

Silicate weathering in temperate forest soils: insights from a field experiment

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Abstract Few studies of silicate mineral weathering have been conducted in carbonate-bearing temperate forest soils. With climate and vegetation held constant, we compared soil mineralogy and major element chemistry of soil waters from a carbonate-free temperate aspen forest site in the Cheboygan watershed, northern Michigan, with that from carbonate-containing soils from experimental tree-growth chambers (low- vs. high- fertility). All soils were well-

drained sands (quartz, Na-rich plagioclase, and K-feldspar) with minor amounts of carbonate present only in the experimentally manipulated soils. The Na^+ concentrations in soil waters corrected for atmospheric deposition (Na^*) were used to compare relative rates of plagioclase feldspar weathering across sites. In natural soil water profiles, maximum concentrations of Na^* , Si, and dissolved organic carbon (DOC) were observed by a depth of 15 cm, a soil zone free of carbonate minerals. Mean Na^* and DOC concentrations were different in the three soils, and increased in the order natural soil < low-fertility chambers < high-fertility chambers. While low pH environments are generally viewed as enhancing weathering rates, here higher Na^* appears to be related to high DOC, which is consistent with observed increases in active organic functional groups as pH increases. Our results suggest that under a specific vegetative cover, the soil carbon environment affects the weathering flux observed. Our study also suggests that disturbed soils provide an enhanced physical and chemical environment for weathering. Generalized silicate weathering models may benefit from including the enhancing effects of organic anions at moderate pH in addition to precipitation and temperature.

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Introduction

The climatic variables of precipitation and temperature play an important role in controlling rates of silicate mineral dissolution and watershed fluxes measured in streams (Drever and Zobrist 1992; Velbel 1993; Bluth and Kump 1994; Brady and Carroll 1994; White and Blum 1995). While fluxes from streams have been highlighted in the literature, relatively little attention has been paid to integrating stream chemistry with that of analyses of soil waters (Cronan et al. 1990; Soulsby and Reynolds 1992; Hughes et al. 1994; Andrews and Schlesinger 2001).

In addition to climate, soil organic matter content, abbreviated here as fertility, may affect weathering rates. Fertility influences below-ground CO_2 production (root and microbial respiration), which generates carbonic acid for weathering. Organic acids are produced in situ as well, by decay of organic matter and through secretion by roots and fungal hyphae. These acids accelerate weathering rates of silicate minerals by decreasing soil pH or by chelating insoluble Al^{3+} (e.g., Lundström and Öhman 1990; Blake and Walter 1996; Stillings et al. 1996; Raulund-Rasmussen et al. 1998). Soil pH, a function of soil mineralogy and organic matter content, is also important in that silicate minerals such as feldspars generally have the lowest dissolution rates at moderate pH (Chou and Wollast 1984).

Studies of river chemistry have established a relation between riverine organic carbon content, vegetative cover, and silicate weathering fluxes. For example, Humborg et al. (2004) and Millot et al. (2003) found increased riverine organic carbon content and increased weathering fluxes in Swedish and Canadian catchments with large proportions of forest and wetland cover, compared with mountainous and periglacial landscapes. Similarly, Moulton et al. (2000) reported increased weathering fluxes from a vegetated compared with unvegetated catchment. Although this previous work has demonstrated the potential importance of soil fertility on mineral weathering rates, direct field manipulations have not previously been conducted.

The purpose of this study is to test geochemical controls on weathering by comparing the composition

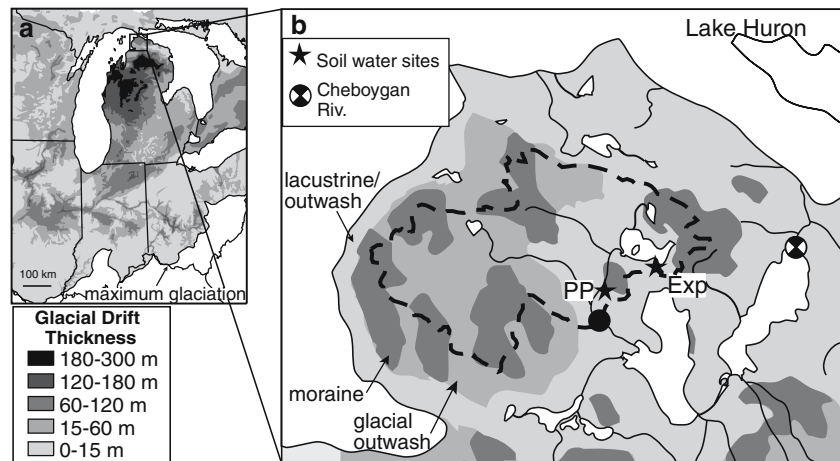
of soil solutions produced in a plot-scale field experiment and in a natural soil profile. While holding climatic variables and vegetation type constant, we examine the effect of carbon transformations in the presence and absence of carbonate mineral buffering on relative weathering rates of Na-plagioclase. In an unbuffered system, we would predict silicate mineral weathering to be enhanced in sites with more fertile soils; however, where pH is buffered by carbonates, H^+ -promoted dissolution may be suppressed. Unlike most watershed studies of mineral weathering conducted in areas underlain by silicates (e.g., Hubbard Brook—Bormann and Likens 1994; Likens and Bormann 1995; Loch Vale—Mast and Drever 1990; Bear Brook—Rustad et al. 1996), we have focused on a recently deglaciated region with soils of mixed carbonate and silicate mineralogy: the Cheboygan watershed, northern Michigan. Previous data from a field experiment in the Cheboygan watershed (Williams et al. 2003) showed an increase in carbonate mineral weathering due to increased atmospheric CO_2 and soil fertility. Here we compare soil solution chemistry and soil gas $p\text{CO}_2$ from the field experiment with a natural forest site and observe differences in carbon dynamics and in rock-derived Na^+ concentrations across sites and depths.

Methods

Field area and sites

The study was conducted in the forested Cheboygan watershed, located in the northernmost Lower Peninsula of Michigan (Fig. 1). In the Great Lakes region, the most recent Wisconsin ice sheet advanced to cover most of the region approximately 11,500 years ago (Futyma 1981). As this final ice sheet retreated, the middle stage of glacial Lake Algonquin covered the area from 11,200 to 10,000 years ago (Larsen 1987). The retreat of the Wisconsin glaciation left Paleozoic carbonates, shales, and evaporites of the Michigan Basin blanketed with sandy glacial drift up to 240 m thick. Thick moraine deposits of mixed carbonate and silicate mineralogy rise up to 100 m above the lowland outwash and lakebed deposits (Fig. 1) (Dorr and Eschman 1970; Department of

Fig. 1 (a) Midcontinent glacial drift thickness and our study area, (b) the Maple catchment (dashed line) of the Cheboygan watershed, northern Michigan. Soils and soil solutions were collected from sites at the University of Michigan Biological Station: *Exp* experimental tree-growth chambers; *PP* the Pellston Plain, a natural aspen forest



Geology, Western Michigan University 1981; Farrand 1982). Carbon cycling dynamics in two mature ecosystems developed in these glacial deposits have been examined by Ku (2001): a lowland aspen forest developed on very well drained lakebed sands (Pellston Plain) and an upland beech-maple forest developed on well-drained loamy sand and sand till (Pearsall et al. 1995). The present study focuses on comparing weathering processes in soils from a field experiment and in Pellston Plain, whose similarity in soil texture, mineralogy, and aspen (*Populus* sp.) vegetation, make them appropriate for comparison.

At the natural Pellston Plain site, soils are of the Rubicon Series (Entic Haplorthod). The forest is composed of trembling and big-tooth aspen, red and white pine, and paper birch (*Populus tremuloides*, *Populus grandidentata*, *Pinus strobus*, *Pinus resinosa*, *Betula papyrifera*) with bracken ferns (*Pteridium aquilinum*) in the understory. We conducted our sampling in an area that was dominantly aspen, with understory ferns.

In the field experiment, conducted within the Cheboygan watershed at the University of Michigan Biological Station, trees were grown in open-topped chambers under manipulated soil fertility and atmospheric CO₂. Twenty open-bottom root boxes (10.9 m² in area, 0.45 m deep) were filled with either low-fertility or high-fertility soil. The high-fertility treatment consisted of 100% Kalkaska sand A-horizon (Typic Haplorthod), while the low-fertility treatment consisted of 80% Rubicon sand

C-horizon (Entic Haplorthod) and 20% Kalkaska sand A-horizon. Both soils are common to the region and sustain aspen. One quadrant of each chamber was planted in 1997 with trembling aspen saplings (*P. tremuloides*), one quadrant with sugar maples (*Acer saccharum*), and one half with a mix. Three saplings were planted per quadrant. Trees were locally derived genotypes and approximately 20-cm tall at planting. Open-topped chambers maintained atmospheric CO₂ at ambient (~350 μatm.) or twice-ambient conditions during the growing season. Further details of the experimental setup are given in Curtis et al. (2000) and Williams et al. (2003). The experiment ran from June 1997 through June 1999. Because our study focuses on the soil fertility treatment, data from the two atmospheric CO₂ treatments were pooled.

Soil solutions and gases

Soil solutions and soil atmosphere were collected from both the natural and experimental sites. The aspen quadrant of each chamber was instrumented with a ceramic-cup tension lysimeter (SoilMoisture Corp.) placed at 15 cm depth, from which soil solution was collected periodically. Eight chambers contained stainless steel needles (1/8 in. ID) at five depths (10–125 cm) for the extraction of soil atmosphere. In the aspen forest site on the Pellston Plain, three groups of ceramic-cup tension lysimeters were installed at 15, 75, 125, and 250 cm-depth. Two groups of soil gas needles (5–125 cm) were installed at the site.

Solutions were collected in plastic syringes and filtered (0.45 μm) in the field. Soil solution and soil gas $p\text{CO}_2$ data presented here were collected during several sampling trips in spring 1998, when the greatest number of soil solution samples was collected. The Pellston Plain site was sampled monthly, and the experimental chambers were sampled biweekly (with the exception of CO_2 , which was not sampled in the chambers in May 1998). Major and minor cations were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES; precision $\pm 3\%$) and anions by ion chromatography (precision $\pm 2\%$). Total alkalinity (equivalent to HCO_3^- concentration at the measured pH) was determined by electrometric endpoint titration, dissolved inorganic carbon (DIC) by gas chromatography following acidification and headspace equilibration, and dissolved organic carbon (DOC) by platinum-catalyzed oxidation with infrared detection (precision $\pm 5\%$). Solution pH was measured in the field with an Orion Ross electrode, given sufficient sample volume, or in the laboratory on the alkalinity aliquot with a Radiometer electrode. The pH of soil solutions from the experimental chambers was measured infrequently due to fluid volume constraints. The $p\text{CO}_2$ of the soil atmosphere was analyzed by gas chromatography (precision $\pm 5\%$). Analytical methods are described in further detail in Williams et al. (2003), Ku (2001), and references therein.

Analyses of soil mineralogy

Soil mineralogy and carbon content were determined by X-ray diffractometry (XRD) and coulometry, respectively, on two depth profiles of Pellston Plain soils and bulk samples of chamber soils. Samples were ground using a mortar and pestle and passed through a 200-mesh sieve. XRD scans were performed in a continuous scan from 4° to $34^\circ 2\theta$, at a rate of 1°min^{-1} , and integrated with Scitag software. Standard curves were generated using analyses of mixtures of quartz, albite, and microcline. Calculated wt.% feldspars were precise to $\pm 2\%$ and accurate to $\pm 10\%$. Inorganic and total carbon contents were determined on a Coulometrics carbon coulometer, with precision of each method $\pm 0.3\%$, and organic carbon calculated as the difference. Inorganic and organic carbon

contents were converted to weight percentages of CaCO_3 and CH_2O , respectively. An exponential function based on one Pellston Plain depth profile was used to estimate CaCO_3 and CH_2O on the other depth profile of Pellston Plain samples, which were not analyzed for carbon. Error introduced by this estimation is minimal for the feldspars ($< 2\%$), given the low carbon contents.

Because XRD analysis is generally considered a semi-quantitative method of determining bulk soil mineralogy, lithium metaborate (LiBO_2) digests were performed in concert with electron microprobe analyses of plagioclase grains to further constrain the plagioclase content of the soils. A 0.1-g soil sample was mixed with 1 g of LiBO_2 flux, melted at $1,100^\circ\text{C}$, quenched and dissolved in 60 mL of 5% HNO_3 . Samples were analyzed for major elements by ICP-OES (Perkin Elmer Optima 3300 DV; further details in Nezat et al. 2004). Results were blank-corrected for elemental contributions from the LiBO_2 flux. The LiBO_2 digest method typically yields accuracy within 7% for major cations.

Electron microprobe analysis was performed to determine Na content (albite fraction) of plagioclase in the soils. Thin sections of soil grain mounts from two depths at Pellston Plain and two experimental chambers (one of each fertility treatment) were scanned. The analysis was conducted at 15 kV and 10 nA in raster mode to minimize alkali mobility. Standardization was performed for quantification of Na, Ca, Al, Si, Sr, Mg, K, Rb, and Ba. Oxygen was calculated as oxides of major and minor elements. Mineral elemental totals were $100 \pm 1.4\%$. Between eight and ten plagioclase grains were analyzed per slide, and three analyses were performed on different parts of each grain. Using the elemental compositions of plagioclase and assuming that plagioclase was the sole mineral source of Na^+ in the digests, the Na^+ contents from the digests were converted to wt.% plagioclase. Plagioclase contents determined by XRD and LiBO_2 digests were then normalized to soil volume to permit a comparison based upon the amount of plagioclase encountered by soil solution. To this end, weight percent plagioclase was multiplied by soil bulk density (U.S. Department of Agriculture 1991) yielding grams of plagioclase per unit volume.

Calculation of Na^*

Incongruent dissolution of plagioclase releases Na^+ to solution, while Al^{3+} and most of the mineral's Si are retained in secondary aluminosilicates. However, catchment mass balances of Na^+ are also influenced by atmospheric deposition and anthropogenic salt contributions. The Na^+ and Cl^- derived from anthropogenic salts were minimized in this study by using a sparsely populated catchment and by placing lysimeters at a distance from roads. Soil solution concentrations were corrected to obtain Na^+ derived from weathering (Na^*), using the volume-weighted annual average Na^+/Cl^- ratio in atmospheric deposition at the University of Michigan Biological Station. Although Cl^- has been used for many years in biogeochemical studies as a relatively conservative tracer, recent research has suggested that Cl^- is more involved in biological cycling than previously appreciated (Lovett et al. 2005; Öberg and Sandén 2005), and this warrants additional discussion below.

Na^+ concentrations were corrected by subtracting Cl^- concentration multiplied by the Na^+/Cl^- ratio of wet atmospheric deposition [0.68 ± 0.06 for the study years 1997–1999; National Atmospheric Deposition Program (NRSP-3)/National Trends Network 2003] to yield Na^* . Atmospheric deposition generally accounted for 20% of the chamber soil solution Na^+ concentration and 45% of the Pellston Plain Na^+ concentration. Occasionally, slightly negative values for Na^* were obtained, indicative of error inherent in the method. Negative values were included in statistical calculations without further correction.

In using the Na^+/Cl^- ratio of atmospheric deposition to calculate Na^* , we assume that Cl^- behaves conservatively, with any biological transformations occurring at steady state. However, Lovett et al. (2005) have shown that after ecosystem disturbance, a net release of Cl^- may occur during organic matter degradation followed by a period of accumulation of Cl^- in biomass as the ecosystem is aggrading. Additionally, Cl^- takes part in transformations to and from organochlorine compounds (Öberg and Sandén 2005; Öberg et al. 1996), though the magnitude and significance of this process is only beginning to be understood. Neither Cl^- nor organic chlorine in biomass was quantified in

this study. Solution Cl^- concentrations in the natural and experimental sites were compared statistically in order to gage whether the aggrading experimental ecosystems might strongly affect our approach to calculating Na^* . Differences between mean site Cl^- concentrations were not significant ($p > 0.05$), although higher maximum Cl^- concentrations were reached in the chambers than in the natural site. Given these caveats, the additional error introduced by Cl^- cycling into calculation of Na^* is expected to be minor.

Excessive evaporation of soil waters was also ruled out because correlations between Na^* and Cl^- and Na^* and solution volume (statistical analyses performed using SYSTAT), yielded no statistically significant relationships except in the low-fertility soil waters where Na^* was negatively related to solution volume ($r = -0.38, p < 0.0001$). In addition, natural and experimental soil water Cl^- concentrations were similar, though Cl^- did reach higher values in the experimental soils, suggesting that similar processes were acting on the natural and experimental sites. Three outliers from Pellston Plain with Cl^- concentrations $>150 \mu\text{M}$ were considered evaporated or contaminated and were excluded from the analysis. Precision in calculating Na^* was determined to be within 7% of reported values, based on pooling the precision of cation and anion analyses.

Results

Soil chemistry and mineralogy

Pellston Plain and experimental chamber soils were predominantly quartz, plagioclase feldspar and K-feldspar (Table 1). While Pellston Plain lacked carbonate minerals to 250 cm depth, the chamber soils contained minor amounts (0.15–0.18 wt.% CaCO_3), which permitted observation of the dissolution products of both carbonate and feldspar weathering in chamber soil solutions. Although new reactive mineral surfaces may have been exposed during mixing of natural soils for the chamber fill, the chamber treatments all contain the same soil and are thus fully comparable. Organic carbon contents at Pellston Plain were

<2.5 wt.% CH₂O at the surface and declined rapidly with depth. The low-fertility soil was comparable to Pellston Plain with organic carbon contents of <1 wt.%, while the high-fertility soil contained 4 wt.%, consistent with how the treatments were generated. Microprobe analyses yielded plagioclase compositions of 83 ± 9 mol.% albite at 13 cm depth and 76 ± 9 mol.% albite at 324 cm depth at Pellston Plain. In the chambers, plagioclase compositions were 73 ± 15 mol.% albite and 90 ± 12 mol.% albite in the low-fertility and high-fertility soils, respectively. Volume-normalized plagioclase content (Tables 1, 2) determined by XRD and LiBO₂ agree within several weight percent, though XRD consistently yields slightly lower values. When taken together, the analyses illustrate that although plagioclase content was variable in the natural and experimental soils, the range of plagioclase contents encountered in the chambers and natural soils was similar, permitting meaningful comparisons of soil solution chemistry.

Soil solution chemistry

Chamber soil solutions were dominated by carbonate mineral weathering (Fig. 2a). Carbonate mineral dissolution by carbonic acid produces a 2:1 ratio of HCO₃⁻:Ca²⁺ + Mg²⁺. This ratio was observed in the low-fertility chambers. Deviation from the ratio in the high-fertility chambers is attributed to excess Ca²⁺ + Mg²⁺ that charge-balances NO₃⁻ produced during decomposition of organic matter in the first months of the experiment (see Johnson et al. 1995; Williams et al. 2003). The pH of chamber soil solutions was buffered to typical values of 7.6 in both the low-fertility and high-fertility soils by carbonate mineral dissolution, which proceeded to equilibrium (Williams et al. 2003). Pellston Plain solution chemistry reflected the lack of soil carbonate minerals, with very low concentrations of HCO₃⁻ and Ca²⁺ × Mg²⁺, as well as slightly acidic pH values of 5.8 ± 0.1 at 15 cm depth. DIC concentrations were very similar to alkalinity concentrations because at moderate pH, HCO₃⁻ is the predominant species comprising DIC. DOC concentrations showed no trend with DIC among sites (Fig. 2b), but DOC concentrations, roughly reflected differences in soil organic carbon contents of the sites.

As an illustration of the need to correct for atmospheric contributions, the chemical trends represented by evaporation of rain or of road salt (halite) are superimposed on a graph of Na⁺ versus Cl⁻ in the soil solutions (Fig. 3). After correcting for Na⁺ added by atmospheric deposition as detailed above, a net excess of Na (Na*) remained, which we attribute to the weathering of feldspars.

Though Na-feldspar dissolution produces both Si and Na*, the incongruent reaction sequesters some Si in a solid phase, such as kaolinite. Additionally, Si may be biologically cycled (e.g., Derry et al. 2005). For these reasons, Na* is a more useful tracer than Si of silicate weathering in the soils (Fig. 4). By 15-cm depth in the natural Pellston Plain soils, mean Na* was 16 ± 12 μM, compared to 60 ± 47 μM in the low-fertility soil solutions and 87 ± 52 μM in the high-fertility soil solutions (Fig. 5). Na* was positively correlated with Si in the chamber soil solutions (low-fertility— $r = 0.76$, $p < 0.001$; high-fertility— $r = 0.66$, $p = 0.11$) at a 1:2 mole ratio of Na*:Si in the high-fertility and a 1:3 mole ratio in the low-fertility soils. For comparison, incongruent dissolution of albite to kaolinite produces a 1:2 ratio in solution. The Na*:Si mole ratio was not found to correlate significantly with Si in the natural soil waters ($r = 0.26$, $p = 0.44$). Furthermore, Si concentrations at Pellston Plain overlapped with values in the chambers, while Na* values were lower. Si concentrations tended to decrease in variability and magnitude with depth at Pellston Plain (Fig. 5e), consistent with precipitation of a secondary aluminosilicate phase.

Trends of Na* with DOC were used to explore the possible influence of DOC on aluminosilicate weathering (Fig. 4b). The concentrations of both Na* and DOC in chamber soil solutions, where pH was higher, were greater than those in the natural soil solutions (see Table 3 for statistical details). Additionally, solutions from the high-fertility soils had significantly higher DOC and Na* concentrations than those from the low fertility soils (mean DOC of 3.0 ± 1.0 and 2.0 ± 0.8 mM in high- and low-fertility soils, respectively; mean Na* given above). In the natural Pellston Plain soil profiles, DOC concentrations decreased slightly with depth and averaged 1.1 mM (Fig. 5d), while Na*

Table 1 Bulk mineralogy of experimental chambers and natural Pellston Plain soils determined by X-ray diffraction and carbon coulometry

Soil site ^a	Depth (cm)	Quartz	Ksp ^b	Plag. ^c (wt.%)	CaCO ₃	CH ₂ O ^d	Bulk density ^e (g cm ⁻³)	Volumetric plag. content ^f (g cm ⁻³)
Shallow soils								
PP-42	0–10	89.0	7.2	2.3	0.00	1.6	1.40	0.032
PP-44	0–7	91.5	3.9	1.0	0.01	2.6	1.40	0.014
PP-44	14–21	89.3	6.8	1.8	0.01	2.2	1.45	0.026
PP-44	28–35	90.9	7.3	0.7	0.01	1.0	1.45	0.010
PP-44	64–74	90.4	6.8	2.8	0.00	0.0	1.45	0.041
PP-pit	10–15	95.7	1.1	1.1	NA ^g	2.0	1.45	0.016
PP-pit	15–20	96.1	1.6	0.5	NA	1.8	1.45	0.008
PP-pit	20–25	95.9	2.2	0.4	NA	1.5	1.45	0.005
PP-pit	25–30	93.3	4.2	1.3	NA	1.3	1.45	0.019
PP-pit	36–41	90.8	6.3	1.9	NA	1.0	1.45	0.028
PP-pit	46–51	88.7	4.0	6.5	NA	0.7	1.45	0.094
PP-pit	56–61	92.9	3.6	2.9	NA	0.5	1.45	0.042
PP-pit	66–71	89.1	7.3	3.2	NA	0.4	1.45	0.046
Deep soils								
PP-42	109–120	87.6	6.6	5.7	0.00	0.2	1.53	0.087
PP-44	99–105	87.6	9.7	2.7	0.01	0.0	1.53	0.041
PP-44	152–158	90.3	6.8	2.8	0.00	0.2	1.53	0.043
PP-44	224–231	90.4	4.8	4.8	0.00	0.0	1.53	0.073
PP-pit	76–81	92.8	3.3	3.6	NA	0.3	1.53	0.055
PP-pit	86–91	93.0	4.0	2.8	NA	0.2	1.53	0.042
PP-pit	102–104	94.2	2.0	3.7	NA	0.1	1.53	0.057
Chamber low-fertility		87.8	9.7	2.5	0.18	0.8	1.50	0.038
Chamber high-fertility		81.4	11.8	6.8	0.15	3.9	1.35	0.092

^a Data from discrete samples are presented. Natural site (Pellston Plain) soil samples were collected by hand auger (PP-42 and PP-44) and from a soil pit (PP-pit). Experimental chamber soils for XRD analysis were split from a bulk sample of homogenized low-fertility and high-fertility soils, prior to chamber construction

^b Ksp = microcline

^c Plag. = plagioclase feldspar

^d Measured values, except for PP-pit soils, whose organic carbon content was estimated using an exponential function fitted to the data from sites PP-42 and PP-44

^e Estimated from soil survey data (U.S. Department of Agriculture 1991)

^f Calculated as bulk density multiplied by wt.% plagioclase

^g NA = not analyzed, and assumed negligible

concentrations were less depth-dependent, with a maximum value of 29 μM at 75 cm, and means of 9–16 μM at other depths. Shallow mean DOC concentrations did not vary directly with soil organic carbon in that Pellston Plain soils had slightly higher organic carbon contents but lower DOC than the low-fertility chamber soils. The high-fertility soil, however, had both the highest shallow DOC concentration and highest organic matter content of the sites.

Soil CO₂

Soil atmosphere $p\text{CO}_2$ values (Fig. 6) were higher in the chambers than at Pellston Plain, and as presented in Williams et al. (2003), soil fertility had a significant effect on $p\text{CO}_2$ values in the experimental chamber soils. In contrast, the atmospheric CO₂ treatment in the chambers did not result in a significant difference between soil atmosphere CO₂ concentrations in ambient

Table 2 Plagioclase content of natural and experimental chamber soil samples calculated from LiBO₂ digests of bulk soil in concert with electron microprobe analysis of plagioclase

Sample ^a	Na (mmol kg ⁻¹) ^b	Albite fraction of plag. ^c	Calculated wt.% plag.	Bulk density (g cm ⁻³) ^d	Volumetric plag. content (g cm ⁻³)
Shallow soil PP-42, 0–13 cm	109	0.83	3.5	1.4	0.049
Deep soil PP-42, 324 cm	221	0.78	7.5	1.53	0.115
Chambers low-fertility					
MC 3-4 (AL) Jun. 1997	274	0.73	10.0	1.5	0.150
MC 5-3 (AL) Jun. 1997	215	0.73	7.8	1.5	0.118
MC 4-2 (EL) Jun. 1997	111	0.73	4.1	1.5	0.061
MC 1-2 (AL) Jun. 1999	224	0.73	8.2	1.5	0.122
MC 4-1 (AL) Jun. 1999	211	0.73	7.7	1.5	0.116
MC 1-4 (EL) Jun. 1999	264	0.73	9.7	1.5	0.145
MC 5-1 (EL) Jun. 1999	202	0.73	7.4	1.5	0.111
Chambers high-fertility					
MC 1-3 (AH) Jun. 1997	464	0.90	13.6	1.35	0.184
MC 4-3 (AH) Jun. 1997	206	0.90	6.1	1.35	0.082
MC 2-3 (AH) Jun. 1999	358	0.90	10.5	1.35	0.142
MC 1-3 (AH) Jun. 1999	425	0.90	12.4	1.35	0.168
MC 3-2 (EH) Jun. 1999	327	0.90	9.6	1.35	0.130
MC 2-2 (EH) Jun. 1999	336	0.90	9.8	1.35	0.133

^a Data from discrete samples are presented. Natural site (Pellston Plain) samples for digests were collected by hand auger (PP-42). Experimental chamber soils for digests were collected from two low-fertility and three high-fertility chambers in 1997 and from four low-fertility and four high-fertility chambers in 1999. Chamber samples are identified by chamber ID (e.g., MC 1-3) and experimental treatment. MC 1-3, for example, means Block 1, Chamber 3. Treatment IDs are as follows: *AL* ambient atmospheric CO₂, low soil fertility; *EL* elevated CO₂, low fertility; *AH* ambient CO₂, high fertility; *EH* elevated CO₂, high fertility

^b Determined by LiBO₂ digest

^c Fraction of plagioclase composition described by albite endmember. Determined by electron microprobe analysis of soil plagioclase grains

^d Estimated from soil survey data (U.S. Department of Agriculture 1991)

^e Calculated as bulk density multiplied by wt.% plagioclase

compared with elevated CO₂ chambers (Williams et al. 2003). A maximum concentration was reached at 50 cm in the chambers, just below the bottom of the root box. In contrast, at Pellston Plain *p*CO₂ continued to increase toward the depth of the water table (~4 m), but reached a local maximum at 100 cm.

Discussion

We observed increased concentrations of Na⁺ in the chamber soils compared with the natural sites, and additionally, higher concentrations of Na⁺ in the high-fertility compared with the low-fertility chambers. In the following discussion,

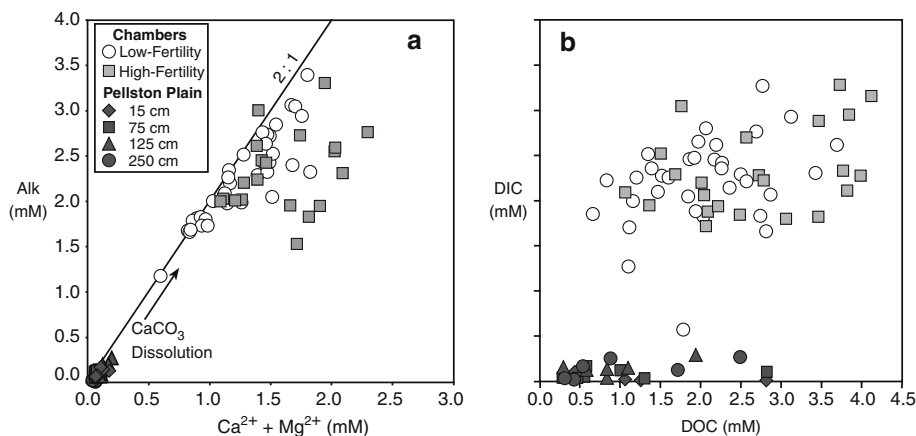


Fig. 2 (a) Soil solution concentrations of HCO_3^- versus $\text{Ca}^{2+} + \text{Mg}^{2+}$ from Pellston Plain and low- and high-fertility experimental chambers. Solid line indicates the 2:1 ratio obtained from reaction of carbonate minerals with

carbonic acid. (b) Soil solution concentrations of DIC versus DOC. Data shown are from repeated sampling events of ten low-fertility and ten high-fertility chambers and three groups of lysimeters at Pellston Plain

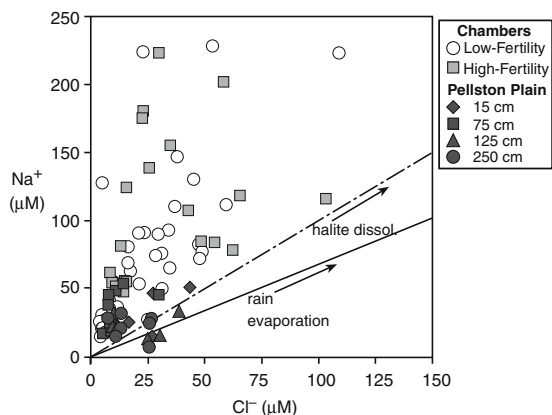


Fig. 3 Soil solution concentrations of Na^+ versus Cl^- in comparison with trajectories obtained from evaporating rainwater or dissolving halite. Na^* indicates Na^+ attributed to rock weathering and is defined on the graph as the vertical distance between Na^+ concentration and the rainwater evaporation line. Data shown are from repeated sampling events of ten low-fertility and ten high-fertility chambers and three groups of lysimeters at Pellston Plain

we address several possibilities to explain this observation.

Soil mineralogy and cation exchange

Comparison of the Na^* concentrations in natural and experimental soils requires consideration of the proportion of reactive feldspar in the different soils. The soil textures in the natural and

experimental sites were similar in that they were both sandy and well drained. The most significant compositional difference between the natural site and experimental soils was the presence of carbonate minerals in the experimental soils. Additionally, the natural soils and experimental soils exhibited a range of several weight percent in plagioclase contents, with high-fertility soils at the upper end of the range. However, the high-fertility soils had a lower bulk density due to higher organic carbon content and a finer grain size generating higher porosity. When mineral weight percents are normalized to soil volume (taking into account bulk density differences), the mass of plagioclase per volume of soil in both the experimental soils falls within the range exhibited in the natural soils (Tables 1, 2). Differences in feldspar content may be important if feldspar dissolution proceeds at rates far from equilibrium and is governed by kinetics. In such a case, the Na^* content of the soil solutions would be dependent on the feldspar content of the soils. However, our evidence at the natural site suggests that a quasi-equilibrium solubility of feldspar (e.g., incongruent dissolution to produce an aluminosilicate) is reached in the upper soils, at very shallow depths in the soil water's flowpath. However, regardless of whether feldspar dissolution was limited kinetically or by solubility, the similarity of feldspar contents in

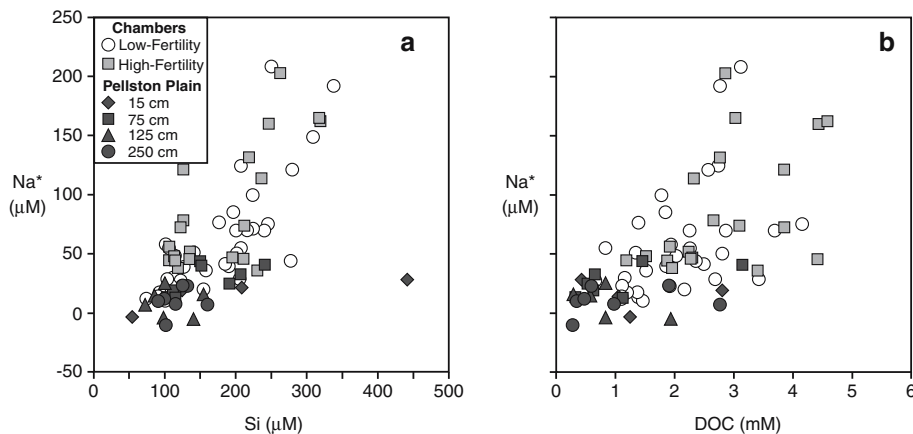


Fig. 4 Soil solution concentrations of Na^+ versus Si (**a**) and versus DOC (**b**) from Pellston Plain and low- and high-fertility experimental chambers. Data shown are from

repeated sampling events of ten low-fertility chambers, ten high-fertility chambers, and three groups of lysimeters at Pellston Plain

the natural and experimental soils once normalized to soil volume allowed a comparison of soil solution chemistries.

The exchange pool in soils serves as storage for cations in a form that is relatively available to plants. At our sites, the exchange pool was not measured directly, but cation exchange analyses of similar, though more clay-rich soils from the E.S. George Reserve in southeastern Lower Michigan (relatively low $3\text{--}6\text{ cmol kg}^{-1}$ (pers. comm., Lixin Jin, Department of Geology, University of Michigan)) suggest that soils in our sites would have even a lower exchange capacity. At shallow depths, Ca^{2+} tends to dominate the exchange pool because it is translocated by plants while Na^+ , which is excluded by plant roots, accumulates on exchange sites deeper in the profile (Jobbágy and Jackson 2004). George Reserve soils reflect this trend, with the exchange pool dominated by Ca^{2+} in the upper 5 cm of mineral soil and by Na^+ deeper (40 cm) in the profile. Ca^{2+} is also more strongly bound to the exchange sites than Na^+ because of its smaller ionic radius and higher charge. However, if carbonate mineral dissolution dominates weathering reactions, high solution concentrations of Ca^{2+} would flood exchange sites with Ca^{2+} and drive off more weakly held ions like Na^+ , increasing the apparent Na^+ .

An exchange mechanism as described above cannot be completely ruled out in explaining differences in Na^+ between the natural Pellston Plain soils and the experimental chambers. At

Pellston Plain, where carbonate minerals have been dissolved away from the upper 250 cm of the soil profile, this mechanism would not be important. However, carbonate was present in both the low-fertility and high-fertility chamber soils. Because of differences in the two soil treatments, it is difficult to explain the higher Na^+ concentrations observed in the high-fertility compared with low-fertility soils using a cation exchange model. Given that the high-fertility soil was 100% A-horizon, its exchange pool would likely have a high Ca^{2+} content, while the dominantly C-horizon low-fertility soil would have an exchange pool saturated by Na^+ . Thus, under a scenario of increased Na^+ for Ca^{2+} exchange from carbonate weathering, the apparent Na^+ due to cation exchange should be higher in the low-fertility than high-fertility soils, opposite of what we observed. This argument suggests that cation exchange, though an important mechanism in soils, is not the dominant process producing Na^+ in our field sites.

Carbon, soils, and driving mechanisms for mineral weathering

Organic and inorganic carbon are generally separated from each other in developed soil profiles. The upper horizons of spodosols (characteristic of moist, temperate, forested areas) are generally enriched in organic matter to

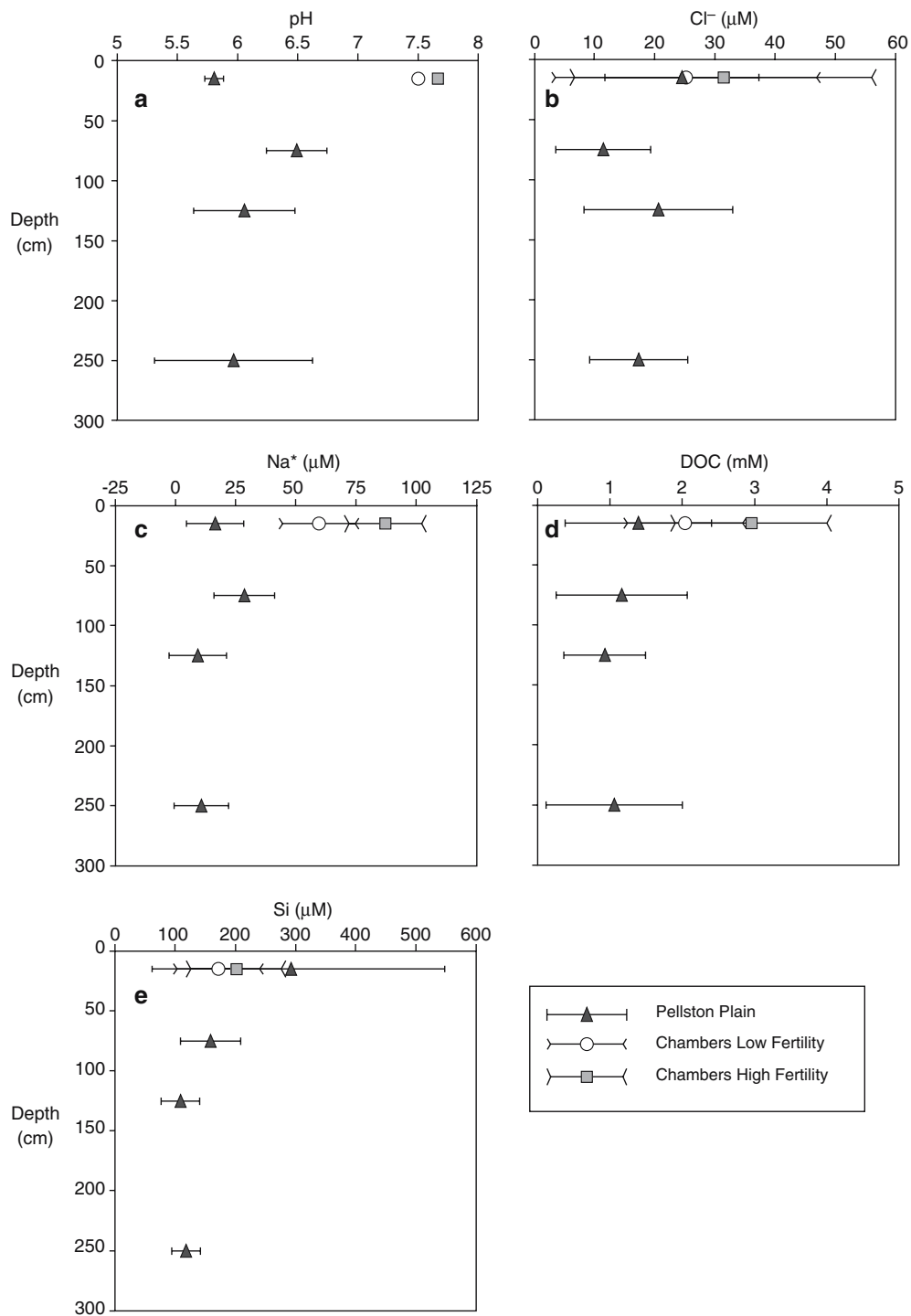


Fig. 5 Depth profiles of mean soil solution chemistry at Pellston Plain compared with the low- and high-fertility experimental chambers. Bars indicate 1 SD. Sample sizes are as follows: high-fertility ($n = 29$), low-fertility ($n = 42$),

Pellston Plain—15 cm depth ($n = 5$), Pellston Plain—75 cm ($n = 9$), Pellston Plain—125 cm ($n = 6$), Pellston Plain—250 cm ($n = 7$). Means are pooled from repeated samples at each site

Table 3 One-way analysis of variance for Na⁺, Si, and DOC soil solution concentrations at 15 cm depth by site (high-fertility chambers, low-fertility chambers, and Pellston Plain)

Source of variation	Na ⁺ df	MS	F ^a	Si df	MS	F	DOC df	MS	F
Site	2	15,853.037	7.820***	2	10,349.582	1.239	2	13.621	16.700***
Error	67	2,027.279		73	8,351.602		75	0.816	

Sample sizes varied by site: high-fertility chambers ($n = 29$), low-fertility chambers ($n = 42$), and Pellston Plain ($n = 5$), and represent repeated sampling of lysimeters in ten chambers of each fertility treatment and three lysimeters at Pellston Plain. Not all lysimeters yielded water during each sampling event

df = degrees of freedom

Statistical significance indicated by *: $p < 0.001$

^a A post-hoc Tukey's HSD test of pairwise differences between means was conducted for Na⁺ and DOC across the three possible pairs of sites. For Na⁺, the pair Pellston Plain–high-fertility was highly significant at $p < 0.001$; Pellston Plain–low-fertility was significant at $p < 0.05$; and low-fertility–high-fertility was marginally significant at $p < 0.1$. For DOC, all three pairs were highly significant at $p < 0.001$

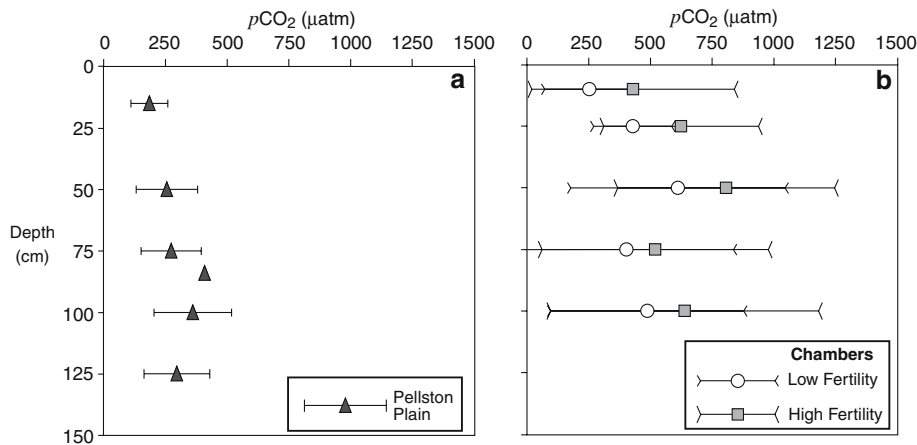


Fig. 6 Profiles of mean soil gas $p\text{CO}_2$ in spring 1998 from Pellston Plain compared with the experimental chambers. Soil gas samples from Pellston Plain were collected from two sets of gas needles during three sampling events. For averaging, Pellston Plain data were pooled by sample depth ($n = 4$ – 6 for different depths). Soil gas samples were collected from four low-fertility and four high-fertility

experimental chambers on four dates. A fifth high-fertility chamber was sampled once. Chamber soil gas data were pooled by soil fertility treatment and sample depth. Pooled sample sizes were $n = 14$ – 15 for each depth in the low-fertility soils, and $n = 13$ – 17 for each depth in the high-fertility soils. Bars indicate 1 SD

depths of ~20–30 cm (Brady 1990). In carbonate-rich soils, inorganic carbon is found in the lower soil horizons, and carbonate minerals may increase in abundance in the profile dramatically (e.g., Reardon et al. 1979), indicative of a reaction front. This is the case in our study area, where calcite and dolomite occur at depths below 1–3 m (below 3 m at Pellston Plain).

The separation of organic carbon from inorganic carbon in the solid phase of the soil allows for different weathering processes to operate at different depths in the soil profile.

Soil organic matter decomposes to produce CO_2 gas and dissolved organic compounds, a fraction of which is comprised of organic acids. Organic acids may affect weathering rates by decreasing soil pH or by providing ligands to chelate insoluble Al^{3+} , effectively increasing silicate mineral solubility. In turn, the soil gas $p\text{CO}_2$, derived from root and microbial respiration and organic matter oxidation in upper soil horizons, is the source for carbonic acid that aggressively attacks carbonate minerals lower in the profile. Thus, in developed soil profiles containing

carbonates and silicates, silicate dissolution mediated by DOC would occur at shallow depths in the profile, while carbonic acid-promoted dissolution occurs at the depths where carbonates are present. If, however, carbonate and silicate minerals were mixed together in the profile, soil solution pH would be buffered. In this case, based on the pH-dependence of silicate mineral weathering, we would expect silicate weathering rates to decrease in the absence of organic acids.

Weathering and carbon transformations

The presence of high concentrations of DOC in the soil solutions may help explain the observed differences in Na^+ among the field sites. DOC was readily available at shallow depths in both the chambers and the Pellston Plain site, with concentrations averaging 3 mM in the high-fertility and 2 mM in the low-fertility chamber soils, and 1.5 mM in the shallowest Pellston Plain soils. Mean Na^+ concentrations decreased in the same order. Though our concentration data are not direct measurements of weathering rates, the similarity of the field soils in their sandy texture and short soil solution residence times may permit relative comparisons of weathering rates on these short timescales.

While laboratory studies have made links between DOC and weathering rates, few field studies have attempted to make this comparison, perhaps in part because the composition of organic carbon can be quite variable between sites. Field studies have made the connection between weathering rates and vegetative cover, however. Several studies have shown that weathering rates on vegetated terrain are higher than on bare terrain (e.g., Bormann et al. 1998; Moulton and Berner 1998; Moulton et al. 2000). For example, using a mass balance approach, Bormann et al. (1998) found that mineral weathering rates were increased ten times in plots planted with red pine compared with an unvegetated plot. Accumulation of Ca^{2+} and Mg^{2+} in the growing plant tissue was measured in addition to fluxes in drainage water. Even though Na^+ is not a plant nutrient, we would expect that increased weathering of nutrient-cations from feldspar would accelerate the

weathering release of Na^+ as well. Our results indicate further that when controlling for vegetation, soil fertility and the amount of organic matter and DOC produced can influence weathering rates.

The concentration of DOC does not directly correspond to its reactivity in terms of functional groups (e.g., Blake and Walter 1996; Ochs 1996; Vance and David 1991), and our analysis of specific biochemical reactions is limited by lack of chemical characterization of DOC. Drever (1994) has questioned whether ligand concentrations are high enough in bulk soil solution to have a measurable effect on weathering rates. With increasing pH, however, the reactivity of organic functional groups may actually increase as H^+ dissociates from organic molecules (Oliver et al. 1983; Perdue et al. 1984; Cronan and Aiken 1985; Vance and David 1991). In our case, the presence of carbonate minerals in chamber soils served to buffer pH, and may have enhanced the complexing capacity of the DOC, potentially increasing silicate weathering rates. We used the Vance and David (1991) model for organic anion charge density, calibrated with northern hardwood forest floor leachates, and average DOC and pH from our sites, to estimate the equivalents of charge contributed by DOC across our sites. The results (160 $\mu\text{eq. L}^{-1}$ in the natural, 260 $\mu\text{eq. L}^{-1}$ in the low-fertility, and 370 $\mu\text{eq. L}^{-1}$ in the high-fertility site), were more than adequate to balance the Na^+ concentrations observed across the sites. The presence of Na^+ and Si at 15 cm depth in the soil profile suggests that weathering of feldspars is occurring at very shallow depths in the soil profile, where DOC is at its maximum, and despite circum-neutral pH values.

The effect of carbon cycling rates cannot be ignored in explaining differences between soil solution chemistries in the chambers and Pellston Plain. The chambers represent rapidly aggrading ecosystems, in which organic matter in the soils served to fertilize growing trees. It should be noted that the slightly higher organic carbon content of the shallow Pellston Plain soils compared with the low-fertility chamber soils was not reflected in their respective $p\text{CO}_2$ values or DOC concentrations. Previous research has found soil carbon content to be a useful predictor of DOC flux from watersheds (Hope et al. 1997).

Higher DOC concentrations in the low-fertility soils than in the natural site may reflect differences in carbon cycling rates in the aggrading versus mature ecosystem. Similarly, enhanced soil $p\text{CO}_2$ values in the aggrading chambers compared with the natural site may have facilitated carbonic-acid-mediated mineral weathering, though carbonic acid would first react with highly soluble carbonates until equilibrium was reached.

Higher concentrations of Na^* , Si, and DOC in the experimental soils compared with the natural soils also suggest that mineral weathering occurs at accelerated rates in disturbed soil profiles. The physical mixing of the chamber soils may have allowed more reactive mineral surfaces to be exposed, analogous to soils in glaciated regions. This type of result has been seen frequently in the literature comparing natural and experimental weathering rates. Increased experimental rates have often been attributed to fresher mineral surfaces, where oxyhydroxides have not accumulated (e.g., Petrovich 1981; White and Blum 1995). Soil disturbance may also have accelerated decomposition of the accumulated organic matter in the soil profile (Bormann et al. 1998), releasing more organic acids for weathering. Large-scale soil disturbance in the form of cultivation was reported by Raymond and Cole (2003) to explain part of an increased alkalinity flux observed in the Mississippi River. Our results similarly suggest that landscape disturbance, such as from agriculture, may increase silicate weathering rates.

Summary and conclusions

Keeping climate and vegetation constant, we were able to compare mineral weathering products in soil solutions of natural soils with those in experimentally manipulated soils of low or high fertility. Plagioclase feldspar was present in all soils, and the largest mineralogical difference between the soils was the presence of carbonate minerals in the experimental soils, which resulted in circum-neutral soil pH, while natural soils had a lower pH. The Na^+

concentrations in soil waters corrected for atmospheric deposition (Na^*) were used to compare relative rates of plagioclase feldspar weathering across sites. In natural soil water profiles, the maximum concentrations of Si and DOC were observed by a depth of 15 cm, and Na^* by 75 cm depth. Mean Na^* and DOC concentrations were different in the three soils, and increased in the order natural soil < low-fertility chambers < high-fertility chambers.

Our results suggest an interplay of fertility, pH, and soil disturbance in influencing mineral weathering rates. Ample supplies of organic carbon in the experimental soils, in addition to disturbance of the soil, may have effected the higher Na^* concentrations observed compared with the natural site. Our results also suggest that higher Na^* in the chambers may be related to high DOC, reflecting the increase in active organic functional groups as pH increases.

These results have implications for large-scale weathering studies. First, unlike the larger river studies that have compared weathering in vegetated versus headwater and periglacial catchments, our manipulated experiment holds vegetation type constant while varying soil fertility. Under this controlled condition, we found that higher soil fertility resulted in higher DOC concentrations and enhanced silicate weathering. This suggests that the soil carbon environment plays an important role in contributing to the weathering observed under a specific vegetative cover. Second, our results are compatible with Raymond and Cole's (2003) finding that cultivation plays a role in increased weathering fluxes from rivers. The soil disturbance caused by activities such as cultivation not only may expose new weathering surfaces, but also may increase organic matter decomposition and DOC production, and may increase the pH of vegetated soils (either by mixing or by liming). Our results suggest that these physical and chemical conditions may increase weathering rates in disturbed compared with naturally occurring soils. Generalized silicate weathering models may benefit from including the enhancing effects of organic anions at moderate pH in addition to precipitation and temperature.

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