

## Effects of CO<sub>2</sub> and nutrient availability on mineral weathering in controlled tree growth experiments

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[1] We sought to determine the effect of elevated atmospheric CO<sub>2</sub> on mineral weathering reactions in midlatitude carbonate-bearing forest soils of differing nutrient availability. Increased plant growth and soil respiration under elevated atmospheric CO<sub>2</sub> suggest increased rates of carbon cycling, which may affect mineral weathering. A randomized complete block experiment was conducted, where aspen and maple saplings were grown in open top chambers under two levels of atmospheric CO<sub>2</sub> and soil N. Soil solution chemistry and soil gas PCO<sub>2</sub> profiles beneath aspen were collected from planting (1997) to harvest (1999). Carbonate mineral weathering products (Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>) dominated solutions, which were saturated with respect to calcite. Soil PCO<sub>2</sub> values at 25 cm depth were 41% higher in high N soils, but CO<sub>2</sub> treatment was not significant. An ANOVA model tested treatment effects on spring 1998 solution chemistry. CO<sub>2</sub> treatment had a significant effect on DIC, which was 12% higher in elevated than ambient CO<sub>2</sub> chambers. Little effect of CO<sub>2</sub> treatment was observed in low N soils. In high N soils, solutions had higher concentrations of carbonate weathering products (DIC, 15%; HCO<sub>3</sub><sup>-</sup>, 27%; Ca<sup>2+</sup>, 3%, not significant; Mg<sup>2+</sup>, 5%, not significant). Soil N availability had a significant, positive, effect on mean concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and DOC. The soil N treatment difference in solutes may result from differences in PCO<sub>2</sub> and, additionally, NO<sub>3</sub><sup>-</sup> from organic matter decomposition. Our results suggest that increased carbonate weathering may occur under increased atmospheric CO<sub>2</sub> and in fertile soils. *INDEX TERMS*: 1030 Geochemistry: Geochemical cycles (0330); 1045 Geochemistry: Low-temperature geochemistry; 1886 Hydrology: Weathering (1625); 1615 Global Change: Biogeochemical processes (4805); 1806 Hydrology: Chemistry of fresh water; *KEYWORDS*: mineral weathering, carbonates, soil solution, DOC, DIC, elevated carbon dioxide

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### 1. Introduction

[2] Through fossil fuel burning, human activity is presently transferring carbon at the rate of 6 Pg yr<sup>-1</sup> from geologic reservoirs to the atmosphere. The global response to this mass transfer is not yet fully understood, but on the timescale of human concern (hundreds of years), the carbon emitted must be distributed among earth-surface reservoirs (estimated reservoir size): atmosphere (750 Pg C), terrestrial (2060 Pg C), and oceans (35,900 Pg C [Sundquist, 1993;

Schlesinger, 1997]). Recent research [Ciais *et al.*, 1995; Fan *et al.*, 1998; Schimel *et al.*, 2001] has suggested the existence of a northern midlatitude terrestrial carbon sink. This terrestrial sink likely is composed of a combination of forest biomass, soils, and groundwaters [Dixon *et al.*, 1994; Nadelhoffer *et al.*, 1999; Schimel *et al.*, 2000].

[3] The growth of trees and other plants has been found in numerous studies to increase in response to elevated atmospheric CO<sub>2</sub>, especially under optimal nutrient, light, and water conditions [e.g., Hungate *et al.*, 1997; Curtis *et al.*, 2000; Andrews and Schlesinger, 2001]. Previous results from open-top chamber studies of *Populus tremuloides* by Pregitzer *et al.* [1995], Curtis *et al.* [2000], Pregitzer *et al.* [2000], and Zak *et al.* [2000] indicate increased rates of photosynthesis, tree growth, soil respiration, and fine root growth and turnover under twice ambient atmospheric CO<sub>2</sub>. These results suggest that increased atmospheric CO<sub>2</sub> may result in increased rates of carbon cycling in forest ecosystems.

[4] Through respiration, the terrestrial biosphere delivers to the soil atmospherically derived CO<sub>2(g)</sub>. Soil gas CO<sub>2</sub>

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dissolves in the soil solution to form carbonic acid, which is available for mineral weathering. The solubility of carbonate minerals increases with PCO<sub>2</sub>, so that in shallow soils that are open to CO<sub>2</sub>, the higher the PCO<sub>2</sub>, the more intense the weathering of carbonate minerals. Silicate mineral weathering can also occur by the action of carbonic acid, although rates of silicate mineral weathering have been found to respond more strongly to organic ligands, components of dissolved organic carbon (DOC [e.g., *Lundström and Öhman*, 1990; *Drever and Vance*, 1994; *Blake and Walter*, 1996; *Berg and Banwart*, 2000]).

[5] Mineral weathering reactions that occur in soil solutions are important from the standpoint of carbon cycling because they convert CO<sub>2(g)</sub> to dissolved forms. On geologic timescales, the weathering of silicate minerals is thought to regulate atmospheric CO<sub>2</sub>, but on shorter timescales (i.e., the residence time of ocean waters) the weathering of carbonate minerals may serve as a sink for atmospheric CO<sub>2</sub> [*Berner and Kothavala*, 2001]. In addition, rates of carbonate mineral weathering are orders of magnitude faster than those of silicate weathering [*Holland*, 1978; *Berner and Berner*, 1987; *Roy et al.*, 1999]. If atmospherically derived carbon is processed through the biosphere and soil at increased rates under higher atmospheric CO<sub>2</sub>, then where carbonate minerals are present, their weathering reactions will be extremely important in converting respired CO<sub>2</sub> to dissolved forms. This dissolved carbon can then be sequestered in shallow groundwater reservoirs or returned to the large ocean reservoir via rivers.

[6] The present study sought to determine the effect of elevated atmospheric CO<sub>2</sub> on mineral weathering reactions mediated by carbon cycling in midlatitude carbonate-bearing forest soils of differing nutrient availability. We hypothesized that mineral weathering rates would increase under increased atmospheric CO<sub>2</sub> and under increased nutrient availability in response to higher rates of soil respiration. Trees were grown in open-top chambers under two treatments of atmospheric CO<sub>2</sub> and soil N availability. Our study used soils from the forested Cheboygan watershed, northern Michigan, which unlike many studied watersheds located in silicate terrains (e.g., Hubbard Brook and the Duke Forest [*Bormann and Likens*, 1994; *Likens and Bormann*, 1995; *Bormann et al.*, 1998; *Andrews and Schlesinger*, 2001; *Schlesinger and Lichter*, 2001]) is a system established atop thick carbonate-bearing glacial drift. Increased atmospheric CO<sub>2</sub> was hypothesized to lead to faster tree growth, higher root respiration rates, and therefore higher PCO<sub>2</sub>, which would increase carbonate mineral weathering rates and solute concentrations. We hypothesized a similar response of mineral weathering to the soil N treatment, and were additionally interested in the interaction between the CO<sub>2</sub> and soil N treatments.

[7] Soil gas PCO<sub>2</sub> and the chemical composition (cations, anions, and organic and inorganic carbon parameters) of soil solutions were monitored over the duration of the experiment. Soil samples were analyzed for organic and inorganic carbon content before and after the experiment. To test the hypothesis of increased mineral weathering under elevated CO<sub>2</sub> and soil N, weathering product concentrations in soil

solutions from the different experimental treatments were compared.

## 2. Methods

### 2.1. Experimental Design

[8] Chamber experiments were conducted at the University of Michigan Biological Station, in the Cheboygan watershed, located in the northernmost part of the Lower Peninsula of Michigan. The experiment followed closely a previous set of chamber experiments described by *Curtis et al.* [2000], and the design of the chamber experiments was optimized for study of the response of trees to differing treatments of CO<sub>2</sub> and N-availability. A two-way factorial randomized complete block design was used to vary four treatments with five replications, for a total of 20 experimental chambers. Twenty square, open-bottom root boxes (3.3 m diameter by 0.45 m depth) were filled with either low-N-availability or high-N-availability soil. Soil treatments were made by mixing Rubicon sand and Kalkaska sand, soils both native to the Cheboygan watershed and common in northern Michigan [*Alfred et al.*, 1973; *Tardy*, 1991]. High-N-availability soil consisted of 100% Kalkaska sand A horizon and had a texture of 11% gravel, 76% sand, 10% silt, and 3% clay. Low-N-availability soil consisted of 20% Kalkaska sand A horizon, and 80% Rubicon sand C horizon and had a texture of 4% gravel, 93% sand, 2% silt, and 1% clay. Root boxes were filled in the fall of 1996. Each root box was fitted with an open-top chamber in early spring 1997 in order to control atmospheric CO<sub>2</sub>. Ambient daytime CO<sub>2</sub> (~350 µatm) was maintained in half of the chambers, and twice ambient in the other half. The CO<sub>2</sub> treatment was sustained during the growing season (May–October). Chamber treatments are abbreviated in the text as follows: AH = ambient atmospheric CO<sub>2</sub>, high N-availability; AL = ambient atmospheric CO<sub>2</sub>, low N-availability; EH = elevated atmospheric CO<sub>2</sub>, high N-availability; EL = elevated atmospheric CO<sub>2</sub>, low N-availability.

[9] In June 1997, trembling aspen (*Populus tremuloides*) and sugar maple (*Acer sacharum*) saplings were planted in each chamber. One fourth of each chamber was planted with aspen, one fourth with sugar maple, and one half with a mix of aspen and sugar maple. Three saplings were planted per quadrant. Soil gas needles and lysimeters were placed in the trembling aspen quadrant of the chambers because aspen had been used in previous chamber experiments. Each chamber contained a shallow tension lysimeter (SoilMoisture Corporation) with a ceramic tip placed at 15 cm depth. Soil gas sampling needles (one eighth inch in diameter) were installed in two blocks of the experiment (eight chambers) at depths of 10 cm, 25 cm, 50 cm, 75 cm, and 125 cm. Sampling of soil gases began in April 1998. Trees were allowed to grow until June 1999, when they were harvested. At the time of harvest, many of the trees were more than 3 m tall.

[10] Trees were watered with groundwater during the first growing season, after which time they received only natural rainfall and snowfall. On average, the region receives 82 cm of precipitation per year. The climate in the Cheboygan watershed region is temperate, with mean summer temper-

atures of 18°C and winter temperatures of -6°C [National Oceanographic and Atmospheric Administration, 1985].

## 2.2. Sampling and Analyses of Soil Solutions and Soil Gases

[11] To collect soil solution, tensions of 500 kPa were pulled on each lysimeter with a manual pump between 3 and 24 hours prior to sampling. Water samples were collected in plastic syringes. Aliquots for analyses (except dissolved inorganic carbon) were filtered through 0.45 µm nylon or nylon + glass filters. Dissolved organic carbon (DOC) and cation aliquots were acidified in the field. Given sufficient sample volume, pH was measured in the field with an Orion Ross combination electrode. Otherwise, pH was measured on the alkalinity aliquot (when available) in the laboratory.

[12] Major element chemistry was measured by inductively coupled plasma atomic emission spectroscopy and ion chromatography. A Leeman Labs, Inc. Plasma-Spec ICP-AES 2.5 was used to analyze for Na, K, Mg, Ca, and Si. Anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>) were analyzed on a Dionex 4000I series ion chromatograph (IC) with an AS14 column.

[13] Total alkalinity was measured by electrometric endpoint titration using a Radiometer TitraLab automated titration system. The HCO<sub>3</sub><sup>-</sup> concentration was calculated as equivalent to total alkalinity, given measurement precision (±0.01 meq/kg), pH range of the samples, and ionic composition of the solutions. Dissolved inorganic carbon (DIC) was determined by gas chromatography, following headspace equilibration and acidification to convert all carbonate species to CO<sub>2</sub> [see *Kling et al.*, 1992, 2000]. DOC was measured using a high-temperature platinum-catalyzed combustion followed by infrared detection of CO<sub>2</sub> (Shimadzu TOC-5000) [see *Kling et al.*, 2000].

[14] A charge balance was performed on water chemistry data to check for internal consistency among the various analyses. On average,  $(\sum \text{cation charge} - \sum \text{anion charge}) / (\sum \text{cation charge} + \sum \text{anion charge}) \times 100$  was  $1.5\% \pm 3.8$ , for the 54 samples with complete analyses of 153 samples total. In addition to using titration methods, alkalinity (HCO<sub>3</sub><sup>-</sup>) was also determined by charge balance. If the alkalinity of a sample was not measured, or if charge balance calculated using total alkalinity left an imbalance of ±10%, the HCO<sub>3</sub><sup>-</sup> by charge balance was used in graphs and calculations. HCO<sub>3</sub><sup>-</sup> calculated by charge balance was used for 24% of the samples from spring 1998 (the focus of this paper).

[15] Soil gas samples were extracted in the field using 20-mL nylon syringes fitted with Viton O-rings to reduce sample leakage. Samples were immediately transferred to pre-evacuated 4-mL glass serum vials. Soil gas PCO<sub>2</sub> was measured by gas chromatography.

## 2.3. Soil and Mineralogical Characterization

[16] Samples of chamber soils were collected prior to tree planting (June 1997), and at the end of the experiment before tree harvesting (June 1999). In June 1997 a bulk sample (approximately 0–10 cm depth) was taken from one chamber of each of the four combinations of experimental treatments. In June 1999 a 50-cm push-core of soil was taken from each chamber. Both sets of soil samples were

used for determinations of carbon content, and the June 1997 set was used to estimate bulk soil mineralogy by x-ray diffraction.

[17] Coulometry was used to determine the inorganic and organic carbon content of the chamber soils at both the beginning and end of the experiment. Starting soil samples included splits from the bulk samples collected in spring 1997. Ending soil samples comprised splits from the cores collected in spring 1999. Two cores from each chamber treatment (eight cores) were used for coulometry. Samples were taken from the top and bottom of the experimental soils in each of the 8 cores, with care taken to avoid the underlying native soil.

[18] Coulometric analyses were performed on a Coulometrics, Inc. Model 5011 CO<sub>2</sub> Coulometer, Model 5020 Total Carbon Apparatus, and Model 5030 Carbonate Carbon Apparatus. Total carbon content was determined by combustion of the bulk sample (~0.1 g) at 950°C for 10 min to oxidize all the carbon present to CO<sub>2</sub>. Inorganic carbon content was determined by coulometric titration in 20-min runs, in which sample splits (0.05 g to 0.5 g) were acidified to dissolve carbonate minerals and release CO<sub>2</sub>. Weight percent organic carbon was calculated as the difference between wt % total carbon and wt % inorganic carbon. Coulometric precision for both total and inorganic carbon measurements was ±0.3% of analyzed wt %.

## 2.4. Statistical Analyses

[19] The experiment was designed for use of analysis of variance (ANOVA) modeling to test for experimental treatment effects on chemical variables of interest. Analyses were conducted using the SAS GLM procedure, and significance was set at  $\alpha = 0.05$  for all analyses.

[20] Treatment differences in soil inorganic and organic carbon before and after the experiment were tested using separate ANOVAs for 1997 and 1999. Dependent variables included organic and inorganic C content from spring 1997 bulk samples ( $n = 4$ ), and average organic and inorganic C content from cores ( $n = 8$ ). Average values were determined by pooling carbon content of the 0–10 cm and 20–30 cm intervals of each core. Fixed effects in both models included CO<sub>2</sub> treatment (ambient and elevated) and soil N availability (low and high). The CO<sub>2</sub> × soil N interaction was included in the ANOVA of the initial (1997) data, but was omitted from the analysis of final (1999) data because degrees of freedom were insufficient.

[21] Statistical tests were performed on the soil solution chemical compositions obtained during spring 1998 to test for an effect of CO<sub>2</sub> and soil N availability treatments. ANOVA models included experimental block (1–5), CO<sub>2</sub> treatment, soil N availability, and the CO<sub>2</sub> × soil N interaction as fixed effects. Average spring 1998 chemical concentrations of soils solutions from each chamber were used as dependent variables in the models. This approach was used because while soil solutions were sampled on several occasions during spring 1998, water distribution was uneven, such that each chamber was not sampled the same number of times. Average concentrations of the chemical species of interest were determined for each of the 20 chambers, to yield one observation per chamber for modeling. Eleven models were run with the following



dependent variables: average spring 1998 concentrations of DIC, HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Si, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and DOC. Multiple comparison of means was performed using the Tukey-Kramer test to compare the difference between mean chemical concentrations at ambient and elevated atmospheric CO<sub>2</sub> within the two levels of soil N availability. Least-squares means were calculated for this test to take into account missing values.

[22] Soil gas PCO<sub>2</sub> averages at 25 cm depth were tested over two time periods: (1) spring 1998, to compare with soil solution data; and (2) April 1998 through June 1999, the entire duration of soil gas sampling. The statistical analysis of spring 1998 data was conducted identically to that of the soil solutions, described above, except that CO<sub>2</sub> was measured in two (rather than five) experimental blocks. The ANOVA analysis of the entire PCO<sub>2</sub> data set included experimental block (1–2), time (1–16), CO<sub>2</sub> treatment, soil N treatment, and CO<sub>2</sub> × soil N as fixed effects. Data were not pooled for this latter analysis.

### 3. Results

#### 3.1. Solution Chemistry, PCO<sub>2</sub>, and Composition of Chamber Soils

##### 3.1.1. Soil Composition

[23] Bulk soil mineralogy of the starting high- and low-N-availability soils was predominantly quartz, with microcline (K-feldspar) and albite (Na-feldspar). The high-N-availability soil exhibited a higher feldspar to quartz ratio than did the low-N-availability soil. Both soil types contained a small fraction of carbonate minerals. At planting, the high-N-availability soil had a slightly lower (not significant) inorganic carbon content (0.003 wt %) than the low-N-availability soil (0.009 ± 0.004 wt %; Table 1). At the end of the experiment, experimental treatment did not have a significant effect on inorganic carbon content ( $p = 0.5$  for CO<sub>2</sub>,  $p = 0.7$  for soil N,  $p = 0.3$  for CO<sub>2</sub> × soil N,  $n = 8$ ). The high-N-availability soil contained approximately 4 times more C<sub>org</sub> than the low-N-availability soil (significant at  $p = 0.012$ ,  $n = 4$ , initial data;  $p = 0.035$ ,  $n = 8$ , final data), corresponding to the proportionate mixtures of soil making up the low- and high-N-availability treatments. CO<sub>2</sub> treatment did not have a significant effect on organic carbon content at the end of the experiment ( $p = 0.14$ ,  $n = 8$ ).

##### 3.1.2. Soil Solution Chemistry

[24] Soil solutions were collected periodically from July 1997 (a month after tree planting) through June 1999 (just prior to harvesting). The most intensive sampling took place in 1998, but as shown in Figure 1, the greatest quantity of samples was obtained in July and November 1997 and the spring of 1998. The lysimeters were dry on many sampling occasions, especially in the latter part of 1998 and spring 1999, and certain lysimeters yielded water more frequently than did others [Williams, 2000]. Soil solutions collected were predominantly Ca<sup>2+</sup>-Mg<sup>2+</sup>-HCO<sub>3</sub><sup>-</sup> solutions (Figure 1).

[25] NO<sub>3</sub><sup>-</sup>, charge-balanced by Ca<sup>2+</sup> and Mg<sup>2+</sup>, was an important constituent of soil solutions during the first year of the experiment, especially in high-N-availability soils where concentrations up to 20 mM were reached (compared with <1 mM in nearby natural forest sites [Ku, 2001]). By spring 1998, NO<sub>3</sub><sup>-</sup> concentrations had declined to <2 mM in

**Table 1.** Comparison of Inorganic and Organic Carbon Content of Open-Topped Chamber Soils Prior to Tree Planting (Initial, Spring 1997) and at Harvest (Final, Spring 1999)

Treatment <sup>a</sup>	Depth, cm	Mean Wt % C <sub>inorg</sub> ± s.d. <sup>b</sup>	
		Initial	Final
<i>Low N</i>			
AL	0–10	0.009 ± 0.004	0.042 ± 0.013
	20–30		0.012 ± 0.001
EL	0–10	0.009 ± 0.004	0.013 ± 0.001
	20–30		0.031 ± 0.010
<i>High N</i>			
AH	0–10	0.003 ± 0.000	0.007 ± 0.004
	20–35		0.008 ± 0.003
EH	0–10	0.003 ± 0.000	0.012 ± 0.005
	20–30		0.053 ± 0.064
Treatment <sup>a</sup>	Depth, cm	Mean Wt % C <sub>org</sub> ± s.d. <sup>b</sup>	
		Initial	Final
<i>Low N</i>			
AL	0–10	0.41 ± 0.02	0.36 ± 0.11
	20–30		0.40 ± 0.09
EL	0–10	0.41 ± 0.02	0.43 ± 0.18
	20–30		0.22 ± 0.08
<i>High N</i>			
AH	0–10	1.52 ± 0.05	1.57 ± 0.06
	20–35		1.42 ± 0.09
EH	0–10	1.52 ± 0.05	1.46 ± 0.11
	20–30		1.29 ± 0.19

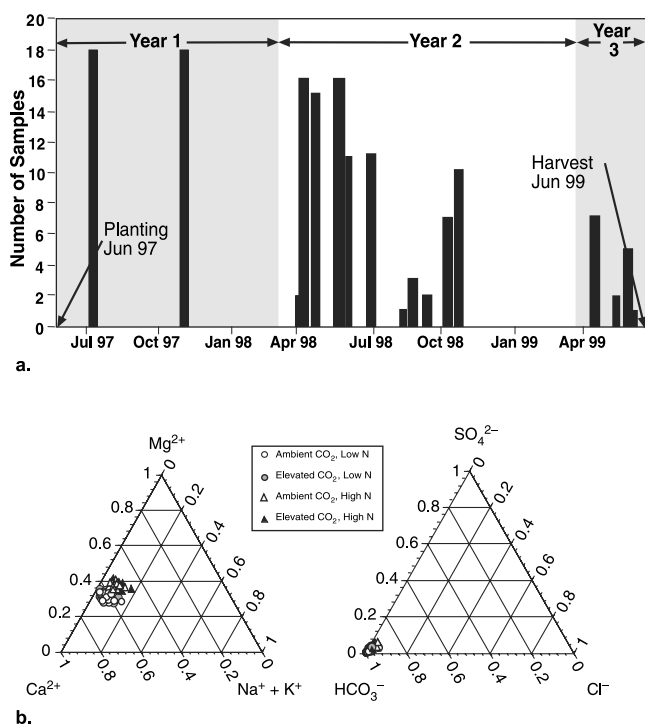
<sup>a</sup>Treatments included low- and high-N-availability soil and ambient and elevated atmospheric CO<sub>2</sub>. AH = ambient CO<sub>2</sub>, high N; AL = ambient CO<sub>2</sub>, low N; EH = elevated CO<sub>2</sub>, high N; EL = elevated CO<sub>2</sub>, low N.

<sup>b</sup>Initial wt.% C<sub>inorg</sub> and C<sub>org</sub> was determined on one sample from each treatment. Initial samples were bulk samples taken from approximately 0–10 cm depth. Final wt.% C<sub>inorg</sub> and C<sub>org</sub> was determined on two soil cores (from different chambers) per treatment, subsampled by depth.

all experimental treatments. In the summer and fall of 1998 and in spring 1999, fewer than half of the lysimeters yielded water, which resulted in difficulties in using ANOVA for statistical tests during these time periods. Soil solutions from spring 1998 were selected to be used in ANOVA tests of treatment effects on chemical concentrations (below). At this time, confounding effects due to the experimental artifacts of uneven water distribution and high NO<sub>3</sub><sup>-</sup> concentrations were minimized.

##### 3.1.3. Soil Gas PCO<sub>2</sub>

[26] Soil gas PCO<sub>2</sub> was measured in eight chambers (two of each treatment) during the growing season in 1998 and 1999, until the trees were harvested. PCO<sub>2</sub> measured at 25 cm depth was followed over time (Figure 2) to compare with chamber soil solution compositions at 15 cm depth. High-N-availability chambers displayed higher soil gas PCO<sub>2</sub> values than did low-N-availability chambers ( $p < 0.0001$ ,  $n = 125$ ; Table 2). PCO<sub>2</sub> in high-N-availability soils was, on average, 41% higher than in low-N-availability soils. A seasonal pattern was also visible ( $p < 0.0001$ ,  $n = 125$ ), with highest concentrations occurring in mid to late June. An additional peak for the high-N-availability chambers appears to have occurred in the beginning of April 1998. Because respiration has been found to respond to temperature and moisture conditions [Reiners, 1968;

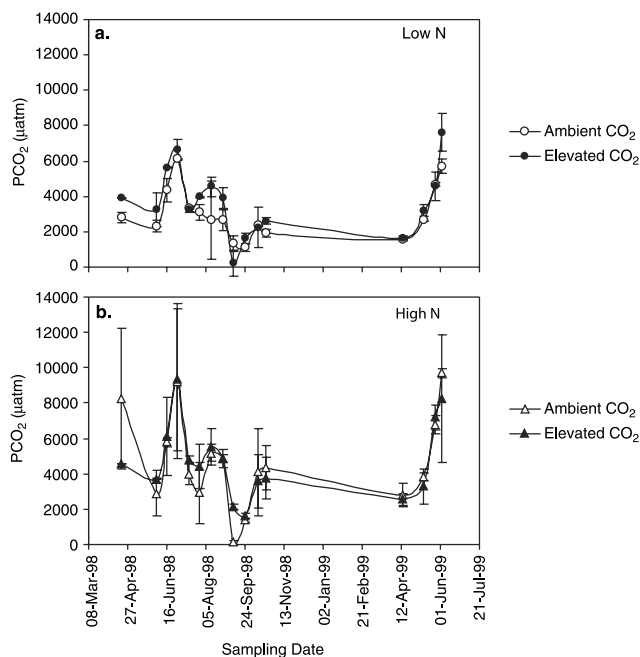


**Figure 1.** (a) The histogram shows the number of soil solution samples obtained from the 20 chambers throughout the course of the experiment. Aspen and maple trees were planted in the chambers in June 1997 and were harvested in June 1999. The two sampling dates in 1997 yielded a large number of samples, but solution chemistries (high NO<sub>3</sub><sup>-</sup>) reflected a transient start-up state of nutrient flushing from the experimental ecosystems. The largest number of samples were obtained in spring 1998. (b) Ternary plots of soil solution chemistry show that soil solution components were primarily of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and HCO<sub>3</sub><sup>-</sup>.

Edwards, 1975; Davidson *et al.*, 1998; Savage and Davidson, 2001], a correlation was performed between mean daily PCO<sub>2</sub> in each experimental treatment and mean daily temperature and past week's precipitation. The correlation coefficient (*r*) between mean daily temperature and mean treatment PCO<sub>2</sub> was as follows: AL = 0.36, EL = 0.34, AH = 0.06, EH = 0.36. Between past 7 days precipitation and mean daily treatment PCO<sub>2</sub>, the following correlation coefficients were calculated: AL = 0.56, EL = 0.62, AH = 0.64, EH = 0.57. Mean soil gas PCO<sub>2</sub> profiles from the chambers in spring 1998 are shown in Figure 3. Profiles reached a maximum PCO<sub>2</sub> by 50 cm depth (just below the maximum depth of the chamber soil fill) and then decreased.

### 3.2. Effects of Experimental Treatments on Chamber Soil Solutions: April–June 1998

[27] Examination of experimental treatment effects on chamber soil solution compositions was complicated by several factors. Results from the first growth season (1997) were obscured by high NO<sub>3</sub><sup>-</sup> concentrations associated with recovery of the experimental system following soil disturbance. Similar problems with NO<sub>3</sub><sup>-</sup> were observed by *John-*



**Figure 2.** Soil gas PCO<sub>2</sub> at 25 cm depth in treatments of (a) low-N-availability soil (ambient versus elevated atmospheric CO<sub>2</sub>) and (b) high-N-availability soil (ambient versus elevated atmospheric CO<sub>2</sub>). Curves connecting sample points do not represent fitted functions. Soil gas PCO<sub>2</sub> was monitored in two chambers of each experimental treatment. Profiles showed higher PCO<sub>2</sub> in high-N-availability chambers. No significant difference was observed between atmospheric CO<sub>2</sub> treatments for a given soil N treatment.

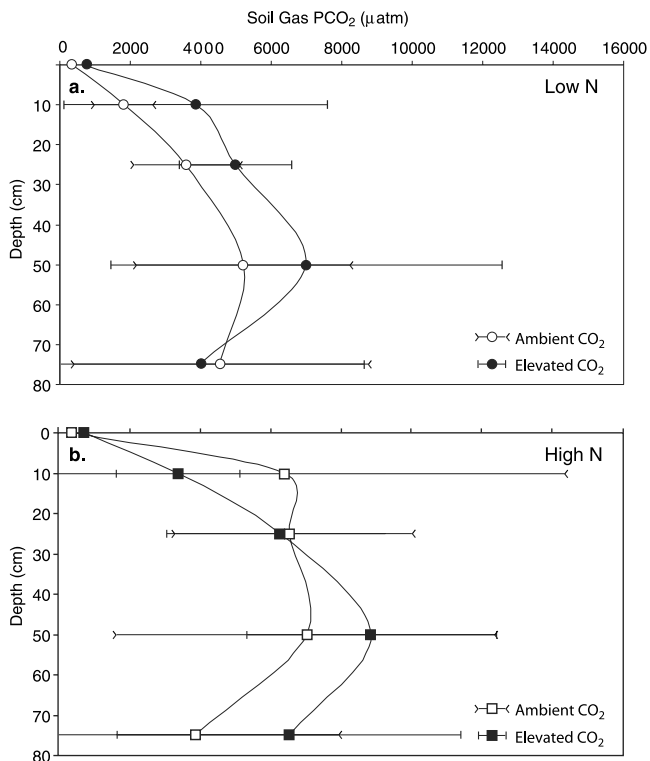
*son et al.* [1995] in a 46-week study of N effects on potted ponderosa pine saplings. In our experiment, because the NO<sub>3</sub><sup>-</sup> was charge-balanced by Ca<sup>2+</sup> and Mg<sup>2+</sup>, an evaluation of Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations during times of high NO<sub>3</sub><sup>-</sup> would have yielded information on soil disturbance rather than on CO<sub>2</sub>-mediated carbonate mineral weathering. Scarcity of samples during the summer and fall of the second growth season (1998) and the third growth season (spring 1999) prevented analysis of data from these time periods

**Table 2.** Results of ANOVA of Atmospheric CO<sub>2</sub> and Soil N-Availability Effects on Soil Gas PCO<sub>2</sub> at 25 cm Depth in Open-Top Chambers

Source of Variation	d.f.	PCO <sub>2</sub> , <sup>a</sup> μatm			Mean Spring 1998 PCO <sub>2</sub> , <sup>b</sup> μatm			
		MS	F	p	d.f.	MS	F	p
Block	1	258280	0.18	0.6759	1	1526296	2.42	0.2178
Time	15	427706918	19.41	<0.0001	—	—	—	—
CO <sub>2</sub>	1	4269186	2.91	0.0912	1	540627	0.86	0.4230
Soil N	1	60646089	41.28	<0.0001	1	8798663	13.94	0.0335
CO <sub>2</sub> × soil N	1	4759081	3.24	0.0748	1	1795197	2.84	0.1903
Error	105	1469251			7	631183		

<sup>a</sup>Analysis was performed on PCO<sub>2</sub> data from two experimental blocks. Data were gathered from spring 1998 through spring 1999.

<sup>b</sup>Analysis was performed on spring 1998 PCO<sub>2</sub> data from two experimental blocks, pooled by chamber.



**Figure 3.** Mean soil gas profiles from the experimental chambers, April–June 1998: (a) low-N-availability soil, (b) high-N-availability soil. Curves connecting sample points do not represent fitted functions. Chambers with elevated atmospheric CO<sub>2</sub> treatments had increased maximum soil gas PCO<sub>2</sub> compared with ambient-CO<sub>2</sub> chambers. Soil PCO<sub>2</sub> profiles showed a maximum concentration at 50 cm depth, much deeper than where soil solution concentrations were measured (15 cm depth). Bars indicate 1 standard deviation.

with the ANOVA method for which the experiment was designed. Spring of 1998 (April–June) provided the most numerous samples after NO<sub>3</sub><sup>-</sup> concentrations had waned, and therefore provided the best opportunity to observe any effects of CO<sub>2</sub> and N treatments on chamber soil solutions.

[28] Mean concentrations of major soil solution elements were determined for each treatment (AL, EL, AH, EH) for the period April to June 1998 by averaging together means from individual chambers. Results from ANOVA modeling are presented in Tables 3 and 4. Experimental block was found to have a significant effect on Ca<sup>2+</sup> ( $p = 0.01$ ), NO<sub>3</sub><sup>-</sup> ( $p = 0.05$ ), and DIC ( $p = 0.02$ ). CO<sub>2</sub> treatment was found to have a significant effect on DIC (elevated > ambient by 12%,  $p = 0.01$ ). For HCO<sub>3</sub><sup>-</sup>, there was evidence of interaction between CO<sub>2</sub> treatment and soil N availability ( $p = 0.02$ ). Soil N availability had a significant effect on mean concentrations of Ca<sup>2+</sup> ( $p = 0.0009$ ), Mg<sup>2+</sup> ( $p < 0.0001$ ), K<sup>+</sup> ( $p = 0.04$ ), Na<sup>+</sup> ( $p = 0.01$ ), NO<sub>3</sub><sup>-</sup> ( $p = 0.0004$ ), SO<sub>4</sub><sup>2-</sup> ( $p = 0.03$ ), and DOC ( $p = 0.007$ ), with higher concentrations observed in the high-N-availability soils (see Table 4 for percentage differences). Spring 1998 PCO<sub>2</sub> at 25 cm depth was also significantly affected by soil N availability, with

50% higher PCO<sub>2</sub> in high-N- than low-N-availability soils ( $p = 0.03$ ; Table 2).

[29] To further examine the CO<sub>2</sub> effect, multiple comparisons of means using the Tukey-Kramer test were made within levels of soil N availability (AL versus EL, AH versus EH; Table 4, Figure 4). No significant differences were observed between mean concentrations of solutions from the AL and EL treatments. Differences in mean concentrations of the AH versus EH treatments were statistically significant for HCO<sub>3</sub><sup>-</sup> ( $p = 0.02$ ) and marginally significant for DIC ( $p = 0.09$ ). Differences between other AH versus EH treatment means (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Si, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, and DOC) were not statistically significant, but they were in the expected direction, with EH means slightly greater than AH means of all species except NO<sub>3</sub><sup>-</sup>.

[30] Figure 4 displays the mean concentrations by experimental treatment of chemical parameters of relevance to C cycling and carbonate mineral weathering, along with  $p$  values from the multiple comparison of means within soil N availability treatment. Mean soil gas PCO<sub>2</sub> values for each treatment at 25 cm depth for spring 1998 are also displayed along with their  $p$  values. The following percentage differences were not statistically significant, except for AH and EH DIC (marginally significant) and HCO<sub>3</sub><sup>-</sup>, as noted above. For carbonate weathering products Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, differences between means of AL and EL treatments were generally small, with EL concentrations 8% to 0.6% lower than AL concentrations. The EL concentrations of DIC were 8% higher than AL concentrations, and average PCO<sub>2</sub> of EL soils was 42% higher than that of AL soils during this time period. High-N-availability soil solutions had higher mean concentrations of all parameters, on average. EH mean concentrations were higher than AH mean concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, DIC, and HCO<sub>3</sub><sup>-</sup> (by 3%, 5%, 15%, and 27%, respectively). Mean PCO<sub>2</sub> was 7% lower in the EH than in the AH treatment. DOC showed minor differences in mean concentration of the EL versus

**Table 3.** Results of ANOVA of Atmospheric CO<sub>2</sub> and Soil N Availability Effects on Mean Soil Solution Chemistry of Open-Top Chambers, April–June 1998 (~1 Year After Tree Planting)<sup>a</sup>

Variable	Error d.f.	Block		CO <sub>2</sub>		Soil N		CO <sub>2</sub> × Soil N	
		F	p	F	p	F	p	F	p
Na <sup>+</sup>	10	0.70	0.6070	0.21	0.6581	8.73	0.0144	0.63	0.4470
K <sup>+</sup>	10	1.72	0.2207	2.72	0.1299	5.48	0.0413	0.04	0.8403
Mg <sup>2+</sup>	10	2.85	0.0819	0.00	0.9885	149.05	<0.0001	2.18	0.1709
Ca <sup>2+</sup>	10	5.35	0.0144	0.05	0.8199	22.01	0.0009	1.39	0.2663
Si	10	0.21	0.9266	1.02	0.3371	2.79	0.1259	0.65	0.4402
Cl <sup>-</sup>	10	0.92	0.4874	0.21	0.6529	0.16	0.6995	0.69	0.4247
SO <sub>4</sub> <sup>2-</sup>	10	1.76	0.2131	3.44	0.0934	5.95	0.0348	3.14	0.1068
NO <sub>3</sub> <sup>-</sup>	10	3.47	0.0502	2.47	0.1473	26.58	0.0004	0.01	0.9113
DOC	11	1.39	0.2989	2.12	0.1732	10.95	0.0070	1.41	0.2593
HCO <sub>3</sub> <sup>-</sup>	10	2.23	0.1384	6.96 <sup>b</sup>	0.0248 <sup>b</sup>	0.39 <sup>b</sup>	0.5461 <sup>b</sup>	7.62	0.0201
DIC	11	4.41	0.0227	8.81	0.0128	0.67	0.4318	0.84	0.3791

<sup>a</sup> $\alpha = 0.05$ . Model degrees of freedom for  $F$  test: Block = 4, CO<sub>2</sub> = 1, Soil N = 1, CO<sub>2</sub> × Soil N = 1.

<sup>b</sup>A post-hoc one-way ANOVA was carried out for the HCO<sub>3</sub><sup>-</sup> response variable due to the significant CO<sub>2</sub> × Soil N interaction. Unbiased  $F$  and  $p$ -values for CO<sub>2</sub> and soil N determined in this manner were as follows: for CO<sub>2</sub>,  $F = 2.71$ ,  $p = 0.1189$ ; for soil N,  $F = 1.64$ ,  $p = 0.2191$ .

**Table 4.** Mean Chemical Compositions (mM) of Soil Solutions Collected From Open-Topped Chambers, April–June 1998<sup>a</sup>

Species	Interaction Least Squares Means <sup>b</sup>				Main-Effect Least Squares Means <sup>b,c</sup>					
	Low Soil N		High Soil N		Soil N			Atmospheric CO <sub>2</sub>		
	Amb. CO <sub>2</sub>	Elev. CO <sub>2</sub>	Amb. CO <sub>2</sub>	Elev. CO <sub>2</sub>	Low	High	% Change	Amb.	Elev.	% Change
Ca	0.85	0.81	0.98	1.0	0.83	0.99	19	0.91	0.91	0.84
(s.e.)	(0.31)	(0.31)	(0.36)	(0.36)	(0.22)	(0.27)		(0.24)	(0.24)	
n	5	5	4	4	10	8		9	9	
Mg	0.44	0.41	0.71	0.74	0.42	0.73	71	0.58	0.58	0.06
(s.e.)	(0.22)	(0.22)	(0.26)	(0.26)	(0.16)	(0.19)		(0.17)	(0.17)	
n	5	5	4	4	10	8		9	9	
Na	0.081	0.074	0.13	0.15	0.078	0.14	77	0.10	0.11	8.5
(s.e.)	(0.18)	(0.18)	(0.21)	(0.21)	(0.13)	(0.16)		(0.14)	(0.14)	
n	5	5	4	4	10	8		9	9	
K	0.040	0.029	0.053	0.045	0.035	0.049	41	0.047	0.037	-21
(s.e.)	(0.0055)	(0.0055)	(0.0064)	(0.0064)	(0.0039)	(0.0048)		(0.0042)	(0.0042)	
n	5	5	4	4	10	8		9	9	
Si	0.17	0.18	0.19	0.22	0.17	0.21	19	0.18	0.20	11
(s.e.)	(0.018)	(0.021)	(0.018)	(0.021)	(0.013)	(0.015)		(0.014)	(0.014)	
n	5	5	4	4	10	8		9	9	
NO <sub>3</sub> <sup>-</sup>	0.31	0.14	0.81	0.66	0.23	0.73	225	0.56	0.40	-28
(s.e.)	(0.089)	(0.089)	(0.12)	(0.089)	(0.063)	(0.076)		(0.076)	(0.063)	
n	5	5	3	5	10	8		8	10	
SO <sub>4</sub> <sup>2-</sup>	0.039	0.040	0.046	0.082	0.039	0.064	62	0.042	0.061	44
(s.e.)	(0.0090)	(0.0090)	(0.0012)	(0.0090)	(0.0064)	(0.0077)		(0.0077)	(0.0064)	
n	5	5	3	5	10	8		8	10	
Cl <sup>-</sup>	0.032	0.023	0.029	0.032	0.027	0.030	11	0.031	0.027	-11
(s.e.)	(0.0069)	(0.0069)	(0.0094)	(0.0069)	(0.0048)	(0.0058)		(0.0058)	(0.0048)	
n	5	5	3	5	10	8		8	10	
HCO <sub>3</sub> <sup>-</sup>	2.2	2.2	2.0 <sup>d</sup>	2.6 <sup>d</sup>	2.2	2.3	2.8	2.1	2.4	13
(s.e.)	(0.092)	(0.092)	(0.13)	(0.092)	(0.065)	(0.078)		(0.078)	(0.065)	
n	5	5	3	5	10	8		8	10	
DIC	2.1	2.3	2.1 <sup>e</sup>	2.5 <sup>e</sup>	2.2	2.3	3.0	2.1	2.4	12
(s.e.)	(0.080)	(0.080)	(0.092)	(0.080)	(0.057)	(0.061)		(0.061)	(0.061)	
n	5	5	4	5	10	9		9	10	
DOC	2.0	2.0	2.5	3.1	2.0	2.8	38	2.2	2.5	15
(s.e.)	(0.22)	(0.22)	(0.25)	(0.22)	(0.15)	(0.17)		(0.17)	(0.15)	
n	5	5	4	5	10	9		9	10	

<sup>a</sup>Amb. = ambient, Elev. = elevated, n = treatment sample size, s.e. = standard error.

<sup>b</sup>Least squares means were calculated instead of arithmetic means to compensate for missing values in the balanced experimental design. Where n = 5 or 10, least squares means were identical to arithmetic means and otherwise, were always within 7% of the arithmetic means.

<sup>c</sup>Statistical significance of main effects means can be found in Table 3.

<sup>d</sup>Interaction means compared within Soil N treatment were significantly different at the 0.05 level.

<sup>e</sup>Interaction means were marginally significantly different at the 0.1 level.

AL treatment (3%). Mean concentrations of DOC in EH treatments were 25% greater than those of AH treatments.

[31] Trends in the mean concentrations of chemical constituents derived from atmospheric deposition (Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were also evaluated within low- and high-N-availability treatments, though no difference was statistically significant. Mean Cl<sup>-</sup> of the high-N-availability treatment was 11% higher than that of the low-N-availability treatment. Within the N-availability treatments, mean Cl<sup>-</sup> in the EL chambers was 30% lower than in the AL chambers and 10% higher in EH than in AH chambers. In contrast, the trends in mean SO<sub>4</sub><sup>2-</sup> concentrations were similar in direction to those observed for the majority of the C-related parameters. SO<sub>4</sub><sup>2-</sup> concentration in the EL treatment was 2% higher than in the AL treatment, and was 80% higher in the EH than in the AH treatment.

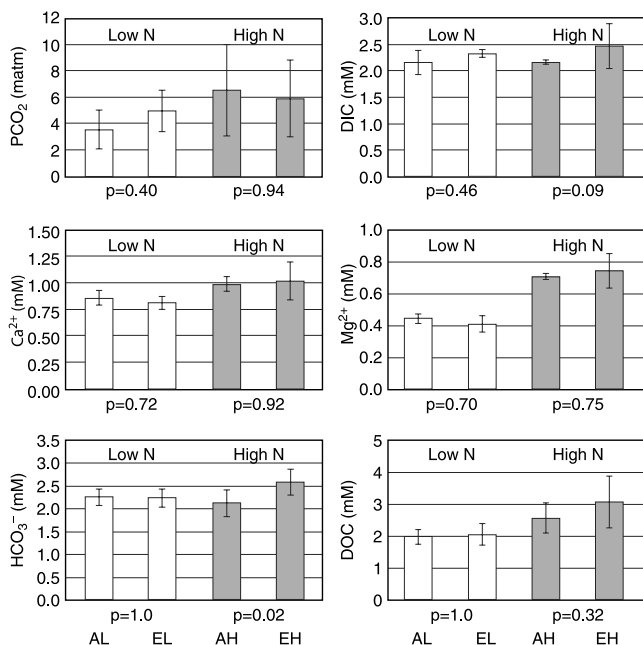
### 3.3. Geochemical Modeling of the Carbonate System

[32] Data from June 1998 were input into SOLMINEQ.88 in order to model PCO<sub>2</sub> and the state of equilibrium with respect to calcite and disordered dolomite in the soil solutions. This time period was selected because (1) by spring

1998, initial high solute concentrations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, NO<sub>3</sub><sup>-</sup>) had flushed through, and (2) pH measurements were available. Measured pH and HCO<sub>3</sub><sup>-</sup> concentrations (from alkalinity or alkalinity calculated by charge balance) are reported in Table 5 with the model results. The K<sub>sp</sub> of disordered dolomite was calculated from the empirical results of *Hyeong and Capuano* [2001], using a solution Mg/Ca ratio of 0.6. Cation and anion concentrations are given by *Williams* [2000]. In spring 1998, solutions from both high- and low-N-availability soils were at saturation to slightly supersaturated with calcite and were close to saturation to slightly undersaturated with disordered dolomite.

[33] A graph of disordered dolomite theoretical solubility with PCO<sub>2</sub> was used to infer the vertical variability of cation concentrations and soil gas PCO<sub>2</sub> where direct measurements were not made (Figure 5). This approach assumes equilibrium with disordered dolomite, which is suggested by the modeled saturation states. To estimate mean PCO<sub>2</sub> at 15 cm, mean observed spring 1998 Ca<sup>2+</sup> + Mg<sup>2+</sup> concentrations from each of the experimental treatments were plotted on the disordered dolomite solubility curve, yielding the following results in units of atm (μatm): AL = 10<sup>-2.88</sup>





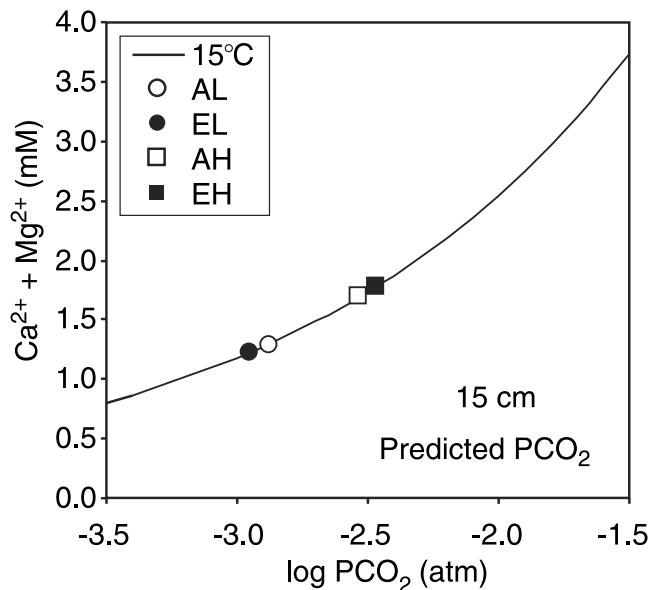
**Figure 4.** Mean spring 1998 concentrations of soil solution and soil gas components related to carbon cycling and mineral weathering (HCO<sub>3</sub><sup>-</sup>, DIC, Ca<sup>2+</sup>, Mg<sup>2+</sup>, PCO<sub>2</sub>, DOC), arranged by experimental treatment. Bars show 1 standard deviation. Multiple comparison of means testing was performed using a Tukey-Kramer adjustment to control overall error ( $\alpha = 0.05$ ). P-values shown in the figure represent the significance of the effect of CO<sub>2</sub> treatment within the two levels of N availability treatments. Treatment abbreviations: AH = ambient atmospheric CO<sub>2</sub>, high-N-availability soil; AL = ambient atmospheric CO<sub>2</sub>, low-N-availability soil; EH = elevated atmospheric CO<sub>2</sub>, high-N-availability soil; EL = elevated atmospheric CO<sub>2</sub>, low-N-availability soil.

(1320); EL = 10<sup>-2.94</sup> (1150); AH = 10<sup>-2.53</sup> (2950); EH = 10<sup>-2.48</sup> (3310).

## 4. Discussion

### 4.1. Soil Carbon

[34] Limited soil carbon data were collected during the experiment. However, our results suggest the lack of an



**Figure 5.** The curve represents the theoretical relation between solubility of disordered dolomite and PCO<sub>2</sub> at 15°C. The relation was used with mean spring 1998 Ca<sup>2+</sup> + Mg<sup>2+</sup> concentrations measured in soil solutions to predict PCO<sub>2</sub> at 15 cm, where PCO<sub>2</sub> was not measured (circles and squares). Treatment abbreviations: AH = ambient atmospheric CO<sub>2</sub>, high-N-availability soil; AL = ambient atmospheric CO<sub>2</sub>, low-N-availability soil; EH = elevated atmospheric CO<sub>2</sub>, high-N-availability soil; EL = elevated atmospheric CO<sub>2</sub>, low-N-availability soil.

effect of atmospheric CO<sub>2</sub> treatment on soil organic carbon accumulation after 2 years, despite previous evidence of rapid carbon cycling in the experimental ecosystem [Prezitzer *et al.*, 2000]. This apparent lack of carbon accumulation tends to support the findings of Schlesinger and Lichter [2001] in a loblolly pine plantation and Hungate *et al.* [1997] in grasslands, and adds to the uncertainty about whether the soil carbon pool will act as a net sink for atmospheric CO<sub>2</sub> [Cox *et al.*, 2000].

### 4.2. Soil Gas PCO<sub>2</sub> and Carbonate Saturation State

[35] Soil gas PCO<sub>2</sub> was examined over the course of the experiment because solubility of carbonate minerals

**Table 5.** Carbonate Saturation State ( $\Omega$ ) Modeling Inputs and Results for Chamber Soil Solutions on June 30, 1998<sup>a</sup>

Chamber ID <sup>b</sup>	Treatment <sup>c</sup>	Temp. <sup>d</sup> °C	pH	HCO <sub>3</sub> <sup>-</sup> , mM	Modeled log $\Omega_{\text{calcite}}$	Modeled log $\Omega_{\text{dis. dolomite}}$	Modeled log PCO <sub>2</sub> , atm
2-1	AL	20	7.62	2.94	0.06	-0.32	-2.40
3-4	AL	20	7.63	2.84	-0.03	-0.40	-2.43
3-3	EL	20	7.66	3.04	0.08	-0.20	-2.42
4-2	EL	20	7.63	3.39	0.13	-0.17	-2.35
4-4	EH	20	7.66	3.29	0.10	-0.03	-2.39

<sup>a</sup>Saturation states were modeled using SOLMINEQ.88. The K<sub>sp</sub> of disordered dolomite was calculated from the empirical equation of Hyeong and Capuano (2001). For comparison, average measured log PCO<sub>2</sub> (atm) on 6/30/98 listed by treatment: at 10 cm depth, AL = -2.95, AH = -2.28, EL = -2.50, EH = -2.47; at 25 cm depth, AL = -2.21, AH = -2.03, EL = -2.17, EH = -2.02.

<sup>b</sup>Chambers were coded by block (1-5) and row numbers 1-4 (4 treatments), for example, Chamber 2-1 indicates block 2, row 1.

<sup>c</sup>AH = ambient atmospheric CO<sub>2</sub>, high-N-availability soil; AL = ambient atmospheric CO<sub>2</sub>, low-N-availability soil; EH = elevated atmospheric CO<sub>2</sub>, high-N-availability soil; EL = elevated atmospheric CO<sub>2</sub>, low-N-availability soil.

<sup>d</sup>Typical late spring/early summer temperature used for modeling purposes. Not measured temperature.



increases with PCO<sub>2</sub>. Soil gas PCO<sub>2</sub> measured at 25 cm depth showed a seasonal pattern, with highest concentrations occurring in June, shortly after the beginning of the trees' growing season (Figure 2), with lower values later in the summer. This suggests a different PCO<sub>2</sub> profile pattern from that presented by the *Reardon et al.* [1979] study of carbonate-bearing soils at Trout Creek, Ontario, where PCO<sub>2</sub> in the rooting zone increased throughout the growing season until early autumn, and then decreased. The different PCO<sub>2</sub> trend observed in the chambers may reflect the difference in stand type and age between the two studies (aspen saplings in chambers compared with a mature mixed conifer-deciduous forest). It is possible that rapid tree growth and root respiration during the early part of the growing season caused the PCO<sub>2</sub> patterns we observed. Additionally, it is possible that soil respiration in the chambers decreased during dry summer periods and increased with soil moisture following rain events [Reiners, 1968; Edwards, 1975; Davidson *et al.*, 1998], when either microbial activity increased or soil gas diffusivity decreased [Davidson and Trumbore, 1995]. Comparison of daily mean PCO<sub>2</sub> at 25 cm depth from each experimental treatment with NOAA climate data from the Pellston area suggest that PCO<sub>2</sub> is weakly positively correlated with daily mean temperature ( $r = 0.06 - 0.36$ ) and total rainfall during the previous week ( $r = 0.56 - 0.64$ ).

[36] Superimposed on the seasonal patterns in PCO<sub>2</sub> observed in all the chamber treatments was a difference between PCO<sub>2</sub> in high and low N-availability soils. The effect of soil N-availability on soil respiration was manifested in the 41% higher PCO<sub>2</sub> at 25 cm depth of high-N-availability chamber soils than low-N-availability soils. This result correlates well with observations from a previous set of chamber experiments using trembling aspen and the same soil N treatments, in which fine root biomass was 137–194% larger and mean rates of soil respiration were doubled in high compared with low-N-availability soil [Pregitzer *et al.*, 2000]. Although part of the difference in PCO<sub>2</sub> between the high- and low-N-availability soil treatments may be due to the finer texture of the high-N-availability soil, the significantly higher root biomass in high-N soil suggests that much of the treatment difference in PCO<sub>2</sub> does reflect differences in soil CO<sub>2</sub> production.

[37] Because the solubility of carbonate minerals increases as PCO<sub>2</sub> increases, higher PCO<sub>2</sub> in the high-N-availability chambers implies a greater capacity for carbonate weathering and accordingly, a higher dissolved inorganic carbon concentration. Silicate weathering was expected to respond less to higher PCO<sub>2</sub> than to increased DOC from higher rates of organic matter turnover observed under increased atmospheric CO<sub>2</sub>, and this topic is being addressed in a separate paper. Geochemical modeling was used to examine the state of the carbonate system during spring 1998, when soil solutions were examined in detail. Mean soil gas PCO<sub>2</sub> values from 10 and 25 cm on June 30, 1998, bracketed the modeled dissolved phase PCO<sub>2</sub> values from 15 cm, providing evidence that the geochemical model accurately describes the natural system (Table 5). The modeling results show that in spring 1998

the carbonate system in the chamber soils was at equilibrium (note that the AH treatment lacked sufficient data for modeling at this time). Soil solutions in June 1998 were at saturation to slightly supersaturated with respect to calcite and approached saturation with disordered dolomite. Soil solutions evolve from initial rain water composition, which is highly undersaturated with respect to carbonate minerals, and progressively react with mineral soil. The fact that chamber soil solutions are at equilibrium with calcite and approach saturation with disordered dolomite at 15 cm depth suggests that weathering of carbonate minerals in the soil has taken place to the point of saturation. These minerals are the most reactive and most soluble phases in the experimental soils, so dissolution of another Ca- and Mg-bearing phase to the point of saturation with calcite or disordered dolomite is not likely. Our results suggest dissolution of dolomite and calcite in the chamber soils and indicate how shallowly in the soil profile, and therefore how rapidly, waters can attain equilibrium with respect to carbonate minerals, when present.

### 4.3. Mean Spring 1998 Soil Solution Chemistry and Implications for an Elevated CO<sub>2</sub> World

[38] Because of the complicating factors of high NO<sub>3</sub><sup>-</sup> in the beginning of the experiment, and scarcity of samples from mid-1998 through 1999, a small window of opportunity, April–June 1998, remained for examining statistically the effect of elevated atmospheric CO<sub>2</sub> on mineral weathering and C concentrations in soil solutions. To test the hypothesis of increased mineral weathering under the elevated CO<sub>2</sub> and high-N-availability treatments, we examined soil solution chemistry as well as soil gas PCO<sub>2</sub> in the different experimental treatments. It was predicted that faster tree growth and higher rates of root respiration under the elevated CO<sub>2</sub> treatment would lead to increased soil gas PCO<sub>2</sub> and thus higher carbonate mineral weathering rates. In addition, increased rates of organic matter turnover under an elevated CO<sub>2</sub> environment would lead to higher DOC concentrations, the respiration of which could further increase soil gas PCO<sub>2</sub> and accelerate weathering rates. Higher tree growth rates in high- compared with low-N-availability soil were expected to enhance mineral weathering in high-N-availability soil. The differences in soil solution chemistry among treatments are assumed to represent differences in mineral weathering, although an ion exchange component is possible (but likely minor in these sandy soils). The differences in concentrations are further assumed to be proportional to differences in elemental fluxes in solutions draining the soil because solution fluxes were not measured.

[39] When treatment means of soil solution chemical compositions were compared, most of the differences in mean concentrations between elevated and ambient atmospheric CO<sub>2</sub> treatments were not statistically significant. A small response of weathering to a doubling of atmospheric CO<sub>2</sub> would be reasonable, given that Pregitzer *et al.* [2000] observed a 19–25% increase in soil respiration rates in their chamber experiments under the twice ambient CO<sub>2</sub> treatment. We observed a significant 12% increase in mean DIC

under the elevated atmospheric CO<sub>2</sub> treatment, and a significant interaction between soil N-availability and CO<sub>2</sub> treatment for HCO<sub>3</sub><sup>-</sup>. In high-N-availability soil, HCO<sub>3</sub><sup>-</sup> and DIC were higher in the elevated CO<sub>2</sub> treatment than in ambient CO<sub>2</sub>. Mean concentrations of soil solution constituents Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, Si, Na<sup>+</sup>, and DOC generally increased in the order AL  $\cong$  EL (or EL < AL)  $\leq$  AH < EH. Mean PCO<sub>2</sub> for the different treatments during April–June 1998 displayed a different pattern than expected: AL < EL < EH < AH, but only the difference between high- and low-N-availability soil was significant.

[40] Atmospheric CO<sub>2</sub> treatment appears to have had little effect on mineral weathering in the low-N-availability soils, with mean concentrations of most carbonate parameters decreasing under elevated CO<sub>2</sub>. In high-N-availability soil the elevated CO<sub>2</sub> treatment appears to be correlated with slightly higher mean solute concentrations (DIC, 15%; HCO<sub>3</sub><sup>-</sup>, 27%; Ca<sup>2+</sup>, 3%, not significant; Mg<sup>2+</sup>, 5%, not significant), suggesting that high soil N magnifies the CO<sub>2</sub> effect. This result is reasonable because PCO<sub>2</sub> and DOC in soils are controlled primarily by root respiration and organic matter turnover, which in turn are directly related to vegetative growth [Raich and Schlesinger, 1992; Kalbitz *et al.*, 2000]. In high-N-availability soil, which has been found to have higher fine-root biomass and higher rates of soil respiration than low-N-availability soil [Pregitzer *et al.*, 2000], increased atmospheric CO<sub>2</sub> would be expected to have a larger effect on tree growth, soil gas PCO<sub>2</sub>, and organic matter turnover.

[41] We found that soil N availability appears to have had a stronger effect on soil solution cation concentrations than did CO<sub>2</sub> treatment. Spring 1998 concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and DOC were all significantly higher in high- than low-N-availability soil. For carbonate parameters Ca<sup>2+</sup> and Mg<sup>2+</sup>, concentrations were 19 and 71% higher, respectively, in high-N-availability soil than in low-N-availability soil. The differences in HCO<sub>3</sub><sup>-</sup> and DIC were 3% (similar in magnitude to the CO<sub>2</sub> effect on Ca<sup>2+</sup> and Mg<sup>2+</sup> in EH versus AH soils), and not statistically significant. It is likely that the continued production of NO<sub>3</sub><sup>-</sup> in the high-N-availability soil in spring 1998 contributed to the observed differences in cation concentrations in the two soil treatments. Though much decreased from fall 1997, the NO<sub>3</sub><sup>-</sup> concentration in the high-N soil in spring 1998 was still 225% higher than in the low-N soil. Therefore, although higher carbonate mineral weathering rates would be predicted in high-N-availability soil because of the observed PCO<sub>2</sub> differences, a definite effect on mineral weathering could not be completely distinguished from the NO<sub>3</sub><sup>-</sup> effect.

[42] The spring 1998 results from the chamber experiments demonstrate that soil solution chemistry responds quickly to changes in organic and inorganic carbon cycling in the soil. Our results suggest a small increase in carbonate weathering rates under a doubling of atmospheric CO<sub>2</sub>, and predict an increase in weathering rates in high-N-availability soil. As atmospheric CO<sub>2</sub> levels continue to rise over the next century, small increases in mineral weathering rates are likely to occur. If weathering inputs to soil solutions increase while overall water fluxes remain constant, the

increase in weathering will correspond to increased cation and carbon fluxes from terrestrial ecosystems.

#### 4.4. The Carbonate System Revisited: Importance of Carbonate Terrains for Drawdown of Atmospheric CO<sub>2</sub>

[43] Theoretical modeling of the carbonate system allows for extension of the observations of soil solution chemistry at 15 cm to predict the chemistry at other depths, up to the maximum PCO<sub>2</sub>. As PCO<sub>2</sub> in the profile increased with depth, assuming equilibrium with disordered dolomite, Ca<sup>2+</sup> + Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations would increase (e.g., 33 to 85% higher at 50 cm than at 15 cm). If these solutions moved downward to a zone of lower PCO<sub>2</sub>, soil solutions would become supersaturated with respect to calcite, which could precipitate, removing Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>, but leaving Mg<sup>2+</sup> in solution. The kinetics of calcite precipitation are slow, however, and a constant Mg/Ca ratio in groundwaters and groundwater-fed streams of northern Michigan [Ku, 2001] suggest that calcite precipitation is not an important pathway for inorganic C loss. These results suggest that carbonate dissolution may be an extremely effective pathway by which atmospherically derived CO<sub>2</sub> may be converted to dissolved forms and transferred to groundwater or ocean reservoirs on a timescale of 10<sup>2</sup>–10<sup>4</sup> years.

[44] Andrews and Schlesinger [2001] recently reported that under a 55% increase in atmospheric CO<sub>2</sub> in a 15-year-old loblolly pine forest in the Duke forest, there was an increase over 3 years in soil respiration, soil gas PCO<sub>2</sub>, soil solution cation concentrations, and alkalinity. Soil solution concentrations observed in their experiment differed markedly from ours because of the differing geological substrate (perhaps coupled with differences in stand ages). Andrews and Schlesinger's experiment was conducted in a silicate terrain with clay-rich soils, where ion exchange and slow silicate mineral dissolution produced the soil solutions observed. Our chamber experiments, in contrast, were conducted in sandy glacial soils with mixed silicate and carbonate mineralogy, and dissolution of reactive carbonate minerals dominated the soil solution chemistry. Alkalinities reported by Andrews and Schlesinger were on the order of 0.1 meq L<sup>-1</sup> at 15 cm and 0.6–1.7 meq L<sup>-1</sup> at 200 cm. Total cation concentrations were 0.4 meq L<sup>-1</sup> at 15 cm and 0.8–2.8 meq L<sup>-1</sup> at 200 cm. By contrast, at only 15 cm in our chamber experiments, mean HCO<sub>3</sub><sup>-</sup> of 2.0–2.6 meq L<sup>-1</sup> and Ca<sup>2+</sup> + Mg<sup>2+</sup> concentrations of 2.4–3.6 meq L<sup>-1</sup> were observed in spring 1998. These results are not directly comparable because carbonate minerals are so reactive that only in disturbed soil profiles would carbonates be encountered at a shallow depth of 15 cm. Nonetheless, the contrast in soil types between the Duke forest and northern Michigan illustrates the higher soil solution concentrations, which mirror higher stream fluxes of the weathering products Ca<sup>2+</sup>, Mg<sup>2+</sup>, and HCO<sub>3</sub><sup>-</sup> typical of carbonate-bearing terrains [e.g., Amiotte Suchet and Probst, 1993; Roy *et al.*, 1999].

[45] Another difference between the two experiments was that much higher PCO<sub>2</sub> values were observed by Andrews and Schlesinger [2001]. They found that in 1998, mean PCO<sub>2</sub> in control plots ranged from 0.7 % at 15 cm to 4.2 %

at 200 cm (0.007–0.042 atm), and PCO<sub>2</sub> in elevated CO<sub>2</sub> plots ranged from 1.0 % to 4.6 % (0.01–0.046 atm) in 1998. These PCO<sub>2</sub> values, which were an order of magnitude higher than those observed in the chambers, reflect the fine clay soil texture, as well as the much larger soil biomass of 15-year-old trees. If the soil solutions at these high PCO<sub>2</sub> values were in contact with carbonate minerals, equilibrium with disordered dolomite at 15°C would produce HCO<sub>3</sub><sup>-</sup> concentrations at 200 cm of 8.2 and 8.4 mM in the ambient and elevated CO<sub>2</sub> treatments, respectively. While this yields only a 3% difference in HCO<sub>3</sub><sup>-</sup> concentrations in ambient versus elevated CO<sub>2</sub> plots, the effect of dissolving carbonate minerals would increase Andrews and Schlesinger's observed weathering flux by at least 3 times, assuming that alkalinity at 200 cm is proportional to flux to lower soil levels and eventually groundwater. From this discussion, one can conclude that in tandem, soil gas PCO<sub>2</sub> and the presence of reactive carbonate minerals have the potential for contributing noticeably to the transport of increased atmospheric CO<sub>2</sub> to groundwaters and stream waters. We propose that under increased atmospheric CO<sub>2</sub>, areas underlain by carbonate-bearing soils will be more effective than silicate-rich areas in drawing down atmospheric CO<sub>2</sub> through mineral weathering reactions.

## 5. Conclusions and Implications

[46] This field-scale experiment set out to evaluate the effects on mineral weathering of atmospheric CO<sub>2</sub> levels that will be encountered within the century. Experimental northern Michigan soils were distinct from soils used in many other weathering experiments (e.g., Hubbard Brook, Duke Forest) in that both carbonate minerals and aluminosilicates occurred together in the soil. Results from spring 1998 soil solution chemistries demonstrated that under a twice-ambient CO<sub>2</sub> atmosphere, concentrations of DIC increased significantly, and HCO<sub>3</sub><sup>-</sup> increased under twice-ambient CO<sub>2</sub> and high soil N. Little CO<sub>2</sub> effect was observed in low-N-availability soils. Soil N availability had a statistically significant positive effect on concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and DOC, but it was difficult to distinguish whether the increased concentrations were related to higher PCO<sub>2</sub> or higher NO<sub>3</sub><sup>-</sup> in the high-N-availability soil solutions. The trend in soil gas PCO<sub>2</sub> at 25 cm in spring 1998 was generally consistent with the soil solution chemistry observed, with PCO<sub>2</sub> increasing in the treatment order AL < EL < EH < AH. Over the course of the experiment, high-N-availability soil had on average 41% higher PCO<sub>2</sub> than low-N-availability soil, but no statistically significant CO<sub>2</sub> treatment effect was observed.

[47] Soil N fertilization and atmospheric CO<sub>2</sub> fertilization are both important controls on mineral weathering, mediated by vegetative production of soil gas PCO<sub>2</sub> and DOC. The experimental results suggest that in a world with elevated atmospheric CO<sub>2</sub>, global weathering fluxes may be increased, especially in reactive carbonate-bearing terrains. Our results demonstrate that when reactive carbonate minerals occur even in trace amounts in the zone of maximum PCO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>-rich groundwater-like solutions result. The fate of the solute-rich soil solutions depends on the kinetics of calcite precipitation

and the shape of the soil gas PCO<sub>2</sub> profile down to the water table. If HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> are able to remain in solution until the soil solutions joined the groundwater system, the dissolution of carbonate minerals at the maximum zone of soil gas PCO<sub>2</sub> would significantly enhance C transport to shallow groundwaters, and the export of C in river systems.

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