Weathering during the Great Oxidation Event: Fennoscandia, arctic Russia 2.06 Ga ago

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9 **Abstract**

10 The establishment of an oxygen-rich atmosphere between 2.4 and 2.0 billion years ago (Ga)
11 is one of the defining events in Earth history; however, the nature of the transition from an
12 anoxic atmosphere is poorly resolved with interpretations relying heavily on empirical evidence
13 that is poorly calibrated and not supported by numerical modeling. In an attempt to characterize
14 the nature, timing, and impact the Great Oxidation Event (GOE) had on Earth's surface, the
15 Fennoscandian Arctic Russia – Drilling Early Earth Project (FAR-DEEP) targeted the Archean-
16 Proterozoic transition exposed in the eastern part of the Fennoscandian Shield. FAR-DEEP
17 recovered more than 400 m of the highly oxidized 2.06 Ga Kuetsjärvi Volcanic Formation
18 (KVF), which is potentially a manifestation of when atmospheric oxygen levels exceeded the
19 ultimate Proterozoic steady state. Identifying the timing and extent of oxidation within the KVF
20 are the primary objectives of this study.

21 The presence of secondary hematite within fractures and amygdales indicates that the
22 elevated oxidation state of the KVF is not a primary feature of the rocks. Immediately below the
23 erosional surface marking the top of the KVF the degree of iron oxidation scales with the degree
24 of chemical weathering, implying that oxidation of the KVF is the result of interaction with
25 oxygen-charged groundwaters during subaerial exposure. The incorporation of rounded clasts
26 with conspicuous hematite rinds into the overlying Kolosjoki Sedimentary Formation indicates
27 that the oxidation of the KVF occurred prior to its deposition.

28 The oxidized regolith recovered in the FAR-DEEP drill cores is more oxidized for the
29 degree of weathering observed compared to older Precambrian- and Archean-aged paleosols, but
30 not anomalously so compared to younger Proterozoic paleosols. This observation suggests that
31 the Kuetsjärvi regolith was created during the progressive increase of pO_2 towards the

Proterozoic steady state. Using a previously published paleosol to infer paleoatmospheric $p\text{CO}_2$ and $p\text{O}_2$ we are unable to provide any useful constraint on the paleoatmospheric $p\text{CO}_2$ and $p\text{O}_2$ levels. We estimate that the paleoatmospheric $p\text{CO}_2$ and $p\text{O}_2$ levels ca. 2.06 Ga ago in Fennoscandia were between 0.4 and 6,500 times present atmospheric level (PAL), and 1×10^{-3} and 12 times PAL, respectively. The wide range in the calculated $p\text{CO}_2$ and $p\text{O}_2$ levels is the result of the $p\text{CO}_2$ model calculations being extremely sensitive to key parameters that are nearly impossible to estimate accurately for ancient paleosols (e.g., the annual precipitation rate, depth to the groundwater table, and the amount of time it took the soil to form).

Keywords: Oxidation, Precambrian oxygen, Precambrian paleosol, Paleoproterozoic, geochemistry, Pechenga Greenstone Belt

1 Introduction

Today, oxygen (O_2) composes 21% of Earth's atmosphere, but in Earth's early history, the atmosphere was virtually devoid of O_2 (Holland, 1984; Rye and Holland, 1998; Lyons et al., 2014). The transition between these two states occurred roughly at the Archean–Proterozoic transition (ca. 2.5 Ga ago), and has come to be known as the “Great Oxidation Event” (e.g., Holland, 1984; Holland and Zbinden, 1988; Holland, 2002; Holland 2006; Kump, 2008; Holland, 2009; Lyons et al., 2014). Despite its name, the “Great Oxidation Event” (GOE) was protracted, spanning perhaps hundreds of millions of years and resulting in an increase in the atmospheric O_2 from vanishingly small values ($<10^{-5}$ of present atmospheric level (PAL)) to up to 10% of PAL (Fig. 1; Kump, 2008; Partin et al., 2013a,b; Lyons et al., 2014; c.f. Ohmoto, 1996; Ohmoto et al., 2006).

Given that the GOE is coincident with the largest global positive carbon isotope excursion in Earth's history (i.e. the Lomagundi–Jatuli positive carbon isotope excursion (LJ–CIE); Baker and Fallick, 1989a,b; Karhu and Holland, 1996; Melezhik et al., 2005), atmospheric oxygen levels may have briefly exceeded their Paleoproterozoic steady–state 2.2 Ga ago (e.g., Kump et al., 201; Bekker and Holland, 2012; Canfield et al., 2013). The positive carbon isotope excursion is interpreted to represent an interval of enhanced burial of organic carbon, because photosynthesizing organisms preferentially utilize the lighter ^{12}C isotope during CO_2 uptake. If the isotopically light organic carbon is buried and not recycled through oxidation, then the remaining carbon pool becomes isotopically heavy and results in a positive $\delta^{13}\text{C}$ isotopic signature of carbonate rocks (e.g., the Lomagundi and Jatulian carbonate rocks). Since the global oxygen budget is strongly linked to the recycling rate of organic carbon, positive isotope excursions are equated to temporary increases in atmospheric oxygen levels for the duration of the excursion (Kump et al., 2011). Using these principles and given the overall magnitude of the excursion, numerical models estimate that atmospheric oxygen levels during the LJ–CIE were likely greater than the putative Paleoproterozoic 10% PAL steady state and may have been as high as modern (Bekker and Holland, 2012; cf. Planavsky et al., 2014).

1.1 Fennoscandian Arctic Russia – Drilling Early Earth Project (FAR-DEEP)

The FAR-DEEP drilling project targeted the Archean–Proterozoic transition (APT) in the eastern part of the Fennoscandian Shield and sampled rocks spanning the GOE in an attempt to better characterize the nature and timing of this remarkable time in Earth's history (Fig. 2; Melezhik, 2013). One of the targets of this drilling project was the Kuetsjärvi Volcanic Formation (KVF) in the Pechenga Greenstone Belt because of its elevated $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. As a result, three FAR-DEEP cores were collected from the KVF intersecting the middle (6A) and

upper (7A and 8B) sections of the formation (Fig. 3; Hanski et al., 2013a, b; Melezhik et al., 2013b). These oxidized Paleoproterozoic volcanic rocks could be a product of the hypothesized ‘overshoot’ (Rybacki et al., 2013), but is exceedingly high atmospheric oxygen really required to explain the oxidized nature of these volcanic rocks? Are there other explanations for volcanic rocks having elevated $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios compared to the other Precambrian volcanic rocks described in the literature, but under atmospheric O_2 levels only a fraction of modern?

To address these questions, we have conducted a detailed petrographic and geochemical study on rock samples collected from FAR-DEEP drill Cores 6A, 7A, and 8B, which intersect the highly oxidized 2.06 Ga old Kuetsjärvi Volcanic Formation. To date, two hypotheses have been presented to explain the anomalously oxidized nature of the KVF: (i) the eruption of the KVF from a highly oxidized magmatic source; and (ii) interaction with oxidizing fluids at Earth’s surface during or just after eruption and possibly during burial (Rybacki et al., 2013). Despite having experienced lower greenschist facies metamorphism, the textural preservation of these rocks is excellent and allows us to determine their pre-metamorphic textures using standard transmitted and reflected light petrographic techniques with a high degree of confidence. We used polished thin sections to examine the distribution of the primary and secondary iron oxide mineral phases, ferric to total iron ($\text{Fe}^{3+}/\Sigma\text{Fe}$) ratios to assess the extent and magnitude of iron oxidation, and whole-rock major element chemistry of the samples to assess the extent of secondary alteration. We use the major element data and the numerical framework proposed by Sheldon (2006) to estimate paleoatmospheric $p\text{CO}_2$, and then infer paleoatmospheric $p\text{O}_2$ using Holland’s R-ratio (e.g., ratio of O_2 demand to CO_2 demand within a paleosol; Holland, 1984).

2 Background Geology

2.1 Regional Geology

The geology of the Pechenga region can be divided into four sedimentary–volcanic successions, referred to as the North Pechenga Group in the literature (Melezhik and Hanski, 2013). For simplicity and to maintain consistency with respect to depositional/eruption environment, we only focus on the two lowermost successions, which are two terrestrial sedimentary sequences separated by two subaerial volcanic units (Fig. 3). To begin, the North Pechenga Group is separated from the underlying Archean basement by a major unconformity. Resting atop this unconformity is the lowermost sedimentary unit, the Neverskrukk Formation, which is composed of terrestrial sedimentary rocks (e.g., conglomerates and sandstones) ranging from <20 m to >300 m in thickness, including conglomerates that are observed filling paleo-valleys. The Neverskrukk Formation is believed to represent alluvial deposition in fault-bounded extensional basins (Melezhik et al., 2013a; Melezhik and Hanski, 2013).

Overlying the Neverskrukk Formation is the ca. 1-km-thick Ahmalahti Volcanic Formation (AVF), composed of massive to amygdaloidal subaerial mafic to intermediate lava flows between 0.5 and 25 m thick (Fig. 3; Melezhik and Hanski, 2013). The individual flows are enriched in Light Rare Earth Elements (LREEs) and low in High-Field Strength Elements (HFSEs; Hanski, 1992). Altogether, the AVF is interpreted to have been erupted in an intraplate environment with significant crustal contamination (Melezhik and Hanski, 2013).

Resting conformably atop the AVF is the Kuetsjärvi Sedimentary Formation (KSF; Fig. 3; Salminen et al., 2013; Melezhik and Hanski, 2013). Much like the Neverskrukk Formation, the KSF varies considerably in thickness (between 15 and 150 m) reflecting syndepositional faulting. The KSF generally consists of siliciclastic sedimentary rocks at the base of the formation that grade into dolostone-dominated sedimentary rocks at the top (Melezhik and

Fallick, 2001; Melezhik and Fallick, 2005; Melezhik et al., 2005a,b; Melezhik and Hanski, 2013). The KSF displays abundant sedimentary structures including soft-sediment deformation features (e.g., ball and pillow structures, flame structures), ripple marks, cross-laminations, scour and fill structures, and possible pseudomorphed sulfate nodules. Many sections of the KSF contain abundant hematite and travertine deposits (Melezhik and Fallick, 2001; Salminen et al., 2013). The upper, dolomite-rich portion of the KSF is characterized by elevated $\delta^{13}\text{C}_{\text{carb}}$ values between +5.8 and +8.9‰ (relative to the Pee Dee Belemnite standard; Melezhik et al., 2005b; Melezhik and Hanski, 2013). The sedimentary structures observed throughout the KSF allow for the reconstruction of paleo-depositional environments with a high degree of confidence. The depositional framework for the KSF is interpreted as sedimentation within an intraplate rift setting atop subaerially weathered AVF basaltic andesites, within fluvial-deltaic and shallow lacustrine environments (Melezhik and Fallick, 2001; Melezhik et al., 2005a,b; Melezhik and Hanski, 2013; Salminen et al., 2013).

The Kuetsjärvi Volcanic Formation (KVF) has a transitional contact with the underlying KSF and is divided almost equally into two parts by a conglomerate member (Fig. 3). The Kuetsjärvi volcanic rocks span a wide range of compositions from picritic to felsic lava flows and include ignimbrites, lava breccias, and bedded tuffs. Many of the lava flows contain abundant amygdales filled with a variety of secondary minerals including adularia, biotite, calcite, chlorite, epidote, hematite, jasper, phlogopite, quartz, sericite, titanite, allanite, and axinite (Hanski et al., 2013a, b; Melezhik and Hanski, 2013; Melezhik et al., 2013a). The KVF displays a very large range in the ratio of ferric iron to total iron ($\text{Fe}^{3+}/\Sigma\text{Fe}$) with a mode of ≈ 0.5 , while the stratigraphically adjacent subaerial AVF has $\text{Fe}^{3+}/\Sigma\text{Fe}$ around 0.2 (Hanski, 2013). The presence of ubiquitous secondary hematite within fractures and amygdales throughout the KVF

suggests that the extensive iron oxidation observed occurred subsequent to eruption (Fig. 4). Moreover, the incorporation of rounded, oxidized clasts derived from the KVF within the overlying Kolosjoki Sedimentary Formation suggests that oxidation of the KVF occurred prior to erosion and deposition of the overlying sediments (Hanski et al., 2013a; Melezhik and Hanski, 2013; Melezhik et al., 2013b; Rybacki et al., 2013).

U-Pb series dating of zircon crystals collected from the conglomerate member within the KVF and the overlying Kolosjoki Sedimentary Formation has precisely constrained the minimum age of the KVF to 2058 ± 6 Ma (Melezhik et al., 2007). Unfortunately, the age of the Kolosjoki Sedimentary Formation is currently unknown. A Rb-Sr age of ca. 2100 Ma has been reported for the Kolosjoki Volcanic Formation, which sits atop the Kolosjoki Sedimentary Formation, and is within error of the minimum age of the KVF (Melezhik and Hanski, 2013). If the Rb-Sr age is a correct reflection of the age of the Kolosjoki Formation, then oxidation of the KVF must have occurred between ca. 2060 and 2100 Ma.

2.2 Geology of FAR-DEEP Cores 6A, 7A, and 8B

Detailed stratigraphic and geochemical descriptions of the rocks recovered by FAR-DEEP drill Cores 6A, 7A and 8B have already been published (e.g., Hanski et al., 2013a, b; Melezhik et al., 2013b) so only a brief, general overview of the recovered core materials will be presented here. As noted above, all of the KVF volcanic and sedimentary rocks recovered by FAR-DEEP Cores 6A, 7A, and 8B have experienced lower greenschist facies metamorphism (Hanski et al., 2013a, b; Melezhik and Hanski, 2013; Melezhik et al., 2013b), but due to the excellent textural preservation the pre-metamorphic nature of the rocks can be determined with a high degree of confidence in many samples.

Drill core 6A samples the middle of the KVF and is 313 m in length (Hanski et al., 2013b). The drill core is composed primarily of volcanic rocks ranging in composition from picrite to rhyolite, and intersects the conglomerate member that divides the KVF into roughly two equal parts (Melezhik and Hanski, 2013). The core is informally divided into seven volcanic units (Units A–H from bottom to top, Fig. 5) based upon composition (Hanski et al., 2013b); however, each unit is composed of multiple lava flows of variable thickness.

Drill cores 7A and 8B intersect the erosional contact marking the top of the KVF (Hanski et al., 2013a; Melezhik et al., 2013b). Core 7A is 93 m in length and recovered 82 m of volcanic rocks from the top of the KVF and the bottom 11 m of the Kolosjoki Sedimentary Formation (i.e., “The Gritstone Member”). These volcanic rocks have been informally divided into four individual lava flows (Flows A–D from bottom to top, Fig. 6) that range in composition from basalt to basaltic andesite (Hanski et al., 2013a).

Core 8B, despite being 336 m in length, recovered only 13.5 meters of the KVF at the base of the core (322.5–336 m core depth; Melezhik et al., 2013b). The overlying 322.5 m of core are part of the Kolosjoki Sedimentary Formation, and is outside the scope of this work. The volcanic rocks recovered in Core 8B are interpreted to represent a single lava flow at the base of the core. Trace element geochemical analyses suggest that this lava flow is equivalent to Flow C of Core 7A (Melezhik et al., 2013b).

Field observations suggest that the site of Core 8B experienced greater amounts of erosion relative to that experienced at the 7A site. This notion is not only supported by the absence of Flow D in Core 8B, but also in the sedimentary rocks overlying the volcanic rocks. For example, the Gritstone Member that overlies the KVF in Core 7A is ~80 m above the volcanic-sedimentary rock contact in Core 8B (Melezhik and Hanski, 2013). The sedimentary rocks in

contact with the KVF are interpreted to represent paleo-canyon and -valley fill in Core 8B (Melezhik et al., 2013b), because outside the immediate vicinity of Core 8B only small pockets of these sediments are observed along the erosional contact between the KVF and Kolosjoki Sedimentary Formation.

3 Methods

The FAR-DEEP core materials were sampled during the Fall of 2011 at the FAR-DEEP core repository in Trondheim, Norway. Our sampling was guided by preliminary geochemical data from the FAR-DEEP Archival dataset (e.g., Melezhik and Hanski, 2013; Rybacki et al., 2013) as well as data obtained during core inspection using a hand-held XRF instrument. The tops of individual lava flows were targeted in hopes of capturing paleo-weathering profiles developed atop the flows. In total, 142 new quarter core samples were collected from the three drill cores (60 samples from Core 6A, 71 samples from Core 7A, and 11 samples from Core 8B).

After collection, samples were cut, cleaned, chipped, and powdered to ≤ 75 μ m. The powdered samples were stored in a triple-rinsed, acid-washed glass vial until analyzed. Sample digestion was completed via fusion with a trace metal grade lithium metaborate flux (100 mg sample/400 mg flux) in a 900°C oven for 10 minutes, and quenched in 100 mL of 5% trace metal-grade nitric acid until completely dissolved (ca. 30 min.). The digested samples were subsequently diluted for analysis. Major element analyses were conducted using a Perkin-Elmer Optima 5300 Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP–AES), while trace elemental analyses were conducted using a Thermo Scientific X-series II Quadrupole Inductively Coupled Plasma – Mass Spectrometer (ICP-MS). A suite of ~~certified~~ USGS rock standards and a suite of matrix matched standard solutions were used to calibrate the ICP-AES and ICP-MS, respectively (Insert Supplementary Tables S1 and S2 here). The ferrous iron (Fe^{2+})

contents of a select subset of samples were determined following the titration procedure of Goldich (1984). To complement the geochemical data, detailed petrographic analyses were conducted on 171 thin sections from Cores 6A, 7A, and 8B. The thin sections were examined using a standard optical microscope in transmitted and reflected light.

4 Results

4.1 Petrography and mineralogy

The Kuetsjärvi volcanic rocks are fine grained, contain abundant amygdales, and are mostly composed of subhedral to euhedral plagioclase laths (albite), euhedral oxides (e.g., magnetite and ilmenite) and chlorite. The primary mineralogy of the Kuetsjärvi volcanic rocks has largely been obscured by secondary minerals that replace the primary plagioclase, olivine, pyroxenes, and oxides, and fill amygdales and fractures. The most common secondary minerals observed within the KVF are biotite, calcite, chlorite, hematite, jasper, phlogopite, quartz, sericite, titanite, allanite, and axinite. Bornite, chalcopyrite and galena are observed in some of the samples within fractures and amygdales.

Hematite is a ubiquitous secondary mineral within Cores 6A, 7A and 8B, and is observed replacing primary Fe-Ti oxides, within randomly oriented, hair-thin, sinuous fractures that terminate at the amygdale edges, as well as within the volcanic groundmass, giving the rocks a dark patchy appearance (Figs. 7A and 7B; Melezhik and Hanski, 2013; Hanski et al., 2013a,b; Rybacki et al., 2013). The sinuous fractures pre-date the larger semi-parallel quartz veins that cut both amygdales and hematite-bearing fractures. In Core 6A, hematization is concentrated along the direction of the flow banding (Fig. 7B), and within the fractures that run perpendicular to the flow bands within the felsic rocks (Fig. 7C). The coarsest grained secondary hematite within the KVF is found as crystals grown on vesicle walls. In the basaltic rocks, euhedral to skeletal

groundmass magnetite grains may be totally hematized and ilmenite needles replaced by hematite and rutile ($2\text{FeTiO}_3 + 0.5\text{O}_2 = \text{Fe}_2\text{O}_3 + 2\text{TiO}_2$). Conversely, below the conglomerate unit in the upper portion of Core 6A some crystals have hematite cores and magnetite rims (Fig. 7D). The least altered oxides, especially in Core 6A, possess intricate internal morphologies (e.g., trellis structuring) with alternating lamellae of magnetite and minor rutile, hematite and/or titanite (Fig. 7E). Besides oxides, hematite is also observed pseudomorphically replacing olivine phenocrysts and chromite crystals within the picritic rocks (Rybacki et al., 2013). Rounded clasts derived from the KVF, which are found within the volcanoclastic gritstone-sandstone interbed in the middle of Core 6A and the lowermost conglomerate bed within Kolosjoki Sedimentary Formation (Hanski et al., 2013a,b; Fig. 7F), possess conspicuous hematite rinds. Altogether, these features suggest that oxidation of the KVF post-dates eruption, but pre-dates the deposition of the overlying Kolosjoki Sedimentary Formation.

In the upper portion of Core 7A, just below the regional unconformity, plagioclase laths have been replaced by a highly birefringent secondary, fine-grained mineral(s) (e.g., chlorite, sericite, and other micas; Fig. 8A). The replacement of plagioclase by this fine-grained material appears to decrease as a function of depth within the core. For example, approximately 10 m below the unconformity, only the rims of the plagioclase crystals have been replaced by the fine-grained material. At depths greater than 20 m, the plagioclase crystals appear to be relatively unaltered (Fig. 8B). These mineralogical trends correlate strongly with the geochemical results presented below.

4.2 Major Element Geochemistry

The majority of the major element data collected in this study is very similar to the previously reported KVF analyses in the FAR-DEEP database (Insert Supplementary Figure S1

and Tables S3–S13 here). Only a few samples from Core 7A possess elevated potassium or iron contents that differ extensively from those reported in the FAR-DEEP database. These ‘altered’ samples, however, were purposely collected from sections of the core interpreted to have been subjected to potassic metasomatism, or that were noted to contain an abundance of amygdales and fractures filled with hematite and/or other secondary minerals.

We can use the major element data to calculate a chemical index of alteration (CIA) for each powdered rock sample. The CIA is a measure of the degradation of feldspars to clays during weathering and has been used in several studies to evaluate the extent of weathering in paleosols (Nesbitt and Young, 1982, 1984, 1989). During weathering, calcium, sodium, magnesium and potassium are preferentially leached from the feldspars, but aluminum is retained in the residual clays. The loss of soluble elements from the chemical weathering of feldspars and retention of aluminum results in an overall increase in the calculated CIA of the sample.

During burial or metamorphism, certain elements (e.g., potassium) that were leached during weathering can be reintroduced to the weathering profile (Nesbitt and Young, 1989; Retallack, 1991; Nesbitt, 1992; Fedo et al., 1995). As a result, some researchers have implemented a modified CIA for samples that have evidence for post-burial potassium addition (e.g., CIA-K; Fedo et al., 1995; Maynard, 1992). In Cores 7A and 8B there are abundant signs of post-burial potassium addition (Hanski et al., 2013a; Melezhik et al., 2013b; Rybacki et al., 2013). Potassium addition is most clearly demonstrated in enrichment-depletion diagrams, utilizing titanium as an immobile element and a parent material equal to the average of the three lowermost samples from Core 7A, which shows potassium enrichments of up to ca. 2,300%, and an average enrichment of around 200% (Insert Supplementary Figure S2 here). Overall, potassium enrichment varies systematically with depth within Cores 7A and 8B with the greatest

addition of potassium (between 100 and 800%) occurring immediately below the erosional boundary marking the top of the KVF. On the individual flow-scale, there are signs of potassium enrichment at the top of each lava flow. Adularia, a low-temperature K-feldspar phase, is observed filling amygdales and within large fractures indicating that potassium addition postdates the eruption of the volcanics (Fig. 4). Because of the extensive evidence for potassium addition we have opted to use the CIA-K to evaluate the extent of alteration *via* weathering within the FAR-DEEP cores. The calculated CIA-K for the KVF samples analyzed by this study range from 51.1–69.8 (average 59.6 ± 4.6), 52.7–79.4 (average 64.1 ± 7.3), and 66.3–82.0 (average 73.8 ± 5.6) for Cores 6A, 7A, and 8B, respectively (Figs. 5 and 6).

The majority of the Core 6A samples lie between the calculated CIA-K for an unweathered basalt (e.g., USGS BCR-2 Columbia River Basalt rock standard) and an unweathered trachyandesite (e.g., USGS AGV-1 rock standard). There are a limited number of samples that exhibit elevated CIA-K's, but sampling was too coarse to reveal any systematic trends (Fig. 5). Conversely, Cores 7A and 8B exhibit considerable variation in terms of the calculated CIA-K, which appears to vary systematically with depth (Fig. 6). The highest CIA-K's are found directly beneath the erosional surface in both cores, as well as near the tops of the lower lava flows within Core 7A. The systematic increase of the CIA-K's near the tops of lava flows suggest that the chemical alteration observed is the result of subaerial weathering, pre-dating metamorphism.

4.3 Iron Oxidation State

The most oxidized rocks within the KVF are found in Core 6A (Fig. 5), where oxidation appears to have been much more pervasive than in the upper part of the formation sampled by Cores 7A and 8B (Fig. 6). The average $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the volcanic rocks in Core 6A is 0.64, but range from 0.2 to nearly 1 (Fig. 5). Excluding Unit B, which is a mafic sill, the measured

Fe³⁺/ΣFe ratios increase steadily from ca. 0.37 to nearly 0.92 through Unit C and remain between 0.63 and 0.96 through Unit D in the bottom half of Core 6A. Units E and F are characterized by lower Fe³⁺/ΣFe ratios between 0.53 and 0.69, but increase through Unit G to nearly 0.87. Conversely, the volcanic rocks in Unit H above the conglomerate member have measured Fe³⁺/ΣFe ratios that are all less than 0.42.

At the base of Core 7A (Flows A and B) the measured Fe³⁺/ΣFe ratios for volcanic rocks are relatively uniform (ca. 0.39). Only in the uppermost flows (Flows C and D), just beneath the overlying Kolosjoki Sedimentary Formation, do the ratios increase to 0.52–0.66 (Fig. 5C). Likewise, the measured Fe³⁺/ΣFe ratios of the Kuetsjärvi volcanic rocks at the base of Core 8B are between 0.44 and 0.70.

5 Discussion

5.1 Origin of the elevated Fe³⁺/ΣFe ratios

The most notable occurrence of hematite is in the form of conspicuous bands that exploit the fragmented lava at the top of the KVF (colloquially referred to as ‘Leopard rock’). As noted above, the concentration of hematite within fractures and amygdales throughout the KVF, and the incorporation of rounded ‘Leopard rock’-like rock clasts into the overlying Kolosjoki Sedimentary Formation, imply that oxidation post-dates eruption, but pre-dated the subsequent erosion of the KVF. Moreover, in outcrop the oxide bands that give the ‘Leopard rock’ its distinctive texture are cross-cut by a network of younger fractures filled with quartz and adularia that crystallized during regional metamorphism, which is very strong evidence that oxidation is not the result of modern surficial processes (Fig. 4). Unfortunately, drill cores 7A and 8B failed to recover samples of the Leopard rock despite their close proximity to the locations where it is known to outcrop at the surface.

The broad shifts in the measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios observed in Core 6A suggest that there were two distinct oxidation events not associated with weathering (Fig. 5). Oxidation appears to have been most intense in regions with high initial porosity and permeability, because the precipitation of secondary hematite is confined primarily to void spaces (i.e., within fractures, amygdales, and lava breccias that mark the top of individual lava flows) within units C, D and G of Core 6A, but is essentially absent in samples from units A, B, E, F and H. Given the lack of correlation between CIA–K and measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, oxidation appears to have not been accompanied by extensive subaerial weathering. In Cores 7A and 8B, however, oxidation of the KVF appears to increase with the extent of chemical weathering (Fig. 6). This suggests that the oxidation of the KVF, at least directly below the erosional surface marking the top of the formation, is closely linked to chemical weathering.

5.2 *Paleosol Identification*

Paleosols are extremely difficult to positively identify within the rock record. For this reason, Rye and Holland (1998) proposed five simple criteria that can be used to identify a pre-Devonian paleosol. If a rock unit is to be considered a paleosol, it must have been developed on a homogenous parent rock, exhibit changes in mineralogy, texture, and chemistry from the parent material to the top of the soils, and there must be identifiable soft-sediment deformation features along the contact between the unit in question and the overlying rocks. In Cores 7A and 8B, we observe unidirectional changes in mineralogy, texture, and chemical composition towards the erosional contact from a quasi-homogenous parental material. However, we do not observe any identifiable soft-sediment deformation features along the contact between KVF and overlying Kolosjoki Sedimentary Formation. The features observed in Cores 7A and 8B meet four out of the five criteria of Rye and Holland (1998), and could be considered ‘likely paleosols’. However,

the absence of discrete soil horizons and only moderate CIA-K values suggests that only the base of the paleosol has been preserved. Therefore, we believe that ‘oxidized regolith’ is a more appropriate classification than ‘likely paleosol’.

There is chemical evidence for poorly developed weathering profiles or regolith atop all of the lava flows sampled by Core 7A (Fig. 6B), however, the elevated $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios appears to be confined to within Flows C and D only suggesting that iron oxidation was contemporaneous with the most recent weathering episode (Fig. 6C). Given the strong evidence in support of synchronous weathering and oxidation prior to the erosion and subsequent deposition of the overlying Kolosjoki Sedimentary Formation, we can calculate the paleoatmospheric CO_2 and O_2 levels in Fennoscandia 2.06 Ga ago using previously published methods (e.g., Holland, 1984; Sheldon, 2006). Unfortunately, although we can constrain the timing of oxidation to have occurred after eruption of the KVF and before the deposition of the overlying Kolosjoki Sedimentary Formation we are not able to confidently resolve the duration of the weathering event that produced the oxidized Kuetsjärvi regolith described above using the available data. Being able to constrain the duration of weathering is very important, because two very different weathering scenarios could plausibly produce almost identical weathering profiles. Stated another way, a weathering profile that developed under low atmospheric $p\text{O}_2$ conditions for an extended period of time (e.g., 500,000 years – 1 Ma) would be indistinguishable from a profile that developed under a high (near modern) atmospheric $p\text{O}_2$ condition in an abbreviated amount of time (e.g., hundreds to thousands of years).

To overcome this ambiguity, we have attempted to quantify the extent of oxidation for the degree of weathering by compiling the CIA-K and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios for several published paleosols. Using the calculated CIA-K’s and measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios as proxies for the extent

of weathering and oxidation, respectively, the KVF samples are anomalously oxidized for the degree of weathering when compared to the data of published paleosols (Fig. 9A). Only samples from the considerably younger Sturgeon Falls Paleosol (ca. 1.1 Ga) and from the least altered portion of the Hokkalampi Paleosol (ca. 2.2 Ga) are more oxidized for the degree of weathering experienced by the rocks (Zbinden et al., 1988; Marmo, 1992; Stafford, 2007). The most oxidized Archean to early Paleoproterozoic paleosol samples, which span the same range of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios measured within the KVF samples, are those that have experienced the most extensive weathering (e.g., CIA-K > 90; Fig. 9A). We interpret these trends to qualitatively indicate that the KVF oxidized regolith formed during the progressive increase towards, but not necessarily above, the Proterozoic steady state $p\text{O}_2$ level.

There appear to be three general weathering trends that describe the extent of oxidation observed within the Archean and early Paleoproterozoic, late Paleoproterozoic, and Mesoproterozoic paleosols (Fig. 9B). Within the Archean to early Paleoproterozoic paleosol samples, the most completely weathered samples are the most oxidized samples. Conversely, the late Paleoproterozoic and Mesoproterozoic paleosol samples exhibit substantial oxidation for all degrees of weathering. This suggests that oxidation occurred only after extensive exposure and weathering at Earth's surface for Archean to early Paleoproterozoic paleosol samples, but accompanied all stages of weathering during the formation of the late Paleoproterozoic and Mesoproterozoic paleosols. Interestingly, the late Paleoproterozoic paleosol samples appear to define a linear trend where the degree of oxidation is roughly equal to the degree of weathering while the Mesoproterozoic samples from the Sturgeon Falls paleosol are all nearly completely oxidized for all degrees of weathering. Interestingly, the Sturgeon Falls paleosol and oxidized Kuetsjärvi regolith both exhibit manganese loss within the weathering profile (Zbinden et al.,

1988), which has been interpreted to reflect atmosphere O_2 levels of $<0.1\%$ PAL (Planavsky et al., 2014). The behavior of other redox sensitive elements within Precambrian paleosols and sedimentary rock sequences, however, qualitatively suggest that the pO_2 levels were much greater than 0.1% PAL during the Proterozoic, and that the atmosphere gradually became more oxidizing during the GOE (Holland, 1984; Holland and Zbinden, 1988; Zbinden et al., 1988; Holland, 2002; Holland, 2006; Kump, 2008; Holland, 2009; Murakami et al., 2011; Partin et al., 2013a,b; Lyons et al., 2014).

5.2.1 Quantifying paleoatmospheric pCO_2 and pO_2

Since soils form in direct contact with the atmosphere, paleosols have long been considered the best sedimentary archive for estimating paleoatmospheric compositions (e.g., Rye and Holland, 1998; Holland, 2006; Holland, 2009; Sheldon and Tabor, 2009). The maturity of a paleosol is typically characterized by examining the textural development and the extent that soluble elements have been leached from the profile relative to an immobile element (e.g., titanium) and the composition of the unaltered parental material (e.g., average of the three lowermost samples from Core 7A for this study). Given that the weathering profile developed atop the KVF described above is classified as a ‘likely paleosol’ according to the criteria of Rye and Holland (1998), we can use the mass balance model of Sheldon (2006) to quantify atmospheric pCO_2 and pO_2 in Fennoscandia 2.06 Ga years ago and more quantitatively assess the “oxygen overshoot” hypothesis (Bekker and Holland, 2012).

5.2.2 pCO_2 model framework and key assumptions

Briefly, the mass balance model of Sheldon (2006) utilizes the depletion profiles of the major elements sodium, calcium, magnesium and potassium, normalized to an immobile element, to estimate paleoatmospheric pCO_2 (Brimhall and Dietrich, 1987; Chadwick et al.,

1990: Anderson et al., 2002). Within the model framework, the mass transfer coefficient, τ_j , for a given mobile element 'j' is defined as follows:

$$\tau_j = \frac{C_{j,w}}{C_{j,p}} \frac{C_{i,p}}{C_{i,w}} - 1 \quad [1]$$

where $C_{j,w}$ is the concentration of element 'j' in the weathered material at a given depth, $C_{j,p}$ is the concentration of element 'j' in the unweathered parent material, $C_{i,p}$ is the concentration of immobile element 'i' in the unweathered parent material, and $C_{i,w}$ is the concentration of immobile element 'i' in the weathered material at a given depth (Brimhall and Dietrich, 1987; Chadwick et al., 1990).

The mass transfer values can be converted to mass transfer fluxes (m) by integrating the τ -plot (τ vs. depth for the weathered zone preserved) for a given element and multiplying by the density (ρ_p) and the initial concentration of element 'j' in the parent material yielding:

$$m_{j,flux}(g/cm^2) = \rho_p \frac{C_{j,p}}{100} \int_{Z=0}^{Z=D_{j,w}} \tau_{j,w}(z) dz \quad [2]$$

where Z is the depth in the soil profile (cm), and $D_{j,w}$ is the total thickness of the weathered zone (equation 9 of Sheldon, 2006). The mass transfer fluxes can then be used to calculate the total flux of CO_2 that was needed to produce the observed extent of cation depletion as follows:

$$M_{CO_2}(moles CO_2/cm^2) = 2 \sum m_{j,flux} \quad [3]$$

(equation 11 of Sheldon, 2006). Using this flux, we can estimate the transport rate of CO_2 into the weathering profile *via* advection and diffusion (Holland and Zbinden, 1988; Sheldon, 2006):

$$\frac{M_{CO_2}}{T}(moles CO_2/cm^2 \cdot yr) = pCO_2^{atm} \left[\frac{rK_{CO_2}}{10^3} \right] + \kappa \frac{D_{CO_2}\alpha}{L} (pCO_2^{atm} - pCO_2^L) \quad [4]$$

where T is the duration of weathering (years), K_{CO_2} is the Henry's Law constant for CO_2 (0.034 mol/atm), r is the annual rainfall rate (cm/year), k is a constant defined as the ratio of seconds in a year divided by the volume per mole of gas at standard temperature and pressure conditions (1.43×10^3 sec·mole/cm³·year), D_{CO_2} is the diffusion constant for CO_2 in air (0.162 cm²/year), α is the ratio of the diffusion constant for CO_2 in soil (0.02 cm²/sec) divided by the diffusion constant for CO_2 in air (0.16 cm²/sec; Holland and Zbinden, 1988), L is the depth to water table (Holland and Zbinden, 1988) or regolith (Brantley et al, 2014), and the terms pCO_2^{atm} and pCO_2^L are, respectively, the partial pressure of CO_2 in the atmosphere and at the water table.

One key assumption is that the pCO_2 of the atmosphere is much greater than the pCO_2 at the water table (Holland and Zbinden, 1988; Pinto and Holland, 1988; Sheldon, 2006; Brantley et al., 2014). By assuming that $pCO_2^{atm} \gg pCO_2^L$ (i.e. the dominant source of CO_2 for the soil is the atmosphere), the pCO_2^L term becomes insignificant and the equation can be solved explicitly for pCO_2^{atm} by collecting terms (equation 13 of Sheldon, 2006):

$$pCO_2^{atm} = \frac{M_{CO_2}}{T \left[\frac{K_{CO_2} r}{10^3} + \kappa \frac{D_{CO_2} \alpha}{L} \right]} \quad [5]$$

While this approach is able to identify sources of error and provides a way to place quantitative constraints on estimates of paleoatmospheric pCO_2 , there are still a few variables that must be specified which are poorly known for Archean and Proterozoic weathering environments (e.g., weathering duration, annual precipitation rates, depth to groundwater table, etc.). As noted above, positively identifying an Archean or Proterozoic paleosol is extremely difficult. Compared to modern soils, preserved and identified Archean and Precambrian paleosols are typically very thick and well-developed, which implies that they required very long exposure times to form. Thinner, more poorly developed Archean- and Proterozoic-aged are

likely preserved within the geologic record, but the lack of root traces and susceptibility to metamorphic overprinting make them nearly impossible to positively identify. Finally, it is important to note that these calculations are intended for an abiotic weathering profile. Cryptobiotic soils likely existed at this time (Gutzmer and Beukes, 1998; Battistuzzi et al., 2004; Watanabe et al., 2004), making the likelihood of elevated $p\text{CO}_2$ in the soil atmosphere from microbial respiration high.

As noted earlier, certain sections of the FAR-DEEP cores have experienced potassium addition during either burial or metamorphism (Figs. 4 and S2). Given that potassium and sodium behave in a chemically similar manner during weathering, we have assumed that the original potassium profile within the paleosol would have been identical to sodium for our mass balance calculations (e.g., Sheldon, 2006). More importantly, since we are not able to properly constrain the duration of soil formation, annual precipitation rate, and depth to the water table, we have carried out multiple calculations for a range of conditions.

In one set of calculations, we varied the annual precipitation rate between 25 (desert) and 350 cm/yr (tropical rainforest) for a suite of soils ranging in age from 5,000 to 100,000 years while holding the depth to the water table constant at 20 m and 11 m for Cores 7A and 8B, respectively (Fig. 10A and B). We interpret these depths to represent the base of the chemical weathering profile and regolith in each drill core. For the second set of calculations, we varied the depth to the water table between 0.1 (e.g., flooded soil) and 100 m (e.g., well-drained soil that formed on a hilltop) for the same set of soil ages, but held the annual precipitation rate equal to the modern global mean annual precipitation rate (e.g., 100 cm/yr; Fig. 10C and D). For all calculations, we use the average composition of the three lowermost samples from Core 7A as our unaltered parent reference material. Modeling the system in this fashion allows us to assess

the sensitivity of the calculated $p\text{CO}_2$ to these poorly constrained variables. The calculated soil $p\text{CO}_2$ for the KVF weathering profile range from 0.4x to 6,500x PAL, but the distribution is skewed right (Insert Supplementary Figure S8 here).

5.2.3 $p\text{O}_2$ Estimation

Paleo- $p\text{O}_2$ levels are first assessed qualitatively by determining if the paleosol retained iron during formation and not subsequently added to or removed from the profile during metamorphism (e.g., Fig. 6D). If iron has determined to have been retained within the paleosol during weathering and not remobilized during metamorphism, then one can quantitatively estimate the minimum soil $p\text{O}_2$ using Holland's R, i.e. the ratio of O_2 demand to CO_2 demand during the degradation of the parent material (Holland, 1984). We can use the soil $p\text{CO}_2$ curves to infer soil $p\text{O}_2$ given that the ratio of Henry's Law constants for O_2 and CO_2 at 15°C is 3.3×10^{-2} (Fig. 11; Holland, 1984). The calculated R for the parental material in Core 7A is 0.042, which is in good agreement with the calculated R's of unweathered basaltic materials by other researchers (e.g., Holland, 1984; Holland and Zbinden, 1988; Pinto and Holland, 1988; Brantley et al., 2014). Using the $p\text{CO}_2$ calculated above, we estimate the soil $p\text{O}_2$ to be between 1×10^{-3} x and 12x PAL for the KVF weathering profile. Since the $p\text{O}_2$ calculations are based upon the calculated $p\text{CO}_2$, the distribution of the calculated soil $p\text{O}_2$'s is skewed right (Insert Supplementary Figure S9 here).

5.2.4 $p\text{CO}_2$ and $p\text{O}_2$ Modeling Results

The majority of the calculated $p\text{CO}_2$'s and $p\text{O}_2$'s for both sets of calculations are <120 PAL and <1 PAL, respectively, when we neglect the long tail of the distribution curves (See Supplementary Figures S8 and S9). These values are in general agreement with previously published results (e.g., Holland and Zbinden, 1988; Pinto and Holland, 1988; Sheldon, 2006;

Murakami et al., 2011). The wide range of calculated soil pO_2 's stems from the uncertainty in the calculated soil pCO_2 's, which are sensitive to uncertainties in the amount of time it took for a paleosol to develop, the annual precipitation rate, and the depth to the water table during formation of the paleosol (Fig. 11). Of these three variables, the duration of the weathering event and depth to the groundwater table appear to have the greatest effect on the soil pCO_2 , and ultimately soil pO_2 , estimates (Fig. 10 and 11). Therefore, it is extremely important to be able to accurately constrain the soil age and depth to the groundwater table. This is especially true when the soil age is expected to be <50,000 yr and/or the groundwater table is believed to have been between 0.1 and 25 m (Figs. 11C and D). Interestingly, the lower end of the groundwater table range (e.g., 0.1–2 m) corresponds with the observed depth to bedrock range within the continental US (Miller and White, 1998). This is significant, because some authors define the depth to the paleo-water table as the base of the weathering profile before compaction (e.g., Holland and Zbinden, 1988), the convention used here. Additionally, the majority of the modern soils fall within this highly sensitive range of soil ages and water table depths. This calls into question the utility of the mass balance model for estimating paleoatmospheric pCO_2 levels. Our results demonstrate the need to either minimize the uncertainty surrounding these variables or to develop a new approach to estimating paleoatmospheric composition.

6 Conclusions/Summary

The anomalously oxidized character of the 2.06 Ga Kuetsjärvi Volcanic Formation is the result of interaction with oxidizing fluids, likely during weathering, near Earth's surface. Oxidation is interpreted to have preceded erosion of the formation and deposition of the overlying sedimentary formation based upon the concentration of secondary hematite within fractures and amygdaloids, and the incorporation of rounded KVF clasts within the overlying

526 Kolosjoki Sedimentary Formation. The oxidized weathering profile interpretation is supported
527 by the close linkage between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and CIA-K's in FAR-DEEP Cores 7A and 8B.
528 Relative to older Precambrian paleosols, the oxidized regolith is more oxidized for the extent of
529 weathering, but not anomalously so when compared to younger Proterozoic paleosols. These
530 observations qualitatively suggest the oxidized Kuetsjärvi regolith was created during the
531 progressive increase towards, but not necessarily above, the Proterozoic steady state $p\text{O}_2$.

532 Our quantitative modeling results suggest $p\text{CO}_2$ and $p\text{O}_2$ levels 2.06 Ga ago in Fennoscandia
533 were between 0.4x and 6,500x PAL, and between 1×10^{-3} x and 12x PAL, respectively. The wide
534 range in the calculated $p\text{CO}_2$ and $p\text{O}_2$ levels is the result of the mass balance model calculations
535 being extremely sensitive to parameters we feel are very difficult to constrain accurately for
536 Precambrian paleosols such as the annual precipitation rate, depth to the groundwater table, and
537 the amount of time it took the soil to form.

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Figure Captions

Figure 1: Timeline of key events during the Paleoproterozoic (modified after Kump (2008)).

Figure 2: Map illustrating the distribution of Paleoproterozoic aged rocks in Fennoscandia. FAR-DEEP Cores 6A, 7A, and 8B were collected from the northeast side of the Pechenga Greenstone Belt located near the top center of the map (modified after Koistinen et al. (2001)).

Figure 3: A simplified stratigraphic column of the lower part of the North Pechenga Group, containing subaerially erupted volcanic rocks of the Ahmalahti and Kuetsjärvi Volcanic Formations (modified after Melezhik and Hanski, 2013).

Figure 4: Map view of leopard rock outcrop (A. Lepland, unpublished). The dark bands are composed of hematite and magnetite. The large orange, semi-parallel fractures that cut across the oxides and the host rock are filled with K-feldspar that crystallized during metamorphism. Scale bar is 60 cm in length.

Figure 5: The detailed stratigraphy of Core 6A showing the volcanic Units A-H and the volcanic conglomerate member, and the variability of CIA-K, $\text{Fe}^{3+}/\Sigma\text{Fe}$, and Fe/Ti ratios as a function of depth. Filled circles represent FAR-DEEP archive data, while the open circles represent the analyses of this study. There appears to be no correlation between CIA-K and $\text{Fe}^{3+}/\Sigma\text{Fe}$. The two vertical black dashed lines represent the calculated CIA-K's of two USGS powdered rock standard. The left line is the Columbia River Basalt (BCR-2) while the right line is a trachyandesite (AGV-1). The gray area represents an “unaltered material” for a rock with a composition between basalt and trachyandesite.

Figure 6: The detailed stratigraphy of Cores 7A and 8B and the variability of CIA-K, $\text{Fe}^{3+}/\Sigma\text{Fe}$, and Fe/Ti ratios as a function of depth. The two black dashed vertical lines represent the calculated CIA-K's of two USGS powdered rock standard. The left line is the Columbia River Basalt (BCR-2) while the right line is a trachyandesite (AGV-1). The gray area represents an “unaltered material” for a rock with a composition between basalt and trachyandesite. For our $p\text{CO}_2$ and $p\text{O}_2$ calculations, we used the average of the three deepest samples analyzed by this study from Core 7A Flow A as the least altered parental material.

Figure 7: (A) Photomicrograph of the hair-thin, randomly oriented, sinuous fractures that are filled with hematite and terminate at the edge of an amygdale filled with secondary minerals. (B) Very fine-grained hematite (silver) with larger magnetite crystals (pink). (C) Jasper (bright red) and quartz (white) filled amygdales and fractures in Core 7A. (D) Partially reduced hematized magnetite crystal. The center is hematite (silver), but the edges are magnetite (pink). (E) Subhedral magnetite crystal with internal trellis structuring. (F) Rounded clasts derived from the KVF possessing conspicuous hematite rinds.

Figure 8: Variability of feldspar alteration textures as a function of depth within Core 7A. **(A)** Completely altered sample from directly below the erosional contact marking the top of the KVF (Sample 3114830-3, Core 7A, depth of 12.61 m). **(B)** Partially weathered sample from approximately 16 meters below the erosional contact in Core 7A (Sample 3114894, Core 7A, depth of 28.9 m).

Figure 9: **(A)** CIA–K vs. $\text{Fe}^{3+}/\Sigma\text{Fe}$ for published paleosols, and the FAR–DEEP samples. In general, the FAR–DEEP samples are more oxidized than older paleosols, but less oxidized than paleosols younger than 2.06 Ga for the degree of weathering (i.e., CIA–K). **(B)** Proposed chemical weathering paths for Archean and early Paleoproterozoic, late Paleoproterozoic, and Mesoproterozoic paleosols. Paleosol data displayed in panel A are from: Grandstaff et al. (1986) for the Dominion and Pre-Pongola Paleosols; Stafford (2007) for the Hokkalampi and Steep Rock Paleosols; Prasad and Roscoe (1996) for the Dennison Paleosol (Hole S–62); Panahi et al. (2000) for the Ville Marie Paleosol; Beukes et al. (2002) for the Hekport Paleosol; and Zbinden et al. (1988) for the Sturgeon Falls Paleosol.

Figure 10: Core 7A and 8B $p\text{CO}_2$ modeling results for the FAR-DEEP weathering profile, varying the annual precipitation rate and depth to the water table for a range of soil ages. Core 7A results are presented in panels A and C, while Core 8B results are presented in panels B and D. The gray-shaded region in panels C and D represent a typical range depth to water table for North America.

Figure 11: Core 7A and 8B soil $p\text{O}_2$ modeling results for the FAR-DEEP weathering profile varying the annual precipitation rate and depth to the water table for a range of soil ages. Core 7A results are presented in panels A and C, while Core 8B results are presented in panels B and D. The gray-shaded region in panels C and D represent a typical range depth to water table for North America.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

A)

B)

Figure 10

Figure 11