**Sedimentary provenance and weathering processes in the 1.1 Ga Midcontinental Rift
of the Keweenaw Peninsula, Michigan, USA**

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ABSTRACT

Fluvial, alluvial, lacustrine, and debris flow sedimentary rocks from the Keweenaw Peninsula (Michigan, USA) are geochemically characterized to examine weathering processes and provenance. These sedimentary rocks result from the erosion, weathering, and redistribution of effusive and plutonic igneous lithologies during periods of volcanic quiescence associated with the failed 1.1 Ga North American Midcontinental Rift. Three units comprising the sedimentary/igneous-mixed Portage Lake Volcanics, coarseness and source-varied Copper Harbor Conglomerate, and the quartz-rich post-rift fill unit of the Jacobsville Sandstone were studied over a geographically-wide and lithologically-varied range of localities across the Keweenaw Peninsula, Michigan. Provenance indicators such as Ti/Zr and Ti/Al ratios and La-Th-Sc ternary diagrams reveal that the Portage Lake Volcanic conglomerates are near-source, and that the Copper Harbor Conglomerate is primarily

derived from felsic uplifted basement and recycled orogen lithologies to the east. The
Jacobsville Sandstone is a combination of pulses of sources from the top to the bottom of the
stratigraphic section: 1) felsic arkosic arenites sourced from the erosion and uplift of
basement orogenic volcanic and plutonic rocks (top), 2) felsic arkosic-subarkosic arenites
sourced from the erosion of uplifted basement, recycled orogeny and reworking of primary
sedimentary and metasedimentary rocks (middle), and 3) quartz arenites eroded from the
cratonic interior (highly mature). This work can consequently aid in structuring a
stratigraphic nomenclature for the Jacobsville Sandstone. Both petrographic data and
weathering indices such as the chemical index of alteration (CIA) and the paleosol
hydrolysis metric ($Al/(Ca+Na+Mg+K)$) indicate low degrees of weathering during syn-rift
deposition at 1.1Ga, but increases with evolution of the rift in post-rift units towards the Late
Mesoproterozoic/Early Neoproterozoic. Values for the CIA throughout the Mesoproterozoic
from this and other localities have the same trend to that of proposed atmospheric CO₂
concentrations derived from paleosol data, demonstrating that characterizing the weathering
trends of floodplain deposits can be a useful addition to deciphering past paleoclimatic
conditions in the Precambrian geologic record.

Keywords: Weathering; Provenance; Mesoproterozoic; Midcontinental Rift; Keweenawan;
Paleoenvironment

1. Introduction

The time frame from 1.8 to 0.8 Ga ago has sometimes been termed the “boring billion” on
the basis of relatively stable marine C isotopes and long-term apparent stability in
atmospheric O₂ levels (Holland, 2002). However, a number of recent studies of marine rocks

(summarized in Lyons et al., 2014) have called into question this relatively simple interpretation of long-term stability, and studies of stromatolite and microbially-induced sedimentary structure diversity and abundance indicate peaks in both during the height of the “boring billion” (Noffke and Awramik, 2013). Post-“Great Oxidation Event” atmospheric O₂ levels now appear to have been much lower than previously thought (10⁻³ times present atmospheric levels; Planavsky et al., 2014), potentially suggesting that rates of oxidative surface weathering may have stayed relatively low until the end of the Precambrian. Simultaneously, a number of Mesoproterozoic paleosols have been identified, which have in turn been used to understand weathering intensity and paleoenvironmental and paleoclimatic conditions of surface environments (e.g., Zbinden et al., 1988; Holland et al., 1989; Maynard, 1992; Rye and Holland, 2000a,b; Sheldon, 2006; Mitchell and Sheldon, 2009, 2010; Mitchell, 2010; Sheldon, 2013). While some of those paleosols are bedrock parented (e.g., Zbinden et al., 1988; Mitchell and Sheldon, 2010) and preserved between basalt flows (e.g., Sheldon, 2013), others are preserved as parts of more permeable floodplain sequences (Mitchell and Sheldon, 2009; Sheldon, 2013), making them potentially more susceptible to post-burial alteration, such as potassium metasomatism (e.g., Fedo et al., 1995; Nedachi et al., 2005) generated by hot fluids from nearby igneous flows and intrusions (Ojakangas et al., 2001). In spite of those complications, paleosols (n = 10) formed from 1.2 to 0.9 Ga consistently indicate low atmospheric pCO₂ levels below 10 times pre-industrial values (Sheldon, 2006; Mitchell and Sheldon, 2010; Sheldon, 2013), which contrasts strongly with Paleoproterozoic (Sheldon, 2006) and Archean (Driese et al., 2011) paleosols that indicate much higher atmospheric pCO₂.

At the same time, paleosols are still comparatively rare in the Mesoproterozoic record, so to validate the notion that atmospheric pO₂ and pCO₂ were both relatively low, it is necessary to look at other terrestrial sedimentary environments. Rocks associated with the

failed ~1.1 Ga Midcontinental Rift (MCR herein) in the present day Lake Superior region (Fig. 1) preserve varied sedimentary environments associated both with the rift event itself and with the pre-rift bedrock that can provide a test of both inferences about the Mesoproterozoic atmosphere. In the MCR, sedimentary rocks are intermixed with effusive igneous lithologies (dominated by basalt) that have remained at the surface mostly unaltered or metamorphosed since their deposition (Ojakangas et al., 2001; Green, 2005). Most of the previous work on the Keweenaw Peninsula has focused on either economic geology of altered sedimentary rocks (e.g., Mauk et al., 1992) or on the igneous rocks preserved there, with relatively few sedimentological studies (e.g., Kalliokoski, 1982, 1986; Elmore, 1984; Nishioka et al., 1984; Elmore et al., 1989), and virtually no geochemical characterization of the sediments (cf. Kalliokoski, 1974). Syn- and post-MCR deposition on the Keweenaw Peninsula is comprised primarily of three units: the Portage Lake Volcanics, the Copper Harbor Conglomerate, and the Jacobsville Sandstone (Figs. 1-2). Here, we study sedimentary rocks from all three units to characterize the weathering trends, provenance, and surface environmental conditions in the late Mesoproterozoic.

2. Geological Setting

2.1. The Midcontinental Rift (MCR)

The ~1400 km long failed MCR reached its climax around 1100 Ma, originating due to tectonic activity associated with a large mantle plume beneath Laurentia (Green, 1983; Vanschmus and Hinze, 1985; Cannon and Hinze, 1992; Davis and Green, 1997; Ojakangas et al., 2001). During the period of rift formation, Laurentia was drifting southwards from 50°N to 20°N (Swanson-Hysell et al., 2009), with the MCR area

situated in the central part of the Supercontinent (Kalliokoski and Welch, 1985; Kalliokoski, 1986). Throughout the course of Keweenaw rifting and volcanism, continental motion was Equator-ward, initially at $33.6 \pm 3.5 \text{ cm yr}^{-1}$ at $1,108 \pm 1 \text{ Ma}$ and slowing to $12.2 \pm 6.4 \text{ cm yr}^{-1}$ by $1,087 \text{ Ma}$ (Swanson-Hysell, 2010), with the slowing corresponding with the end of major volcanic and tectonic forces driving plate motion. A triple junction is thought to have formed to the north of the Lake Superior region (Ojakangas et al., 2001), with the western-most of the three ‘arms’ becoming the failed MCR (Fig. 1). Alternatively, it has been suggested recently that this ‘arm’ was part of an evolving plate boundary system rather than an isolated episode of midplate volcanism (Merino et al., 2013), with the height of activity surrounding the spreading of Amazonia from Laurentia (Stein et al., 2014b). Based upon those new results, a hybrid tectonic model has recently been proposed, suggesting that the MCR began as a continental rift and continued as a large igneous province after extension (Stein et al., 2014), but that idea needs additional testing to be confirmed. Regardless of the specific driving mechanism(s) behind rifting of the MCR, the extension caused by the rifting resulted in subsidence and normal-faulted graben-like basins (Ojakangas et al., 2001). Basalts (and some minor basaltic andesites-rhyolites) were erupted from fissures in a flood-style eruption creating vast thicknesses of extrusive volcanic rocks (Green, 1983; 2005). This activity occurred in two pulses between 1109 and 1105 Ma, and 1100 and 1086 Ma (Paces and Miller, 1993; Davis and Green, 1997), with the main phase of rifting centered around 1100 Ma (Ojakangas et al., 2001). Eruptions occurred intermittently, resulting in a syn-rift sequence of alternating volcanic rocks and dominantly red-bed sedimentary rocks (conglomerates to shales). Rivers flowed into the central areas of the basins from upland areas near the rift margins (Jirsa, 1984; Green, 1989; Ojakangas et al., 2001; Green, 2005). Examples of these intermixed deposits include the North Shore Volcanic

Group (NSVG herein), the Portage Lake Volcanics (PLV herein), and the Copper Harbor Conglomerate (CHC herein; Fig. 2).

Some disagreement exists regarding the reasons for MCR failure; the traditional view is that it failed because of continental collision at the Grenville Front to the east of the rifting zone (Fig. 1; Ojakangas et al., 2001), however new work by Stein et al. (2014) suggests that the MCR became inactive once seafloor spreading was established between Laurentia and Amazonia to the south-west of the MCR region. Compression led to the reactivation of normal faults as reverse faults (for example the Keweenaw Fault; Fig. 1) and thrusts, uplifting the entire rifted basin (Stein et al., 2014a; Ojakangas et al., 2001). Compression is likely to be younger than subsequent post-rift sedimentary sequences, as these steepen on contact with the Keweenaw Fault (Stein et al., 2014) however the precise timing is difficult to constrain. Post-rift sedimentary sequences, which include the Jacobsville Sandstone (J Sst herein) and Bayfield Group (Figs. 1-2), are difficult to date directly; a recent estimate by Stein et al. (2014) suggested most deposition occurred between ~760 – 620 Ma with a maximum age of 959 ± 18 Ma (Stein, 2015) on the basis of comparison of J Sst detrital zircons and the inferred paleolatitude of Laurentia, although earlier workers have assigned an age that is much closer in time to the cessation of rifting.

Present day Lake Superior roughly parallels the orientation of the failed MCR, with lithologies associated with both syn- and post-rift deposition outcropping on both the northern Minnesota and southern Michigan and Wisconsin shores (Figs. 1-2), virtually unchanged since their deposition 1.1 Ga. Correlation of nomenclature of each of these units can be found in Fig. 2.

2.2.Keweenaw Peninsula Geology

The Keweenaw Peninsula on Michigan's Upper Peninsula (Fig. 1) is surrounded by older Paleoproterozoic and Archean metasedimentary and plutonic rocks to the south, by equivalent age Mesoproterozoic deposits to the west, and by younger Paleozoic rocks to the east (Fig. 1; Ojakangas et al., 2001; Mitchell, 2010). The Peninsula is the eastern-most limb of the Lake Superior syncline (Isle Royale being the western limb), and is rich in MCR-related outcrops of volcanic and sedimentary rocks. There are a number of syn- (Bergland and Oronto Groups) and post (J Sst) -rift lithological units associated with the active rifting and cessation of rifting phases, respectively (Fig. 1). The Keweenaw Peninsula represents a greater diversity of MCR-associated sedimentary lithologies in comparison to the western limb in Minnesota and Isle Royale, where differences in paleoenvironment, intrusion frequency, and post-rift faulting mean that sedimentary outcrops are less abundant. An important observation is that the Keweenaw Peninsula preserves post-rift sedimentation, whereas the western shore does not (Ojakangas et al., 2001; Mitchell, 2010).

The Keweenawan Supergroup represents an amalgamation of the MCR units found in the Lake Superior area (Fig. 1). Volcanism within the PLV and CHC is similar to that of the NSVG (Fig. 2) on the western shore (i.e., dominated by tholeiitic basalts with some minor rhyolites; Ojakangas et al., 2001; Green, 2005), suggesting that the mineralogical and geochemical character of resulting sedimentary rocks could show similar characteristics. Volcanic deposits decrease up section in the Keweenawan Supergroup because of waning tectonic forces relating to the failure of the MCR, with deposition instead changing to basin-fill sedimentation (J Sst; Kalliokoski, 1982; Ojakangas et al., 2001; Mitchell, 2010).

2.2.1. Portage Lake Volcanics (PLV) – Bergland Group

The PLV outcrops as a thin band along the central spine of the Keweenaw Peninsula (Fig. 1), with minor outcrops on the Lake coastline in the northernmost part of the peninsula. The PLV consists of a 3–5 km thick pile of predominantly olivine-tholeiite flood-style lavas (Davis and Paces, 1990), dominated by basalts and minor amounts of clastic (conglomerate to sandstone) intervals throughout the succession (Mitchell, 2010). These sedimentary units are laterally continuous across much of the Peninsula, making them important stratigraphic markers (Bornhorst and Rose, 1994). Putative pedogenic caliches (Kalliokoski and Welch, 1985; Kalliokoski, 1986) and some minor rhyolites (Davis and Paces, 1990) are also present. The rhyolites originate from the partial melting of older buried MCR rocks (Vervoort and Green, 1997; Ojakangas et al., 2001). The age of PLV volcanism has been determined by U/Pb methods to be between 1096.2 ± 1.8 Ma and 1094.0 ± 1.5 Ma (Davis and Paces, 1990), thereby making them important syn-rift deposits that correlate well (Fig. 2) with the NSVG sedimentary rocks and with previously described paleosols of Mitchell and Sheldon (2009) and Sheldon (2013).

2.2.2. *Copper Harbor Conglomerate (CHC) – Oronto Group*

The CHC (Fig. 3) is the basal unit of the Oronto Group and outcrops unconformably above the PLV (Figs. 1 and 2). It is stratigraphically below the lacustrine Nonesuch Shale (Nishioka et al., 1984), which outcrops on the southern part of the Keweenaw Peninsula in Michigan and in northern Wisconsin. The CHC consists of a 2 km thick succession of conglomerates with minor amounts of sandstone to siltstone-grade sedimentary rocks (Davis and Paces, 1990). A thick outcrop of CHC conglomerates gives a sharp, elevated relief to the near-central spine of the Peninsula. A minor volcanic constituent, named the Lake Shore Traps, are present near the base of the CHC succession. They consist of 600 m of olivine

tholeiites, tholeiitic basaltic andesites, and tholeiitic andesites exposed in the north of the Keweenaw Peninsula (Bornhorst and Rose, 1994). As the Lake Shore Traps are stratigraphically at the base of the CHC (Ojakangas et al., 2001), they constrain the earliest age of CHC deposition at 1087.2 ± 1.6 Ma (Davis and Paces, 1990). The eruption of the Lake Shore Traps is thought to be the final phase of volcanism associated with active phases of the MCR on the Keweenaw Peninsula (Bornhorst and Rose, 1994; Ojakangas et al., 2001). The CHC fines up stratigraphically and westwards into the basin (Nishioka et al., 1984; Ojakangas et al., 2001) and is represented in the field by conglomerates at the base and a greater proportion of sandstone-shales at the top of the 2 km section. The majority of laterally associated finer grained siltstones and shales are assumed to be beneath the central axis of present day Lake Superior (Elmore, 1984; Ojakangas et al., 2001), but some outcrop in coastline areas in the north. The Oronto Group, particularly the CHC, represents the immediate post-rift erosion of intra-basinal rift material (Ojakangas et al., 2001) in the form of thick and immature deposits of poorly sorted cobble to pebble conglomerates (Nishioka et al., 1984). Sedimentary structures include trough cross-bedded sandstones as well as evidence for microbial colonization of many surfaces indicated by microbially induced sedimentary structures (MISS), and purported microbialite calcitic domes (Elmore, 1984; Nishioka et al., 1984; Mitchell, 2010; Sheldon, 2011; Wilmeth et al., 2014). An age of 1104 ± 2 Ma was determined from detrital zircons within clasts of conglomeratic CHC, indicating that they are at least in part derived from local Keweenawan sources (Davis and Paces, 1990).

2.2.3. *Jacobsville Sandstone (J Sst)*

The J Sst (Fig. 4) outcrops on the southern and eastern shore of the Keweenaw Peninsula (Fig. 1). In the central part of the Peninsula, it is in fault contact (the Keweenaw Fault) with the PLV. The J Sst ranges in thickness (between 30 and 600 m in the south and north of the Peninsula, respectively; Bauman, 2010). There are no igneous rocks associated with the J Sst, and it is interpreted as a post-rift basin-fill deposit in a rift-flanking basin (Kalliokoski, 1982). It is dominated by mixed red and locally reduced fluviatile sandstones, with some localized conglomerate, siltstone, and shale lithologies (Hamblin, 1958; Kalliokoski, 1982; Ojakangas et al., 2001; Bauman, 2010). Based on numerous stratigraphic, sedimentological and associated lithological events, Baumann (2010) suggests the J Sst was deposited in a 100 Ma interval most likely between 950–900 Ma. However, new data from Stein et al. (2014) suggests that deposition of the J Sst may have occurred much later, most likely between 760 and 620 Ma, and with a maximum age of 959 ± 18 Ma (Stein, 2015). A lack of igneous activity and fossils make absolute dating difficult. Regardless of which age model proves to be correct, there was a period of depositional quiescence and cratonic stability between deposition of the CHC and J Sst wherein paleosols formed and were preserved in some areas (Kalliokoski, 1982; Zbinden et al., 1988; Mitchell and Sheldon, 2010).

3. Methods

Following the removal of the upper (at least) 10 cm of surficial material, clean samples of sedimentary rocks and some volcanic rocks (basalt and rhyolites) were collected for geochemical and petrological comparison. For whole rock geochemical analysis, samples were first crushed to powders using a Tema swingmill and Jaw Crusher. Powdered samples were then fused with a lithium metaborate flux within graphite crucibles, melted at 900°C in a muffle furnace, and then digested in a 10% nitric acid solution for major element analysis by ICP-AES. For trace elements, powdered samples were digested in a hydrofluoric and

perchloric acid mix, and then diluted with de-ionized water, and analysed by ICP-MS. Analyses were undertaken on a PerkinElmer Optima 3300RL ICP-AES and an Agilent Technologies 7500 Series CX ICP-MS, respectively, at Royal Holloway, University of London. Analytical uncertainty is <0.1% for major element and <4ppm for trace element analyses. Thirty thin sections were made of both sedimentary and igneous samples. Point count data (500 counts per thin section) were collected on a James Smith Model F Point Count machine. Field observations, geochemical, and point count data can be found in the supplemental material (Tables S1-S2, Data D1-D3).

4. Results and Discussion

4.1. Sedimentology and locality overview

None of the studied lithological units have an obvious ‘parent’ lithology (unlike some paleosols in the Lake Superior region which develop from their underlying weathered basalt parent rock, (e.g. Zbinden et al., 1988; Mitchell and Sheldon, 2010), suggesting that weathering and provenance may have varied across the Peninsula. In addition to this, sites where paleosols have previously been reported or hypothesized were studied (e.g., Bornhorst and Rose, 1994). A brief overview of the sedimentological features of each locality is given in Supplemental Table S2.

4.2. Mineral Composition

4.2.1. Portage Lake Volcanics (PLV)

4.2.1.1. Basalt

The PLV at South Range Quarry consists of a weathered basalt with altered feldspars and minor ferromagnesian minerals (Fig. 5a). Olivines and pyroxenes are rare (8%). The basalt is composed of 27% plagioclase phenocrysts, and 54% plagioclase-based groundmass (some of which are remnants of weathered and altered plagioclase phenocrysts; Fig. 5a). No iron oxide minerals were found. Orthoclase and unidentified zeolites were found in limited amounts (6 and 5%, respectively). In comparison, basalt samples from Hungarian Falls site b) indicate a relatively unaltered basalt with large, unaltered plagioclase feldspars, therefore implying that alteration processes are localized and not widespread in the PLV.

4.2.1.2. Sedimentary rocks

The sedimentary rocks at Hungarian Falls site (b) (Fig. 5b) contain a heterogeneous mix of lithic fragments (felsic 47%, mafic 22%), plagioclase (1%), iron oxides (3%) and a small amount of matrix (12%). The rest is composed of calcitic cement (16%). Clasts are immature and poorly sorted. Plotting data on a quartz-feldspar-lithic (QFL) diagram (Fig. 6a) categorizes Hungarian Falls site (b) sedimentary rocks as lithic arenites.

4.2.2. Copper Harbor Conglomerate (CHC)

The term ‘conglomerate’ is perhaps a little misleading for this sedimentary unit, as it is composed of a variety of grain sizes throughout the section; new fieldwork has found that sand- to mudstone grades are observed just as often as conglomerates in coastal exposures of

the Keweenaw Peninsula (Fig. 3). The parts of the CHC that are conglomerates are a heterogeneous mix of poorly sorted felsic and mafic igneous clasts (~30% average in outcrop), as well as some heavily weathered sedimentary (~20% average in outcrop) and metasedimentary (~10% average in outcrop) cobbles (Fig. 3a, e). Conglomerates are mostly rounded and clast supported, however some localized areas of brecciation are also found (Fig. 3). Sand-, silt-, and mudstones, however, are more homogeneous, and are dominated by quartz (up to 46%), plagioclase feldspar (up to 23%), iron oxides (up to 10%) and a high proportion of matrix (up to 68%; Fig. 5). Lithic fragments are rare (in fine sand- to mudstone grade; Fig. 5d), and there is little post-burial cementation. Black laminations (Fig. 4d), which are frequently observed throughout this sequence (particularly at Horseshoe Harbor), do not appear to be mineral-related and are composed in part of detrital organic carbon (Sheldon, 2012). Non-conglomeratic rocks of the CHC are categorized as a mix of lithic and arkosic arenites (Fig. 6a).

4.2.3. *Jacobsville Sandstone (J Sst)*

The J Sst is dominated by sub-rounded to angular quartz grains, some of which have bifurcated margins and iron oxide-stained rims (Fig. 5). Of ten samples studied in thin section, the average quartz component is 37% (high of 63% in JV4, low of 32% in TRK5) and an average feldspar (all types) component of 30% (high of 40% in TRK1 and TRK2, low of 15% in HF1B), suggesting that there is mineralogical source variation across the Peninsula. Other constituents consist of minor amounts of iron oxides, olivine and pyroxene. Mica (mainly biotite) is present in reasonably large quantities compared to other MCR formations (high of 23% in TRK5; Supplemental Data D3, Fig. 5h), however mica is not present consistently through the unit (Figs. 5f-g) and makes up the constituent difference

when quartz and feldspar contents are low. The matrix component (mainly quartz cement) is variable (ranging from 5 to 27%), and diagenetic cement is mostly absent. Lithic clasts are rare in most J Sst samples, indicating greater maturity. Grain sizes range from coarse sand (minor lenticular beds of granular conglomerate are found at Tamarack; Fig. 4g) to fine sand bordering on siltstone (siltstone rip-up clasts are found in sandstones at Brunette Park; Fig. 4b). J Sst rocks are categorized as a mix of arkosic arenites, subarkose, and quartz arenites (Fig. 6a).

4.3.Geochemistry

Conglomeratic sediments from the PLV at Hungarian Falls site b) exhibit a range of chemical compositions when comparing conglomerate clasts and matrix. For example, a sample of a claystone clast (sample 2HF2) has 9% less Si than its matrix counterpart, the difference being made up of higher percentages of alkali and alkali earth metals in comparison to quartz.

The sedimentary rocks associated with the CHC are far more chemically varied than those belonging to the PLV. Si values for Silver River vary from 44.6% to 70.9%, with a larger variability at Horseshoe Harbor (as low as 28.9% in sample HHA2 and as high as 72.5% in HH4). Relatively large fluctuations also occur for samples from Horseshoe Harbor in Al, Mg, Na and K, with the largest range occurring in Ca (up to 29.8% in sample HHA2, where the average is 6.2%). These large fluctuations in Ca can be attributed to the presence of carbonate stromatolitic-like layers in some of the foreshore outcrops (Mitchell, 2010; Sheldon, 2012; Fig. 3f).

In the J Sst, Si is high (up to 89.9% in some samples at Brunette Park), due to high amounts of quartz grains and Si cement. Totals are very near to 100% as volatile contents

were low (measured as loss on ignition) are present. Al is lower than in other Formations studied (average of 6.9% compared with the CHC 11.5%) because of the dominance of quartz over feldspar. K however remains high in relation to other alkali and alkali earth metals (K average of 4.5%, Ca+Mg+Na average 0.3%), because of the elevated content of microcline and biotite mica.

4.3.1. Chemical Index of Alteration (CIA and CIA-K) and weathering

A useful molecular weathering ratio to determine a measure of the breakdown of feldspars to eventually form clay minerals is the Chemical Index of Alteration (CIA) of Nesbitt and Young (1982), which is calculated on a molar basis as follows:

$$CIA = 100 \times \frac{Al}{Al + Ca + Na + K} . \quad (1)$$

One method of measuring the geochemical changes and consequent mineralogy between proposed parent rocks (in this case, volcanic rocks associated with the main rifting phases of the MCR) and the weathering-derived sedimentary rocks (PLV, CHC, J Sst) is to compare their CIA values. The CIA can also be a useful indicator for changes in weathering rates/types of weathering through time. For example, basalts generally have a low CIA of <45 (e.g., Sheldon, 2003), felsic rocks 55–60, and shales 70–75 (Maynard, 1992; Young and Nesbitt, 1998), indicating that shales are more weathered and mature than their primary ‘parent’ igneous counterparts. Maynard (1992) proposed a variation of equation 1 without K (CIA-K). Enriched potassium, as well as other diagnostic lithologic features, could be an

375 indicator of post-burial alteration by K metasomatism; CIA-K highlights where this may
376 have occurred. Plotting CIA vs CIA-K (Fig. 7a), together with previously documented MCR
377 paleosols from Mitchell and Sheldon (2009) and Mitchell and Sheldon (2010), displays a
378 mainly linear trend in all samples bar the J Sst, indicating no net accumulation of potassium
379 in most of the samples, including all of the paleosol samples. Volcanic rocks from the
380 Keweenaw Peninsula (South Range Quarry) and other MCR associated volcanics (a mix of
381 basalt and rhyolite samples from the NSVG in Minnesota) show a range in CIA values,
382 some with very low CIA values and some exceeding the 'normal' CIA range for igneous
383 rocks, reaching a value of nearly 60. This could suggest minor alteration of the volcanics,
384 however, these data do plot on a linear trend in the dataset, suggesting a process other than
385 K metasomatism was responsible.

386 The CHC sedimentary rocks have CIA values between 9.4 and 56.4, the largest range of
387 the three units studied (Fig. 7a). The variability in both Silver River and Horseshoe Harbor
388 samples is most likely due to the irregularity or the mineral assemblages found in the CHC;
389 both mafic and felsic lithic clasts are frequent, displaying a range in compositions from a
390 variety of sources, therefore giving variable values of CIA corresponding to variations in
391 weatherability. As mentioned previously, some samples from Horseshoe Harbor also contain
392 calcitic domes and laminations purported to be microbialite structures (Mitchell, 2010;
393 Sheldon, 2012; Wilmeth et al., 2014), and there are carbonate cemented alluvial fan deposits
394 throughout the CHC, therefore providing a potential source for both low CIA values and
395 variability of Ca content. The J Sst sedimentary rocks are outliers relative to the rest of the
396 data, with CIA values ranging between 52.3 and 59.8 and CIA-K ranging between 86.1 and
397 96.1, the highest of all Keweenaw Peninsula sedimentary rocks (Fig. 7a). The substantial
398 enrichment of K is the consequence of high proportion of felsic-derived mineral material
399 (such as biotite and microcline), suggesting that it potentially has a different origin than the

PLV or CHC. The J Sst values plot with the MCR rhyolite sample, which further support this idea. Consistently high (in comparison to other sedimentary rocks) CIA values for the J Sst suggest deposition of sediment that had undergone moderate degrees of weathering prior to deposition, and that this weathering was uniform for the J Sst as a whole. It seems unlikely that the J Sst was significantly weathered *in situ* because of the lack of associated pedogenic structures and clays, which would result in significantly higher CIA values (e.g., pure kaolinite has a CIA value of 100; Maynard, 1992).

4.3.2. Provenance of Keweenaw Peninsula sedimentary rocks

Minerals that are sourced from a more felsic source are, for the most part, more stable and difficult to weather in comparison to mafic rocks. Useful indicators of provenance include ratios of an assortment of immobile elements, the most common of which are Ti/Al and Ti/Zr (Fig. 7b), and can also provide additional insights into weathering processes. For example, Zr is only leached from zircons under very acidic conditions, so under normal conditions, its removal reflects physical rather than chemical weathering. Sedimentary rocks from the PLV and CHC are not uniform, but overall indicate an immature source (previously discussed in section 4.2, and because some samples are conglomerate clasts). The NSVG paleosols of Mitchell and Sheldon (2009) also show some variability, indicating parent material sources are not uniform in these either. There is a general correspondence between the NSVG paleosols and CHC and PLV sedimentary rocks, whereas most of MCR volcanic sample data do not follow the same trend (Fig. 7b). The J Sst and rhyolite samples have the lowest values of both ratios, consistent with the J Sst having a more felsic source than the other sedimentary units, and consistent with CIA data and with the idea that the K excess is depositional rather than metasomatic in origin (*section 4.3.1*). The one J Sst outlier

is a grey-green reduction spot (sample JV1). Geochemically, the outlier has elevated concentrations of Ti (2.4 wt% compared with 0.5 wt% average of other samples of J Sst) at the expense of Si (72 wt% vs. 77 wt% average) and Al (8.5 wt% vs. 9.3wt% average). Whether this represents a difference due to the post-depositional processes that lead to the reduction spots or simply a lone unusual sample is unclear with the data available. The Sturgeon Falls paleosol of Mitchell and Sheldon (2010), which is parented by metabasalt, indicates some homogeneity, but again, no close similarity to most samples of mafic MCR volcanic material.

Comparing a provenance indicator (Ti/Al) with a weathering index (CIA) can identify relationships between the degree of weathering and its respective source material. Generally, there is a (weak) negative correlation (Fig. 7c), which indicates increased weathering induces an apparent homogeneity in source material. This is unsurprising, as values above a CIA of 45–50 typically represent a degree of weathering in which easily weatherable minerals (i.e., base cation-rich) are depleted or lost (Nesbitt and Young, 1982), therefore leaving a more homogeneous mix of more resistant minerals. This is particularly evident in the J Sst. Outliers mainly belong to the CHC, and represent lithic-dominated samples from numerous sources and, consequently, degrees of weatherability.

Overall though, the spread of data in Figs. 6b and 7c indicates that the MCR sedimentary rocks originated from numerous source areas. Degrees of weathering in the igneous rocks are varied, probably mostly stemming from original chemistry. This again suggests the Keweenaw Peninsula sedimentary rocks originate from numerous sources both within and outside of the local system. The paleosols from the NSVG (Mitchell and Sheldon, 2009) and Sturgeon Falls (Mitchell and Sheldon, 2010), all thought to be parented primarily by material from a mafic source, form a linear array (Fig. 7c), consistent with

more broadly similar weathering processes and history than the other MCR sedimentary rocks.

Beyond providing constraints on sediment maturity, Ti/Al and Ti/Zr are not sufficient for uniquely determining the source of the CHC, therefore other immobile element relationships can be employed as well. CHC samples from Horseshoe Harbor are dominated by fine sand-siltstone grain ponded and lacustrine-margin deposits that can be better constrained by using a different set of immobile elements, including the REEs La, Th and Sc (Fig. 6c). High-silica source rocks (i.e., felsic) tend to contain higher concentrations of REEs (particularly Th, Hf, and Ba) and lower concentrations of Sc and Cr (which are high in low-silica source rocks (mafic)). Particularly high concentrations of Sc and Cr are in those low-silica source rocks derived from mafic sources, even more so than weathered and re-worked silicic sediments (Cullers, 1994). Fig. 6c suggests that the majority of sand-silt grade rocks at Horseshoe Harbor are derived from a mixed sedimentary source, preferentially from felsic rocks (high La). One outlier is dominated by a higher mafic component (high Sc), which can be attributed to a higher percentage of mafic lithic clasts (Fig. 6a).

5. Paleoenvironmental Interpretation

5.1. Portage Lake Volcanics and the Copper Harbor Conglomerate

The PLV is represented by a coarse cobble–pebble conglomerate at Hungarian Falls site b), containing a mixture of sedimentary and igneous (mafic and felsic) clasts. The ‘chaotic’ and poorly sorted nature of this conglomerate suggests it was deposited in times of tectonic instability, and represents an alluvial-type deposit not related to fluvial processes common in other outcrops of the PLV (for example, no clast imbrication is observed like that seen in the

CHC; Fig. 3e). It seems probable that this conglomerate originates from localized tectonic forces such as a tectonically induced debris flow.

The CHC contains a broad range of sedimentary lithologies, notably thick conglomerate packages at Silver River and Horseshoe Harbor, which are overlying finer grained beds of sand- to siltstone grade. Unlike the conglomerates in the PLV at Hungarian Falls, conglomerates in the CHC contain evidence of fluvial origin (clast imbrication and erosional bases forming scours/micro-channels; Fig. 3d), and are composed of sedimentary lithologies, metasediments, and mixed felsic and mafic lithologies, dominated by plagioclase-rich basalts (not unlike those in the PLV). This chaotic and heterogeneous assortment of lithic material is confirmed by provenance indicators (Figs 6, 7) suggesting that material is from numerous sources, most notably, felsic sources (Fig. 6c). Clast imbrication (Fig. 3e) indicates paleocurrents from the east towards central parts of the MCR basin to the west (Fig. 8); this source is consistent with some pebbles in the CHC conglomerates being clasts of the PLV. The conglomeratic CHC deposits at Silver River and Horseshoe Harbor represent near source, high velocity, braided fluvial channel from a high relief source. The almost synchronous uplift of surrounding hinterland will have provided relief and material carried westwards to coastal parts of the MCR basin, where they will have been eroded and weathered further to deposit as the finer sand-siltstone graded lithologies.

Underlying the thick conglomeratic sequences at each of the localities are fine grained sand-siltstones (Fig. 3). Conglomerates have both a sharp erosional base (at Silver River; Fig. 3d) and a gradational coarsening-up sequence (Horseshoe Harbor; Fig. 3a), implying that networks of smaller braided channels were in operation, some scouring into their surfaces and some grading into higher energy lithologies (conglomerates). The Horseshoe Harbor deposits may be an indication of flooding of fluvial channels onto finer

grained marginally ponded, lacustrine-like environments. Fully lacustrine strata are preserved in the overlying Nonesuch Formation (Fig. 2), and could be the result of either further subsidence post-CHC or of a shift to a wetter climate. The sand-siltstone rocks are heterogeneous, mainly dominated by an assortment of lithics (Fig. 6a) that are proposed to have originated from re-worked metasediments from a typically felsic source (Fig. 6c). This, together with paleocurrent information (Fig. 8), suggests that the sand-siltstone grade CHC rocks may have been sourced from Archean and Paleoproterozoic metasedimentary rocks to the east and south of the Keweenaw Peninsula as opposed to nearby source areas for the conglomerate. The variation in source components is illustrated in Fig. 6b, which suggests reworked CHC originate from both recycled orogen and volcanic-induced (arc) sources. Silver River samples suggest a volcanic (arc) source due to the high proportions of feldspar relative to quartz (Fig. 6a) and low degree of chemical weathering (Fig. 7a, c), indicating a higher degree of remnant parent material. The sand-siltstone grade rocks represents the end of a gradual fining up sequence as large-river system suspended load is deposited in flat, low lying plains as low energy ponds and lacustrine environments. This calmer mode of deposition would then have been interrupted by flash floods and tectonically-triggered landslide events, resulting in the deposition of lenses of conglomerate which scoured into the soft-sediment base.

Desiccation cracks (Fig. 3c) on the surface of some beds at Horseshoe Harbor suggest periodic exposure to the atmosphere, confirming a terrestrial depositional environment with episodic dewatering events.

5.1.2. Jacobsville Sandstone

Upon first glance, the J Sst seems to be a homogeneous package of quartz-dominated fluvial sandstones with large scale sedimentary features (cross-bedding, ripples; Fig. 4) throughout. This study reveals however, that this is not the case. A white coarse sandstone overlays a red/green siltstone at Brunette Park (Fig. 4a-c), indicating that fluctuations in sediment supply/velocity/depositional environment occur at sporadic intervals. The siltstone here could represent a lacustrine or paludal environment (at the present day it sits on the shoreline of Lake Superior, making study difficult), indicating that the J Sst is not as homogeneous as first thought. The rip-up clasts entrained within the overlying white sandstone (Fig. 4b) also indicate it was probably still soft when the sandstone was deposited.

Small scale cross beds are also present in the J Sst outcrop at Hungarian Falls (Fig. 4d), indicating paleocurrents towards the north-east. At Tamarack, small lenses of very coarse-granular rounded lithic fragments (Fig. 4g) are present in an outcrop of medium quartz rich sandstones. These lenses represent times of higher velocity/floods, where lithic grains will have been transported by saltation in the fluvial load and deposited with channel-fill sands. Cross bedding again is common (Fig. 4f), indicating a north-east paleocurrent (Fig. 8).

At Jacobsville, large-scale cross bedding (Fig. 4e) in medium quartz sandstones is overlain by parallel and horizontally laminated fine-medium quartz sandstones (Fig. 4e). This sequence represents the waxing and waning of a large fluvial system, with a decrease in velocity/larger sediment input responsible for the stagnation of flow/filling of the fluvial channel, resulting in horizontal deposition.

The J Sst at Sturgeon Falls unconformably overlies the Sturgeon Falls paleosol (Zbinden et al., 1988; Mitchell and Sheldon, 2010). This is the most mature and quartz-rich of all the J Sst studied (Fig. 6a, 7a), which is surprising considering that the J Sst is thought to prograde (i.e., young) into the MCR basin (Hamblin, 1958; Bauman, 2010). Basal deposits

547 of J Sst in other part of the Peninsula are dominated by a conglomerate (Hambin, 1958),
548 suggesting that at Sturgeon Falls, this basal unit may have been erosively removed before
549 deposition of the quartz sandstone (balls and rip-up clasts of the Sturgeon Falls Paleosol
550 have become entrained within the J Sst here (Zbinden et al., 1988; Mitchell and Sheldon,
551 2010), and that J Sst deposition was not solely a simple case of a prograding and maturing
552 basin-ward sequence.

553 Due to varying proportions of quartz:feldspar with almost constant lithic component
554 through the J Sst sequences studied, Fig. 6a shows a sedimentary classification and maturity
555 ranging from arkosic arenite (Tamarack, Hungarian Falls, Brunette Park) through subarkose
556 (Jacobsville) to quartzarenite (Sturgeon Falls), with Tamarack the least mature and Sturgeon
557 Falls the most mature. What is interesting about this is that that sandstone maturity seems to
558 increase from North to South, contrary to paleocurrent data and to what would normally be
559 expected for an onlapping basin-fill fluvial sequence. Paleocurrents (Fig. 8) from the J Sst
560 indicates that, on the whole, fluvial systems were transporting material from a source area in
561 the south-west towards the north-east. Figure 6c suggests this is a highly felsic source (high
562 La, low Sc), mostly different to the source of the CHC (high La, higher Th) and outside of
563 the regular trend of provenance in the dataset as a whole, which is generally reflective of
564 more mafic compositions. Only Tamarack sources are very variable, suggesting mixed
565 sedimentary source (concurs with conglomeratic input). Jacobsville sources are similar to
566 that of the CHC, suggesting that these deposits could either a) be derived from some of the
567 same source material as the CHC, or b) have a component derived from the CHC itself. The
568 Keweenaw Fault disrupts a complete stratigraphy of the J Sst (Hambin (1958) states that re-
569 activation of the Keweenaw Fault is post-J Sst and possibly even post-Devonian, with Stein
570 (2015) concluding faulting occurred ‘much later’ than 1.06 Ga) , making observations of the
571 later finer grained lacustrine deposits associated with the J Sst difficult to locate. Provenance

indicators (Fig. 6c) indicates that three main pulses or sources of material are prevalent in the Keweenaw Peninsula J Sst: 1) a common source (basement uplift and recycled orogeny of previous emplaced volcanic and plutonic lithologies) providing a mainly felsic (quartz, feldspar (microcline, orthoclase) and biotite mica) constituent in arkosic arenites outcropping in the northern-most studied localities (Brunette Park, Hungarian Falls, Tamarack (Fig. 6c, provided by conglomeratic clasts of nearby volcanics), 2) basement uplift and subsequent recycling of the orogeny creating a source to arkosic-subarkosic arenites, with this source similar to that of the silt-sandstone grade rocks associated with the CHC, and 3) a source from the erosion of the cratonic interior producing quartz arenites almost entirely composed of quartz, held together with a quartz cement. Fig. 6d and Fig. 7a indicate little to no weathering has occurred to the deposits since deposition, so any sorting and destruction of easily weatherable mineral (e.g., feldspars) will have occurred at the time of weathering of the parent rock. Limited *in-situ* weathering is also supported by the lack of soil (paleosol) formation within the PLV, CHC or J Sst units studied, although there may be potential of finding paleosols in suitable outcrops of lacustrine rocks associated with the uppermost part of the J Sst.

6. Linking weathering rates and paleoatmospheric compositions during the Mesoproterozoic and beyond

6.1. Paleoclimate and weathering of the Jacobsville Sandstone

Large river systems present during the deposition of the J Sst could be an indication of a fluctuating climate with a long, drawn out phase of increased water run-off in comparison to earlier in the Mesoproterozoic (and other formations studied in this paper). This could

support the Equator-ward paleopole studies by Swanson-Hysell et al., (2009, 2010), that suggest Laurentia's subsequent movement to tropical climate belts. CIA weathering data however, does not indicate values consistent of heavily weathered, tropical values of the modern-day (Maynard, 1992; Sheldon and Tabor, 2009). This is due, in part, to the action of multicellular plants (e.g., Cotton et al., 2013) and their contribution towards weathering in the intensely weathered climate zones, something that was obviously lacking in the Mesoproterozoic. Without extensive vegetation on floodplains and the subsequent trapping of bedload in transit, sediment loads in large river systems, such as those in the J Sst, will have short residence times during their transport, which is supportive of a low degree of chemical breakdown of minerals and therefore the low CIA (compared with large, tropical river systems of the present day such as the Amazon and Orinoco which have a CIA 74–82 (Gonzalez-Alvarez and Kerrich, 2012)).

A high maturity of the J Sst is indicated from provenance studies and could indicate that residual 'easily weatherable' minerals that are typically enriched in unstable cations were removed earlier in the weathering process leaving deposition of only the most resistant minerals. Furthermore, because the J Sst originates from a felsic source, alkali and alkali earth containing minerals were not in large quantities in the first place. This would explain the discrepancy between moderately low CIA values and high maturity being recorded by the same samples.

6. 2. Mesoproterozoic atmospheric O₂ and CO₂ concentrations

6.2.1. Oxidation vs hydrolysis chemical weathering

622 Despite the lack of new paleosols present within the units studied on the Keweenaw
623 Peninsula, other fluvial and lacustrine deposits can contribute towards paleoatmospheric
624 inferences. Sedimentary units on the Keweenaw Peninsula have a varied and mixed
625 mineralogy (Fig. 5), which is generally attributed to their source and catchment areas. Little
626 in the way of *in-situ* weathering and secondary mineral phases are present (Supplemental
627 data D3), as would be expected in weathered saprolites or paleosols. Yet, as demonstrated in
628 *section 4.3.1* and Fig. 7, because these sedimentary rocks have not undergone significant
629 alteration (metasomatism), they can still contribute to paleoatmospheric reconstructions.
630 Minerals that are normally the product of oxidative weathering reactions (e.g., hematite,
631 goethite, and limonite), or, those minerals containing elements that are sensitive to levels of
632 atmospheric O₂ (Sheldon, 2013), are largely absent (Fig. 5) in comparison to unstable, easily
633 weatherable minerals such as feldspars and Mg silicates (e.g., olivine). This suggests that
634 Fe²⁺ was leached from easily weatherable minerals, and was not retained and subsequently
635 oxidized to form oxides and oxyhydroxides because during modern oxidative weathering,
636 Fe²⁺ that is leached during oxidative weathering generally is translocated within the
637 weathering environment (e.g., down profile) and reprecipitated as Fe³⁺ bearing minerals such
638 as goethite, resulting in little or no net Fe loss for the saprolite or soil as a whole. In contrast,
639 the Sturgeon Falls paleosol has a high Fe loss of 83% relative to its metabasalt parent
640 (Mitchell and Sheldon, 2010) and other MCR paleosols exhibit substantial Fe loss as well.
641 This pattern of loss of oxidation-sensitive elements such as Fe and Mn rather than
642 redistribution is also evident throughout other MCR sedimentary rocks (Fig. 9), with
643 samples from all of the sites being low Fe+Mn, regardless of their provenance. About the
644 same degree of loss is evident also in Ca+Na+Mg, illustrating that rates of chemical
645 weathering (i.e., hydrolysis) are greater than those of oxidation. Al is abundant because of
646 its immobility in relation to the other end members. This is particularly true for the J Sst,

which has a high proportion of Al-rich minerals (more resistant feldspars, like microcline) and a lack of Ca+Na+Mg-bearing minerals (less resistant feldspars, like anorthite or other plagioclases). Retention of Al is also evident from the higher concentrations in sedimentary samples compared to ‘parent’ volcanics (Fig. 9).

Even fine grained lithologies from Horseshoe Harbor that were deposited stably in lacustrine and ponded settings over a long period of time (evidence of microbially induced sedimentary structures (MISS) and microbialite-like domes and swirls (Mitchell, 2010; Sheldon, 2012) suggests geomorphological stability for these organisms to grow for extended periods of time) do not exhibit concentrated *in situ* weathering and mineralogical evidence of oxidative weathering. In light of this, it seems likely that the dominant contributor to chemical weathering of MCR related sedimentary rocks was CO₂ (which could have had a minor local contribution from volcanic emissions through the weathering column), albeit in small amounts, and that O₂ played a minor part generally in Mesoproterozoic weathering (under a low O₂ atmosphere, a much higher CH₄:CO₂ ratio is possible; Haqq-Misra et al., 2008; Robertson et al., 2011; Tian et al., 2011; Sheldon, 2013).

Soils are generally not red at the time of formation, except under some tropical weathering regimes or with some mafic parent materials. Instead, oxidized Fe is typically present as “brown” minerals ferrihydrite or goethite. During burial and diagenesis, dehydration reactions remove water and red minerals such as hematite are formed, however the redox state of the Fe within the Fe-bearing minerals (i.e., Fe³⁺ versus Fe²⁺) is not typically changed, so the presence of diagenetic reddening generally points to the presence of authigenically oxidized Fe minerals (Retallack, 1991). So, while the presence of red color and of “red beds” in the MCR sets a minimum pO₂ value of ca. 10⁻⁵ times present atmospheric levels (Holland, 1984), they do not provide a more quantitative constraint than that because the general red coloration of MCR sedimentary rocks represents a diagenetic

remnant of the original oxidation state (Retallack, 1991). This is confirmed by the general intact nature of, where present, minerals sensitive to oxidative weathering (e.g., olivine and pyroxene).

6.2.2. *Hydrolysis (CO₂ driven chemical weathering)*

The chief chemical weathering process governing the consumption of silicate minerals is hydrolysis. This reaction is controlled by the amount of CO₂ dissolved in pore water, subsequently forming a weak carbonic acid that infiltrates paleosols and freshly deposited sedimentary rocks and preferentially ‘attacks’ and reacts with unstable minerals rich in easily weatherable cations. In sedimentary rocks, hydrolysis can be measured by the following equation:

$$\text{Hydrolysis} = \frac{Al}{Ca + Mg + K + Na}, \quad (2)$$

which is based on the idea that as minerals are weathered, base cations are mobile relative to Al (Retallack, 2001); high values represent highly weathered substrates and values close to 0 represent the least weathered. Similar, the Ba/Sr ratio is commonly used as a measurement of leaching because although Ba and Sr generally behave in geochemically similar ways, Sr is more soluble than Ba, again resulting in higher values in the most weathered samples (Retallack, 2001; Sheldon and Tabor, 2009). Comparison of both weathering proxies (Fig. 10) indicates that with evolution of the MCR, there is an increase in hydrolysis-derived chemical weathering and subsequent leaching in solution. This includes the more weathered state of sedimentary rocks in comparison to various MCR volcanic ‘parent’ lithologies (Fig. 10). The oldest paleosols from the NSVG in Minnesota (Mitchell and Sheldon, 2009) show

little weathering and leaching in comparison to the much younger post-rift J Sst, with the syn-rift CHC, and the Sturgeon Falls paleosol (Mitchell and Sheldon, 2010) in between (Fig. 10). This could be for a number of reasons: 1) long-term recycling of previously weathered material would lead to gradually more weathered sediments as compared with pre- and early stage syn-rift deposition, 2) preferential removal of mobile cations during post-burial alteration in some of the units, or 3) a shift toward more felsic parent materials. Among these, (1) and (3) can be considered the most likely causes because, as outlined above, there is considerable evidence for mixed provenance sediment sources and toward more felsic parent material both in space and time, and because there is little evidence for metasomatic alteration in the MCR (i.e., not scenario (2)).

Furthermore, in light of proposed new age estimates of deposition of the J Sst (760–620 Ma; Stein et al., 2014b), the time between the NSVG sedimentary rocks (and subsequent paleosol formation) and J Sst deposition could be as much as between 340–480 Ma. Thus, there are at least two plausible scenarios to explain the significantly greater degree of chemical weathering. The first is that the J Sst represents a more intense period of weathering closely subsequent to other MCR sedimentary units, with either higher atmospheric $p\text{CO}_2$, more biosphere-related weathering, or both. The second would be that weathering rates did not change appreciably, but that given the extremely long duration of weathering without burial, even modest rates of weathering would result in the degree of leaching observed in the J Sst and would support the alternative interpretation of the J Sst proposed by Stein (2015), who suggested that the J Sst was not actually related to MCR sedimentation. This possibility is further supported by the relatively more felsic mineralogy as compared with other MCR units. The third possibility, that the new age model is incorrect and that the J Sst is closer to >950 Ma in age, would still require (1) or (2) to explain the changes. To address this quantitatively, more and better age constraints are needed,

including more ages from the sedimentary units themselves and from the basalt flows stratigraphically closest above and below the sedimentary units. Placing the new results into a broader context makes it possible to assess scenario (1) versus scenario (2), and will be explored in the next section.

6.2.3. Expanding atmospheric reconstructions of CO₂-promoted weathering to fluvial and floodplain sedimentary rocks

The contribution of CO₂ to weathering throughout the Mesoproterozoic can be expanded beyond the paleosol and microfossil data collated in Sheldon (2013). CIA data mimics that of CO₂ atmospheric concentration (Fig. 11) when comparing a range of sedimentary units (data from Gonzalez-Alvarez and Kerrich (2012) including data from the Keweenaw Peninsula), which all indicate a similar degree of chemical weathering and of changes in chemical weathering through time. Long-term chemical weathering (CIA) shows a sharp increase after 1.1 Ga, at a time when atmospheric CO₂ was also increasing. Between 1.9 Ga and 1.4 Ga, CIA is fairly steady with small fluctuations, with a sharp drop-off after 1.4 Ga; this may be because of the lack of data between 1.4 and 1.15 Ga showing an apparent dip, or it could somewhat ‘fill in the gap’ of paleosol-derived CO₂ data, indicating that there was not a smooth decrease from 1.8 Ga to 1.1 Ga as hypothesized by Sheldon (2013; his Fig. 3), but a fluctuating weathering system and a final rapid decrease around 1.4 Ga. Careful description of other floodplain successions and discovery of new paleosols would allow for further testing of this pattern, but it is reassuring that there is such a high degree of coherence between different types of CO₂ proxies, even if they are not equally quantitative. One other general conclusion that can be drawn is that the terrestrial biosphere, while clearly present in the MCR (Elmore, 1984; Sheldon, 2012; Wilmeth et al., 2014), may not have been either as

extensive in other regions and/or may have played only a limited role in increasing weathering rates. In particular, if the “young J Sst” scenario is correct, and regional burial history (i.e., essentially no burial) is well-understood, then if anything, the degree of weathering in the J Sst is surprisingly weak given the potential duration of weathering of >300 Ma.

7. Conclusions

By using a combination of physical sedimentological and geochemical proxies, it is possible to reconstruct the provenance, weathering intensity, and depositional setting for sedimentary rocks associated with the 1.1 Ga failed Midcontinental Rift system on the Keweenaw Peninsula, Michigan, USA. Conglomerates from the syn-rift Portage Lake Volcanics were not fluvially derived, but instead represent tectonically-induced near-source mass debris flows. In contrast, conglomerates that are part of the Copper Harbor Conglomerate represent high-energy fluvial flood events in an otherwise low relief and arid climate. Finer grained sand-siltstone grade sedimentary rocks near the top of the stratigraphic section represent ponded lacustrine environments that are sourced from a combination of basement uplifted-recycled origin of high relief, felsic-rich hinterland to the east that is a mixture of primary igneous material as well as recycled sedimentary rocks and metasediments. The petrographic and geochemical data from the Jacobsville Sandstone suggest three main pulses of source material: 1) a common source (basement uplift and recycled orogen of previous emplaced volcanic and plutonic lithologies) providing a felsic constituent in arkosic arenites outcropping in the northern-most studied localities, 2) basement uplift and subsequent recycling of orogen creating a source to arkosic-subarkosic arenites from the re-working of primary sedimentary units as well as mixed igneous lithologies in the central Peninsula

(similar to that of the CHC), and 3) a source from erosion of the cratonic interior producing quartz arenites.

Weathering of the syn-rift Keweenaw Peninsula sedimentary rocks is generally minimal, mainly occurring pre-deposition and as the result of hydrolysis reactions, with little evidence of oxidative weathering occurring. However, over the course of the rifting event hydrolysis increases by 25x and therefore either more intense weathering from the formation of the NSVG paleosols to deposition of the J Sst or a very long duration of weathering up to 340 Ma later. The former possibility could potentially be linked to increases in atmospheric CO₂ into the Neoproterozoic, whereas the latter would suggest long-term, low atmospheric pCO₂ and minimal biospheric enhancement of weathering. CIA data from this study indicates that weathering of floodplain sedimentary rocks is similar to that of the weathering occurring in paleosols, and that these weathering trends mimic the paleosol-derived long term CO₂ estimates. There is no evidence of paleosol formation within the PLV, CHC or J Sst rocks studied, but the in-depth characterization of sediments in the Jacobsville Sandstone herein indicates that there is potential for finding them higher in the stratigraphic sequence. Two main constraints have been deduced for the formation of paleosols in the Midcontinental Rift system: 1) felsic sources carried a large distance dominate the Keweenaw Peninsula sedimentary rocks, meaning that high Si, K, Na (stable) minerals, transport, and sorting decrease the odds of soil formation even before deposition; and 2) paleosols developed in the North Shore Volcanic Group (Minnesota) are near source and predominantly derived from local Keweenaw basalts, indicating that high Ca, Mg, Fe (unstable) mineral assemblages are pivotal for paleosol development in the Mesoproterozoic during a time of relatively low atmospheric pCO₂ and pO₂.

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Figure 1

Figure 2

Figure 3 - colour (ONLINE)

Figure 3 - B&W (PRINT)

Figure 4 - colour (ONLINE)

Figure 4 - B&W (PRINT)

Upper white quartz sandstone

a

Lower red/green sand/siltstone

b

c

Paleocurrent direction

d

e

f

g

h

Figure 5 - COLOUR (ONLINE)

Figure 5 - b&w (PRINT)

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11 - COLOUR (ONLINE)

Figure 11 - B&W (PRINT)

Figure captions Keweenaw Paper

Figure 1

Location and geological maps of the Keweenaw Peninsula, Upper Peninsula of Michigan. A: The modern extent of the MCR system, reaching ~1300 km south to Kansas. B: Geologic map of the Keweenaw Peninsula. Localities described in the text are shown with closed circles; populated urban areas are represented by open circles. Key to lithologies and scales are shown. Modified from USGS (compiled by King (1974)), Ojakangas et al., (2001), Finley-Blasi (2006), Mitchell and Sheldon (2010), and Mitchell (2010).

Figure 2

Simplified lithostratigraphic correlation of formations on the north (Minnesota) and south (Wisconsin and Michigan, including the Keweenaw Peninsula) shores of Lake Superior. The shaded formations feature in this study. The unknown age initial age and duration of deposition of the Jacobsville Sandstone is addressed in the text. Adapted from Mitchell and Sheldon (2010), Ojakangas et al., (2001), and Cannon and Nicholson (1992).

Figure 3

Outcrop photos of the Copper Harbor Conglomerate from a range of sites across the Keweenaw Peninsula. A: Fine sandstone and siltstone grading into cobble-grade conglomerate at Dan's Point (Horseshoe Harbor). B: Fine sandstone and siltstone beds gently dipping towards the shore of present day Lake Superior. C: Desiccation cracks (circled) on some bedding planes indicate dry periods. D: Abrupt lithology changes at Silver River; overlying conglomerates erosively scour into underlying finer-grained lithologies. E: Clast imbrication at Silver River. F: Fine sand-siltstone grade lacustrine deposits at Horseshoe Harbor with evidence of black organic laminations (black arrows) and calcitic 'domes' and swirls, representing small stromatolite and/or microbialites in profile (white arrows). Scales: Backpack (40 cm length), pen nib (1cm length), hammer (30 cm length), hammer head (12 cm length).

Figure 4

Outcrop images of the Jacobsville Sandstone on the Keweenaw Peninsula. A: Contact of the lower red and green sand-siltstone and upper white coarse quartz-dominated sandstone at Brunette Park. B: Rip up chips of the lower red/green unit in the quartz sandstone at Brunette Park (arrows). C: Paleocurrent direction from dune ripples and cross beds at Brunette Park. D: Weak cross bedding and bleached cross bed horizons at Hungarian Falls. E: Meter-scale cross bed sets overlain by horizontally laminated sandstones at a lakeside locality just outside of Jacobsville. Lighter areas represent post-depositional bleaching and/or Fe-reduction processes. F: Minor cross bedding and reduction spots in coarse sandstones at a road section outside of Tamarack. G: Coarse portions of sandstones at Tamarack (circled). H: Position of the Jacobsville Sandstone along the banks of the Sturgeon River, stratigraphically below the Sturgeon Falls paleosol (Mitchell and Sheldon, 2010), which is preserved as a paleo-hill with valley fill composed of Jacobsville Sandstone. Localities can be found in Figure 1. Scales: Hammer (30 cm length), hammer head (12 cm length), trowel (15 cm length), fingernail (1 cm length).

Figure 5

Petrographic thin section photos from the Portage Lake Volcanics (A, B), Copper Harbor Conglomerate (C, D, E) and Jacobsville Sandstone (F, G, H). A: Basalt belonging to the PLV from South Range Quarry (sample ASR2). B: Coarse clastics (dominated by lithic fragments) from Hungarian Falls site b (sample 2HF3). C: Roughly laminated (crenulated) fine sandstones from the CHC at Horseshoe Harbor (sample HH1); black 'matrix' probably contains organic material associated with degraded microbial mats. D: Finely laminated siltstones within the CHC at Horseshoe Harbor (sample HH4). E: Coarse feldspathic and quartz-mixed sandstones from within the CHC at Silver River (sample SR4). F: Medium-coarse quartz-rich sandstones from within the J Sst at Sturgeon River (unconformably overlying the Sturgeon Falls Paleosol); microcline and localized alternating calcitic/quartz cement is also present (sample SF13). G: Coarse, quartz-rich, clast supported sandstone from the J Sst at Hungarian Falls (sample HF1). H: Biotite-rich, poorly sorted, quartz sandstone from within the J Sst at Tamarack (TRK5). f=feldspar, ol=olivine, ml=mafic lithic, fl=felsic

lithic, sl=sedimentary lithic, q=quartz, mc=microcline, ca=calcite, b=biotite. Scale bar is equal to 1 mm.

Figure 6

Various examples of provenance from ternary diagrams. A: QFL (quartz-feldspar-lithic clasts) diagram displaying the assortment of arenite types (modified from Pettijohn (1975)). B: Tectonic origin of sedimentary samples from QFL information (modified from Dickinson (1979) and (Dickinson et al., 1983)). C: Potential sources of sediment based on differences in the REEs La-Th-Sc (modified from Bhatia and Crook (1986)). D: Al-Ca+Na-K diagram for J Sst samples only, indicating the lack of Na and Ca and consequently, no enrichment in Al, therefore meaning little weathering and destruction of feldspars (n.b. data points not the same symbol as in key).

Figure 7

Graphs indicating different chemical weathering and provenance trends from across the Keweenaw Peninsula. A: CIA vs CIA-K, indicators of weathering. The nearly linear trend for most of the data indicates little alteration by K-metasomatism of most samples; off-trend J Sst samples are discussed in the text. B: Ti/Al vs Ti/Zr. Both of these ratios are indicators of provenance from immobile elements. C: Ti/Al vs CIA. This graph indicates the relationship between the provenance of sediments versus their degree of weathering (dashed line represents the near linear trend observed in the NSVG and Sturgeon Falls paleosol/s).

Figure 8

Map showing paleocurrent data obtained from both on the north and south shore of Lake Superior. The paleocurrent direction for South Range Quarry is a crude flow direction from the orientation of calcitic amygdales, and the Temperance River flow direction is from pahoe-hoe. All others represent paleocurrents from sedimentary structures (arrows). Bedding orientations (strikes and dips) are also shown (dip figures can be found in Supplemental Table 2 in the Data Repository). Paleocurrent directions indicate a filling of the sedimentary basin (present day Lake Superior) from continental interiors. Sites are identified as follows:

SF=Sturgeon Falls, SR=South Range Quarry, Jv=Jacobsville, HFb=Hungarian Falls site B, TRK=Tamarack, HFa=Hungarian Falls site a, BP=Brunette Park, ASR=Silver River, HH=Horseshoe Harbor.

Figure 9

Ternary diagram comparing Fe+Mn, Ca+Na+Mg, and Al (oxidation sensitive elements, bases lost during hydrolysis, and immobile Al, respectively). Fe+Mn is low in all paleosols and sedimentary units, indicating limited retention of oxygen-sensitive elements that remained soluble and were lost. Ca+Mg+Na loss is low to moderate, particularly in the J Sst, indicating that these labile elements were chemically weathered and lost from the sedimentary units. Conversely, sedimentary units and paleosols are enriched in Al because of its immobility in these sedimentary systems (high Al in the J Sst is the consequence of high proportions of microcline and biotite mica rather than the dominance of mafic minerals at other sites). All plotted sedimentary samples are enriched in Al compared to parent felsic and mafic volcanics. Felsic 'parent' volcanics concur with other observations of low base cation concentrations.

Figure 10

Graph displaying leaching (Ba/Sr) against hydrolysis ($\text{Al}/(\text{Mg}+\text{Ca}+\text{K}+\text{Na})$). A general trend is observed indicating that as weathering (hydrolysis) increases, so does leaching. There is also a general trend of younger lithologies associated with active syn-rift processes (NSVG paleosols, CHC) having a lower degree of weathering compared with end and post-rift (Sturgeon Falls paleosol and J Sst) sedimentation respectively. The Sturgeon Falls paleosol is assumed to be nearer the J Sst in age than the CHC, as depositional characteristics at the base of the unconformably overlaying J Sst at Sturgeon Falls suggests the paleosol was still soft when the J Sst was deposited (Zbinden et al., 1988; Mitchell and Sheldon, 2010).

Figure 11

Comparison of Mesoproterozoic CO₂ constraints (from Sheldon, 2013) with Mesoproterozoic CIA values from sedimentary rocks (from Gonzalez-Alvarez and Kerrich

(2012); black diamonds); paleosol data from Mitchell and Sheldon (2009, 2010), and MCR sedimentary rock data from this study (open white circles). J Sst is shown as 0.69 Ma, or the mid-point of the 0.76 – 0.62 Ma age range proposed by Stein et al., (2014)). There is a broad correspondence between CIA values at the reconstructed $p\text{CO}_2$ value, including a minimum in both during the time of MCR, followed by a relatively rapid increase back to “typical” values for both the Mesoproterozoic and Paleoproterozoic. The black line indicates CIA trend, and the grey line indicates CO_2 reconstructions through the Precambrian (dashed line indicates the error window around the $p\text{CO}_2$ reconstruction). Bars represent estimates from microfossils of Kaufman and Xiao (2003; spotted) and Kah and Riding (2007; lined).

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