entire profile to be studied.

Fe and Al show overall loss through the entire profile (up to 83% and 58% respectively). The loss of Al contrasts with some previous work on Precambrian paleosols (e.g., Driese, 2004; Driese et al., 2007), but it has regularly been documented in modern volcanic soils forming in tropical and paratropical areas (Kurtz et al., 2000; Chadwick et al., 2003), and the MCR was at appropriate paleolatitudes (Swanson-Hysell et al., 2009) during the formation of the Sturgeon Falls paleosol to result in paratropical conditions. Iron oxides are the dominant source of iron in Keweenaw sediments, however these are largely absent from the Sturgeon Falls paleosol and the Fe content of the parent metabasalt is relatively low at 2.1 wt%, so Fe loss, while high as a percentage of the original value (Fig. 7), is not high in an absolute sense.

Ca and Na fluctuate throughout the profile, with Na below 0.1 wt% throughout the whole profile. The addition of Ca at 740 cm depth is explained by an elevated amount of calcitic cement (19%) at this particular level in comparison to the rest of the paleosol (for example, see Fig. 4). Zbinden et al. (1988) discussed the presence of dolomite within the paleosol profile; however the Ca addition at the bottom of the profile seems unlikely to be caused by dolomite as there is not a corresponding peak in Mg. Instead the Ca in the form of detrital calcitic cement was likely derived from the weathering of pre-pedogenic calcite veins in the metabasalt, as the metabasalt is depleted in Ca in comparison to the surrounding sedimentary rocks, and the only samples that exhibit an addition in Ca are sedimentary rocks between metabasalt boulders.

Other elements such as K and Mg show losses (up to 58% and 81% respectively), but apparent gains towards the bottom of the profile. This is presumably an addition directly from the weathering of metabasalt boulders in the R horizon, and the relocation of weathering remnants from higher in the profile.

The apparent ‘addition’ of material in the lower ~350 cm of the profile could be re-precipitation of minerals from elements derived from higher in the profile. This is supported by the high leaching values in Fig. 6.

5.4. Metasomatism?

A common feature of Precambrian paleosols is enriched K content caused by post-burial metasomatism (Maynard, 1992; Fedo et al., 1995). To demonstrate that paleosols are useful for paleoclimatic and paleoatmospheric reconstructions, it is important to distinguish alteration from pre-existing textures and chemical composition. The MCR-related sedimentary rocks surrounding Lake Superior have never been substantially buried, however, the Keweenaw Peninsula hosts hydrothermally produced ore minerals (Nicholson et al., 1992), including copper and minor amounts of silver, which could have led to post-burial alteration of sedimentary rocks on the Keweenaw Peninsula. Also, other putative MCR paleosols (Kalliokoski, 1974) have been disputed on the basis evidence for alteration (Lewan, 1976).

Using data from the Sturgeon Falls paleosol, a variety of calculations can be performed to assess the degree of metasomatic alteration. The difference between CIA and CIA-K is consistent down-profile (Fig. 4), indicating that if K has been added to the profile, it has not been added to one particular horizon or along a lithological contact, but to the profile as a whole. CIA and CIA-K are highly correlated ($R^2 = 0.93$); Data Repository Supplemental Fig. 2), to a similar degree to that of modern soils ($R^2 = 0.97$; Maynard, 1992) suggesting that K has not been added to the profile. Mass balance calculations (Fig. 7; Section 5.2) shows a loss in K throughout the profile, with only a small addition at the bottom near the “R” horizon, which is presumably because of addition from surrounding metabasalt. Other elements have also been redistributed downward in the paleosols profile, indicating that this phenomenon is not specific to K, and therefore seems unlikely to be due to metasomatism.

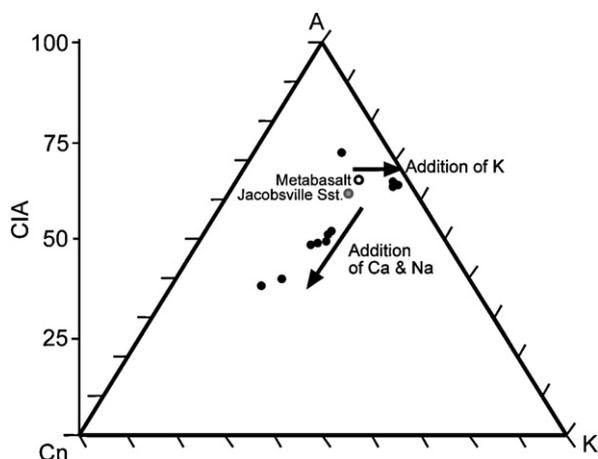


Fig. 9. A–Cn–K plot for the Sturgeon Falls paleosol. A: Al_2O_3 ; Cn: $\text{CaO} + \text{Na}_2\text{O}$; K: K_2O . This plot indicates any addition of each element in relation to each other. There is a greater range in values compared to the NSVG paleosols of Mitchell and Sheldon, 2009. There is addition of Ca and Na which is supported from mass balance data. Addition of K is limited to a few samples. The range in CIA is also shown. Open circle = metabasalt, Grey circle = Jacobsville Sandstone.

K and Rb are chemically similar elements, so addition of one should be matched by addition of the other, however, there is also no evidence for the addition of Rb to the profile (*Data Repository Supplemental Fig. 3*). An A–Cn–K plot (Fedó et al., 1995) in Fig. 9 shows no evidence for the addition of K to the system, whereas an addition of Na and Ca were added to some parts of the paleosols, which is consistent with the mass balance results for those elements (Fig. 7), which indicated some redistribution. Finally, an upward increase in K_2O through a paleosol profile, is a characteristic of metasomatism and diagenetic alteration (Maynard, 1992). There is no such increase in the Sturgeon Falls paleosol.

5.5. $p\text{CO}_2$ reconstruction

Sheldon (2006b) proposed a new method for calculating atmospheric CO_2 levels using mass balance calculations based on Precambrian paleosols; comprehensive discussion of the method and of the uncertainties can be found in Sheldon (2006b) or Sheldon and Tabor (2009), but a brief summary is presented here. Once $\tau_{j,w}$ values (Section 5.3) are calculated for Ca, Mg, Na, and K (which account for essentially all CO_2 consumption during weathering), they can be converted into fluxes as follows:

$$m_{j,\text{flux}}(\text{g cm}^{-2}) = \rho_p \frac{C_{j,p}}{100} \int_{Z=0}^{Z=D_{j,w}} \tau_{j,w(z)} dZ, \quad (6)$$

where the values are defined as before and where Z is the decompacted (Sheldon and Retallack, 2001) paleosol thickness. For each mole of cation that is weathered, two moles of CO_2 are consumed (e.g., Zbinden et al., 1988; Holland et al., 1989):

$$M(\text{moles CO}_2 \text{ cm}^{-2}) = 2 \sum m_{j,\text{flux}}. \quad (7)$$

With a limited or surface-only biosphere in the Precambrian, the time-averaged CO_2 flux is the product of two distinct sources, CO_2 in the atmosphere added by rainfall to the soils (X_{rain}) and CO_2 added to the soils by direct diffusion (X_{diff}). Zbinden et al. (1988) quantified X_{rain} and X_{diff} as follows:

$$\frac{M}{T}(\text{mol cm}^{-2} \text{ year}^{-1}) = X_{\text{rain}} + X_{\text{diff}} \approx p\text{CO}_2 \left[\frac{K_{\text{CO}_2} r}{10^3} + \kappa \frac{D_{\text{CO}_2} \alpha}{L} \right], \quad (8)$$

where $p\text{CO}_2$ is the partial pressure of atmospheric CO_2 (atm), K_{CO_2} is the Henry's Law constant for CO_2 , r is rainfall rate (cm year^{-1}), D_{CO_2}

is the diffusion constant for CO_2 in air ($0.162 \text{ cm}^2 \text{ s}^{-1}$; CRC Handbook), α is the ratio of diffusion constant for CO_2 in soil divided by the diffusion constant for CO_2 in air, L is the depth to the water table, and κ is a constant which is the ratio of seconds in a year divided by the number of cm^3 per mol of gas at standard temperature and pressure ($1.43 \times 10^3 (\text{s cm}^3)/(\text{mol year})$). Eq. (8) can then be re-arranged to solve for the atmospheric $p\text{CO}_2$ at the time that the soil formed:

$$p\text{CO}_2 = \frac{M}{T \left[\left(\frac{K_{\text{CO}_2} r}{10^3} \right) + \kappa \left(\frac{D_{\text{CO}_2} \alpha}{L} \right) \right]}. \quad (9)$$

Uncertainty for $p\text{CO}_2$ estimates is about a factor of three, which represents a substantial improvement over previous methods (e.g., Rye et al., 1995) that had uncertainties of at least an order of magnitude (Sheldon, 2006b). Previous estimates for the time period between ~ 1100 and 940 Ma ago using this estimate were uniformly low ($< 10 \times$ pre-industrial levels; Sheldon, 2006b).

The final consideration is the composition of the parent material. As noted in Section 5.1 above, the Sturgeon Falls paleosol appears to have been derived from a mixed, though chemically nearly homogeneous (Fig. 8), source because of evidence for both weathering of mafic material and the presence of quartz. The most straightforward scenario is to consider a parent material composed of 50% metabasalt and 50% sandstone with the chemical composition of the overlying Jacobsville Sandstone. Using the mass-balance results (see *Data Repository Supplemental Table 4*) to a depth of 660 cm (the depth where basaltic corestones begin to be more common than finer grained weathered material), the present-day global mean annual precipitation of $1000 \text{ mm year}^{-1}$, assuming a formation time of 50,000 years for the paleosol (see Sheldon, 2006b for sensitivity analysis of formation time uncertainty), the resulting $p\text{CO}_2$ value is $4.14 \times \text{PAL}$ (pre-industrial atmospheric level). This is very similar to the value that Sheldon (2006b) calculated for the 980 Ma old Sheigra paleosol (6.89 PAL), which suggests that this is a robust result for this time period. Changing the mean annual precipitation by $\pm 50\%$ results in a shift of just $0.3 \times \text{PAL}$, so the calculated $p\text{CO}_2$ value depends little on that assumption. End-member scenarios result in $6.07 \times$ (100% metabasalt) and $3.61 \times \text{PAL}$ (100% sandstone), with more realistic mixing scenarios of 75% basalt and 25% basalt giving $5.48 \times$ and $4.08 \times \text{PAL}$, respectively. Thus, regardless of the precise starting parent material composition, $p\text{CO}_2$ levels at ~ 1100 Ma ago are fairly tightly constrained to have been between $4 \times$ and $6 \times \text{PAL}$.

5.6. Implications

The Sturgeon Falls paleosol shows many similarities with the penecontemporaneous Good Harbor Bay paleosols of Mitchell and Sheldon (2009), both in terms of the overall weathering environment and the maturity of the respective paleosols. The Sturgeon Falls paleosols is more highly leached and has lower salinization values than the Good Harbor Bay paleosols, both results that are consistent with higher precipitation at the Sturgeon Falls site. Overall though, both sites indicate moderately intense weathering in a climatic setting that was neither overly warm nor wet (Sheldon and Tabor, 2009), which is consistent with paleolatitude range indicated by recent paleomagnetic work (Swanson-Hysell et al., 2009). At the same time, results from both sites on opposite sides of the rift are also consistent with relatively low levels of atmospheric CO_2 , a result that is further validated by comparison to quantitative estimates of CO_2 from the slightly younger Sheigra paleosols in present-day Scotland. Thus, the weathering results are consistent with the modelled atmospheric composition and indicate that the high levels of greenhouse forcing indicated by Paleoproterozoic paleosols (Sheldon, 2006b) were no longer present by the mid-late Mesoproterozoic.

6. Conclusion

New data from the ~1.1 Ga Sturgeon Falls paleosol suggests that the paleosol is not as altered as previously thought. The studied profile has been extended from that of Zbinden et al. (1988) to 12 m thickness including a ~6 m thick eroded basal “C” horizon. The paleosol is moderately mature, and dominated by quartz, with significant clay formation and a lack of feldspars. The relative maturity of the paleosols is supported by the moderate CIA and hydrolysis values and high leaching values near the top and middle of the profile. Evidence for salinization is limited based on the constant and low salinization ratio values. Mass balance data indicate that losses occurred from the paleosol in every element, though in some cases, the elements were redistributed downward in the paleosol profile rather than completely removed. Provenance ratios indicate that the paleosol had a homogeneous parent material composition. In contrast to Zbinden et al. (1988), our data including mass balance, A–Cn–K, and comparing with Rb with K show that there was not significant addition of K to the profile. As a result, the chemical composition of the Sturgeon Falls profile was used to calculate an atmospheric $p\text{CO}_2$ value of 4–6× PAL, which is consistent with previous results for 980 Ma old Sheigra paleosols (Sheldon, 2006b). This result is also consistent with penecontemporaneous records of weathering from the Good Harbor Bay paleosols of Mitchell and Sheldon (2009) from the (modern) northwest limb of the Keweenaw Rift. The modelled atmospheric compositions indicate that the high levels of greenhouse forcing suggested by Paleoproterozoic paleosols (Sheldon, 2006b) were no longer present by the mid-late Mesoproterozoic.

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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.precamres.2010.09.003](https://doi.org/10.1016/j.precamres.2010.09.003).

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