Patterns of Ca/Sr and $^{87}Sr/^{86}Sr$ variation before and after a whole watershed $CaSiO_3$ addition at the Hubbard Brook Experimental Forest, USA

Carmen A. Nezat [a,1], Joel D. Blum [a,*], Charles T. Driscoll [b]

[a] Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109, USA
[b] Department of Civil and Environmental Engineering, Syracuse University, Syracuse, NY 13244, USA

Abstract

Forty-one metric tons of the mineral wollastonite ($CaSiO_3$) was applied to an 11.8 hectare watershed at the Hubbard Brook Experimental Forest (HBEF; White Mountains, New Hampshire, USA) with the goal of restoring the Ca estimated to have been depleted from the soil exchange complex by acid deposition. This experiment provided an opportunity to gain qualitative information on whole watershed hydrologic flow paths by studying the response of stream water chemistry to the addition of Ca. Because the Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of wollastonite strongly contrast that of other Ca sources in the watershed, the wollastonite-derived Ca can be identified and its amount estimated in various ecosystem components. Stream water chemistry at the HBEF varies seasonally due to shifts in the proportion of base flow and interflow. Prior to the wollastonite application, seasonal variations in $^{87}Sr/^{86}Sr$ ratios indicated that $^{87}Sr/^{86}Sr$ was higher during base flow than interflow, due largely to greater amounts of biotite weathering along deeper flow paths. After the application, Ca/Sr and $^{87}Sr/^{86}Sr$ changed markedly as the high Ca/Sr and low $^{87}Sr/^{86}Sr$ wollastonite dissolved and mixed with stream water. The Ca addition provided information on the response times of various flow paths and ion exchange processes to Ca addition in this small upland watershed. During the first year after the addition, wollastonite applied to the near stream zone dissolved and was partially immobilized by cation exchange sites in the hyporheic zone. In the second and third years after the addition we infer that much of this Ca and Sr was subsequently desorbed from the hyporheic zone and was exported from the watershed in stream flow. In the fourth through ninth years after the addition, Ca and Sr from wollastonite that had dissolved in upland soils was transported to the stream by interflow during wet periods when the ground water table was elevated. Between years three and nine the minimum annual Ca/Sr ratio (in late summer base flow) increased, providing evidence that Ca and Sr had increasingly infiltrated to the deepest flow paths. Strong seasonal variations in Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of stream water resulted from the wollastonite addition to upland forest soils, and these ratios have become sensitive to changing flow paths during the annual cycle. Most notably, high flow events now produce large excursions in stream geochemistry toward the high Ca/Sr and low $^{87}Sr/^{86}Sr$ ratios of wollastonite. Nine years after the application we estimate that ~360 kg of Ca from wollastonite has been exported from the watershed in stream flow. The rate of export of Ca from wollastonite dissolution has stabilized at about 11 kg of Ca per year, which accounts for ~30% of the dissolved Ca in the stream water. Given that 19 metric tons of Ca were applied to the watershed, and assuming this current rate of loss, it should take over 1000 years for this added Ca to be transported from the watershed.
© 2010 Elsevier Ltd. All rights reserved.

---

* Corresponding author. Tel.: +1 734 615 3242.
  E-mail address: jdblum@umich.edu (J.D. Blum).
[1] Present address: Department of Geology, Eastern Washington University, Cheney, WA 99004, USA.

1. INTRODUCTION

1.1. Acid deposition and Ca

Accelerated leaching of Ca from the soil exchange complex has occurred in eastern North America for at least the past five decades (e.g., Likens et al., 1996; Huntington et al., 2000; Watmough and Dillon, 2003) due to the effects of acid deposition on pools of plant-available calcium. Despite a decrease since the 1970s in the anthropogenic emissions that cause acid deposition, stream pH and acid neutralizing capacity (ANC) have been slow to recover (Likens et al., 1996). Moreover, a recent survey shows that despite some recovery of surface waters, current inputs of acidic deposition are still resulting in the net loss of exchangeable Ca, with equivalent increases in exchangeable Al in Ca-poor watersheds across the Northeast USA (Warby et al., 2009). Many soils in this region are developed on Ca-poor silicate rocks that undergo weathering at a rate too slow to readily replenish Ca lost from the exchange pool (Likens et al., 1996; Nezat et al., 2004; Blum et al., 2008). It has been suggested that Ca may become a limiting nutrient for vegetation and at low levels may contribute to a decline in the health of some plants and animals in the region. For example, sugar maple decline in non-glaciated watersheds in the Northeast US has been linked to both low concentrations of Ca and Mg (and high concentrations of Mn) in foliage (Long et al., 1997; Horsley et al., 2000; Bailey et al., 2004; St. Clair et al., 2005). In addition, the decline of red spruce has been related to high Al/Ca ratios in the soil exchange complex (Lawrence et al., 1995). At the Hubbard Brook Experimental Forest (HBEF) recent studies indicate that an increase in plant-available Ca improved the health and survival of sugar maple (Juice et al., 2006), decreased winter injury in red spruce (Hawley et al., 2006), and increased snail abundance (Sheldon et al., 2007).

In order to investigate the role of plant-available Ca on the health of flora and fauna in a forest affected by acid deposition, 41 tons of powdered and pelletized wollastonite ($CaSiO_3$) was evenly distributed by helicopter across Watershed 1 (W-1) of the HBEF on October 19th and 20th, 1999 (Peters et al., 2004). The goal of this experiment was to return the base saturation in the soil to pre-acid deposition values, estimated to be about twice the current value (Likens et al., 1998). Because the wollastonite has trace elemental and isotopic ratios (e.g., Ca/Sr and $^{87}Sr/^{86}Sr$) that allow it to be distinguished from other Ca sources in the forest (mineral weathering and atmospheric deposition), the wollastonite-derived Ca can be traced through the ecosystem and quantified in the various ecosystem pools (e.g., stream water, soil water, roots, leaves; Peters et al., 2004; Dasch et al., 2006).

Both base flow and interflow contribute to the stream water chemistry at the HBEF (Hogan and Blum, 2003; Cho et al., 2009). Due to differential mineral weathering rates and differential contributions from atmospheric deposition with soil depth, Ca/Sr and $^{87}Sr/^{86}Sr$ ratios can in many watersheds be used to distinguish base flow from interflow (Bain et al., 1998; Bullen and Kendall, 1998; Land et al., 2000; Hogan and Blum, 2003; Keller et al., 2010). Ca/

Sr and $^{87}Sr/^{86}Sr$ ratios have also been used effectively to distinguish between various sources of Ca in stream water (Bailey et al., 1996; Jacobson and Blum, 2000; Aubert et al., 2002; Tipper et al., 2006; Shand et al., 2007; Pett-Ridge et al., 2009). In this study we modified the chemical signature (Ca/Sr and $^{87}Sr/^{86}Sr$) of interflow in the entire watershed by adding wollastonite, and this allows us to explore the use of Ca/Sr and $^{87}Sr/^{86}Sr$ as flowpath tracers in a unique way.

1.2. Previous studies of Ca addition at Hubbard Brook

Previous studies of the HBEF W-1 wollastonite application determined that wollastonite-derived Ca has been incorporated into tree foliage, tree roots, and understory plants (Dasch et al., 2006; Juice et al., 2006) and that the proportion of Ca derived from wollastonite increased every year for the five years following the application (Dasch et al., 2006). It was also found that pH and Ca concentrations in the surface soil horizons (Oa and Oie) have increased (Fiorentino et al., 2003; Dasch et al., 2006; Fisk et al., 2006; Cho et al., 2010), and Ca derived from wollastonite has been incorporated into snail shells (Sheldon et al., 2007). However, there was no clear evidence that Ca derived from wollastonite had migrated below the forest floor during the first five years following the Ca addition (Dasch et al., 2006).

During the year following the wollastonite addition, most of the wollastonite-derived Ca that was dissolved in stream water originated from the dissolution of pellets that were directly deposited into the stream channel (Peters et al., 2004). Average annual stream water Ca concentrations increased (from 0.87 to 2.6 mg/L), Ca/Sr ratios increased (from 306 to 655 mol/mol) and $^{87}Sr/^{86}Sr$ ratios decreased (from 0.72032 to 0.71818) in the first year following the application. Using the $^{87}Sr/^{86}Sr$ and Ca/Sr ratios of wollastonite and pre-application stream water, Peters et al. (2004) calculated that 401 kg (~64%) of the wollastonite applied to the stream channel had dissolved and was transported out of the watershed by the end of the first year. The ~36% of wollastonite-derived Ca that remained in the stream channel was either present as undissolved wollastonite or, more likely, as Ca that was adsorbed to cation exchange sites in the hyporheic zone. Peters et al. (2004) hypothesized that the Ca adsorbed in the hyporheic zone buffered the stream water chemistry, resulting in relatively constant Ca concentrations even as discharge fluctuated by several orders of magnitude. Cho et al. (2009) investigated the effect of the wollastonite addition on the acid neutralizing capacity (ANC) of W-1 stream water during storm events in 2003. They found that the ANC was positive during storm events (and negative in a reference watershed) due to enhanced Ca supply from wollastonite as the result of interflow along shallow flow paths. This suggests that wollastonite treatment can help to mitigate the intensity of episodic acidification in summer storms (Cho et al., 2009).

In a complimentary experiment of Ca addition to a HBEF stream, Likens et al. (2004) also demonstrated that the hyporheic zone plays an important role in buffering

stream water chemistry. In that study, wollastonite was added to a 50-m reach of stream at a density similar to the W-1 application (336 g $CaSiO_3/m^2$ compared to 350 g $CaSiO_3/m^2$). Relative to a reference reach upstream of this application, the dissolved Ca in the manipulated section remained elevated for ~80 days after the application. Ca was exported via stream water much more slowly than the predicted dissolution rate of $CaSiO_3$ indicating that Ca was adsorbed onto cation exchange sites on stream sediments and/or organic matter (Likens et al., 2004). The amount of Ca absorbed and released from the cation exchange sites in the streambed channel and hyporheic zone appears to be strongly controlled by pH. Hall et al. (2001) added $CaCl_2$ to two HBEF stream channels daily for 2 months, with one of the streams buffered by addition of $NaHCO_3$. In the buffered stream, a net amount of Ca was retained in the reach during the 2-month addition, and released in excess of Cl following the cessation of the $CaCl_2$ addition. Hall et al. (2001) concluded that Ca was adsorbed onto cation exchange sites within the stream channel when pH was neutral (i.e., during the Ca addition while the stream was buffered) and desorbed when stream water pH decreased after the addition.

1.3. Objectives

The specific objectives of this study were to report on long-term changes in the Ca, Sr, and Sr isotope chemistry induced by wollastonite addition to HBEF W-1 and explore the implications of this addition for watershed hydrogeochemistry. We use qualitative interpretations of the stream water time-series to infer watershed-wide processes. Specifically, we investigate: (1) seasonal changes in stream water chemistry due to varying contributions from base flow and interflow; (2) the amount of time for wollastonite deposited directly into the stream channel to dissolve and for the Ca and Sr released to become sequestered in the hyporheic zone exchange complex; (3) the amount of time for the Ca and Sr to be released from the hyporheic zone exchange complex; (4) the extent to which Ca and Sr released from wollastonite deposited on upland forest soil was transported through the soil and into the stream; and (5) the amount of wollastonite-derived Ca that has been exported from HBEF W-1 via stream flow.

2. METHODS

2.1. Site description

Hubbard Brook Experimental Forest (43° 56′N, 71° 45′W) is located in the White Mountains, New Hampshire, USA. The wollastonite application occurred in Watershed 1 (W-1; 11.8 ha), one of a series of stream-gauged south-facing experimental watersheds (Fig. 1). The climate is humid continental with an average annual rainfall of 1300 mm (Likens et al., 1977). The bedrock beneath the eastern portion of HBEF is the Rangeley Formation, a pelitic schist and meta-sandstone, and the Kinsman granodiorite (Barton et al., 1997). The bedrock beneath the watersheds is relatively impermeable so that inputs and outputs of water

and its dissolved constituents can be quantified (Likens et al., 1998). Glacial till, deposited during the retreat of the last continental ice sheets ~14,000 years ago, is composed of local bedrock and averages about 2 m in thickness (Davis et al., 1985; Bailey et al., 2003). Soils are well-drained Spodosols (Haplorthods) about 60 cm deep that have developed in the till (Johnson et al., 1991). The vegetation is northern hardwood forest consisting of sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*), and yellow birch (*Betula allegheniensis*). At higher elevations, red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), and white birch (*Betula papyrifera*) are common.

2.2. Wollastonite addition

Wollastonite was mined from the No. 4 Quarry of the Valentine Mine in the northwestern Adirondack Mountains of New York, crushed to a mean grain size of 16 μm, and formed into pellets (~3 mm in diameter) using a water-soluble lignin sulfonate binder (Peters et al., 2004). Forty-one metric tons of wollastonite was evenly distributed (at ~345 g/m^2) by helicopter to the experimental watershed (W-1) at the Hubbard Brook Experimental Forest on October 19th and 20th, 1999. The wollastonite has Ca/Sr (2870 ± 36, mol/mol, 1σ) and $^{87}Sr/^{86}Sr$ (0.70588 ± 0.00003, 2σ) ratios that are distinct from the other Ca sources in the watershed and allow for the tracking of the wollastonite-derived Ca as it is transported through the ecosystem (Dasch et al., 2006; Peters et al., 2004).

2.3. Stream water collection and analysis

Stream waters were collected weekly in acid-washed LDPE bottles approximately 10 m upstream of the gauging weir. During several late summer periods of the study, stream discharge ceased (Fig. 3) and samples could not be collected. In particular, during August of Years 2 and 3 after the wollastonite application there were no samples collected. This part of the record, therefore, requires extrapolation to make interpretations of seasonal trends. Cation (Ca, Na, Sr) concentrations were measured using an Inductively Coupled Plasma Emission Spectrometer (ICP-OES; PE-3300DV, Perkin Elmer, Norwalk, CT) with a five- to eight-point calibration curve. Replicate analysis of NIST-traceable quality control standards indicate that analytical accuracy was within ±5%. To prepare water samples for Sr isotope analysis, an aliquot containing ~100 ng of Sr was evaporated to dryness and redissolved in concentrated ultrapure HNO_3. This solution was evaporated, redissolved in 3 M ultrapure HNO_3, and loaded onto a quartz column containing Eichrom Sr-Spec resin. The separated Sr was evaporated and dissolved in 0.3 M H_3PO_4 and then loaded onto W filaments using Ta_2O_5 powder. Between 100 and 200 isotope ratio measurements were made per sample using a thermal ionization mass spectrometer (Finnigan MAT 262, Bremen, Germany). To correct for instrumental mass fractionation, the $^{87}Sr/^{86}Sr$ ratios were normalized to an $^{86}Sr/^{88}Sr$ ratio of 0.1194. Multiple measurements of NBS987 yielded an $^{87}Sr/^{86}Sr$ ratio of 0.710252 ± 0.000013 (2σ, $n = 161$).
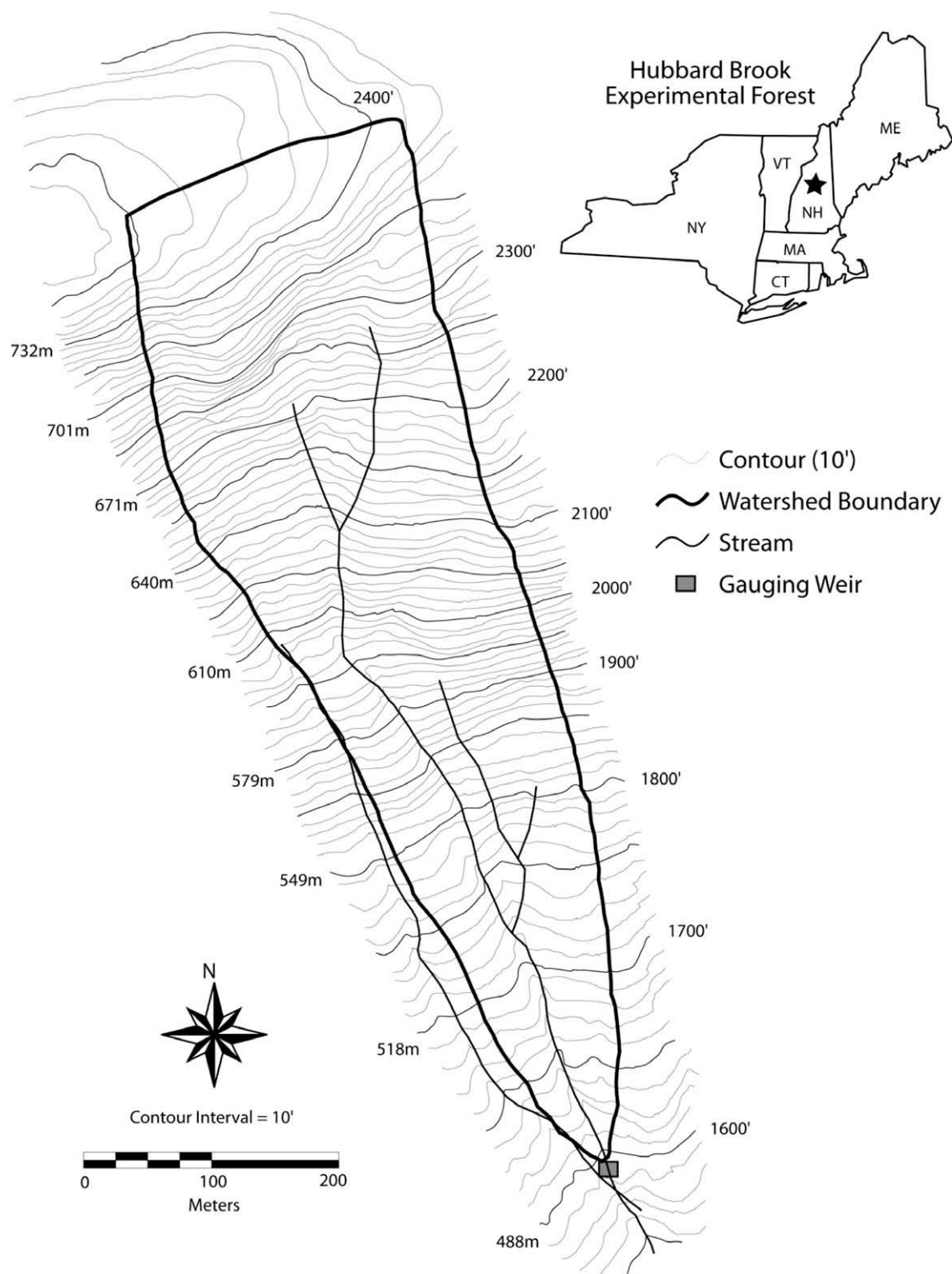
Fig. 1. Topographic map and regional location of Watershed 1 of the Hubbard Brook Experimental Forest.

2.4. Calculation of wollastonite-derived Ca in stream water

To calculate the contribution of Ca in stream water from wollastonite dissolution, a two component isotope solute mixing model was employed where the two endmember components were the chemical compositions of the pre-application stream water and the wollastonite. Mixing of the two components produces a linear relationship between $^{87}Sr/^{86}Sr$ and Ca/Sr ratios of the two endmembers (Peters et al., 2004). The fraction of Sr in stream water (X_{Sr}) from

wollastonite dissolution was calculated from the following equations adapted from Faure (1984):

$$X_{Sr} = \left[\frac{\left(\frac{^{87}Sr}{^{86}Sr}\right)_{Stream} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{Pre\text{-}app}}{\left(\frac{^{87}Sr}{^{86}Sr}\right)_{Wollastonite} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{Pre\text{-}App}} \right]$$

Assuming Sr is a reasonable proxy for Ca, the fraction of Ca in stream water from wollastonite dissolution can be calculated as follows:

$$X_{Ca} = \left[\frac{\left(\left(\frac{^{87}Sr}{^{86}Sr}\right)_{Stream} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{Pre\text{-}App}\right)\left(\frac{Sr}{Ca}\right)_{Pre\text{-}App}}{\left(\left(\frac{^{87}Sr}{^{86}Sr}\right)_{Stream} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{Pre\text{-}App}\right)\left(\frac{Sr}{Ca}\right)_{Pre\text{-}App} + \left(\left(\frac{^{87}Sr}{^{86}Sr}\right)_{Wollastonite} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{Stream}\right)\left(\frac{Sr}{Ca}\right)_{Wollastonite}} \right]$$

The fraction of Ca derived from wollastonite dissolution was multiplied by the weekly stream water Ca fluxes. The calculated amount of weekly wollastonite-derived Ca was summed to determine the cumulative amount that had exited the watershed dissolved in stream water.

3. RESULTS

3.1. Mean annual variations in stream water chemistry

We examined changes in the stream water chemistry of W-1 before and after the watershed-scale wollastonite application. For the two year period before the wollastonite application (Years -1 and -2 on Fig. 2), Ca concentrations remained relatively constant (0.81 ± 0.08 mg/L, 1σ; range = 0.65–1.02 mg/L) even during large seasonal and storm-induced hydrologic changes in the stream discharge. In the year following the wollastonite addition (Year 1) Ca concentrations in the stream rapidly increased to a new mean of 2.34 ± 0.25 mg/L, decreased to 1.76 ± 0.10 mg/L during Year 2, and then leveled off in subsequent years (Fig. 2). The mean Ca concentration in Year 9 (1.30 ± 0.09 mg/L) was still 1.6 times higher than the pre-application value.

Strontium concentrations showed a less dramatic response to the application because the wollastonite has a very low Sr content compared to Ca (Ca/Sr = 2870 ± 36 mol/mol, 1σ; Dasch et al., 2006). Sr concentration increased from a pre-application mean of 5.72 ± 0.58 µg/L to a new mean of 7.88 ± 0.78 µg/L during Year 1, and then decreased until Year 4 when it reached a value that was not significantly different from the pre-application concentration (Fig. 2). The $^{87}Sr/^{86}Sr$ ratio averaged 0.72034 ± 0.00008 for the two years preceding the application. The $^{87}Sr/^{86}Sr$ ratio decreased to an average ratio of 0.71858 during Year 1, and then increased rapidly until Year 4, when it leveled off. During Year 9, the $^{87}Sr/^{86}Sr$ ratio averaged 0.71969 ± 0.00009, which was still significantly lower than pre-application values (Fig. 3).

Na concentrations increased following the application due to a small amount of Na in the wollastonite binder (0.25% Na_2O; Peters et al., 2004). The mean annual concentration after the wollastonite application (e.g., Year 1: 1.03 ± 0.10 mg/L) was, however, only slightly higher than the pre-application value (0.83 ± 0.14 mg/L; Fig. 2).

3.2. Seasonal variations in stream water chemistry

In order to understand the W-1 stream response to the wollastonite addition, we first examined elemental concentrations, Ca/Sr ratios and $^{87}Sr/^{86}Sr$ ratios for the two years prior to the wollastonite application. As noted by Likens et al. (1977), we observed that Ca concentrations in HBEF stream waters changed very little with discharge whereas Na concentrations were more sensitive to discharge due to a dilution effect (Fig. 2). We found that prior to the wollastonite addition Ca/Sr ratios also did not change considerably with discharge (Fig. 3). The $^{87}Sr/^{86}Sr$ ratio displayed variability with changes in discharge, and also exhibited a clear seasonal pattern for each of the two years prior to the wollastonite addition (Fig. 3). In each of the two years prior to the application, the $^{87}Sr/^{86}Sr$ ratio was at its maximum annual value of 0.72050–0.72060 around October 1st, and then within 1–2 weeks decreased rapidly to 0.72025–0.72030. The $^{87}Sr/^{86}Sr$ ratio typically remained low through the winter and reached a minimum annual value of ~0.7202 in April, then gradually increased through spring and summer back to its annual maximum in October.

The Ca/Sr ratio began to exhibit a clear seasonal pattern two years after the wollastonite application. Beginning in Year 2, the Ca/Sr ratio increased markedly within a few weeks of October 1st, and then decreased from mid-October until the following late September or early October, except for brief periods when stream discharge was very high (Fig. 3). During Years 2 and 3, the peak Ca/Sr ratio in November did not reach the highest ratio from the previous fall, indicating that each year the stream chemistry was less influenced by the wollastonite application than during the previous year. Following Year 3, the Ca/Sr ratio increased more gradually from September to November. Starting at the end of Year 3, the minimum annual Ca/Sr ratio increased every year. The maximum Ca/Sr ratio did not show any obvious pattern from year-to-year.

Following the wollastonite addition the $^{87}Sr/^{86}Sr$ ratio decreased markedly to 0.71784 in the first week and then generally increased for three years (Fig. 3). During those three years following the wollastonite addition the seasonal pattern of $^{87}Sr/^{86}Sr$ variation ceased and sharp decreases in
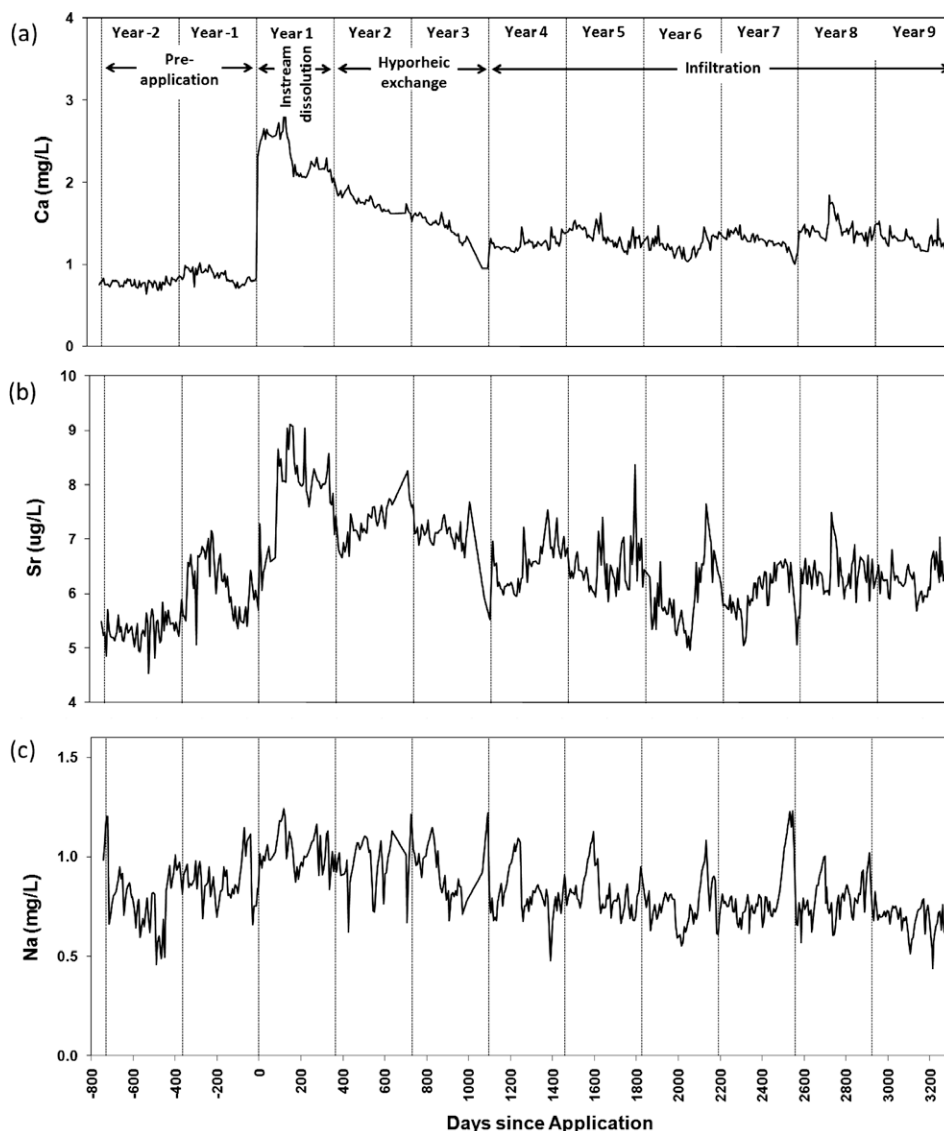
Fig. 2. Stream water concentrations for Watershed 1 prior to and after the wollastonite application. (a) Ca, (b) Sr and (c) Na. The time axis is the number of days prior to or after the application (October 19, 1999). The timing and duration of each of the process periods is indicated. The vertical lines represent October 19st of each year.

the $^{87}Sr/^{86}Sr$ ratio were observed, typically following large discharge events caused by snow melt or rainfall events (e.g., 550 days after the application, Fig. 3). Starting in Year 6, seasonal patterns in the $^{87}Sr/^{86}Sr$ resumed. The $^{87}Sr/^{86}Sr$ ratio reached a maximum around October 1st and decreased rapidly within a few weeks (typically mid-October). The $^{87}Sr/^{86}Sr$ generally stayed low through the winter and increased during the spring and summer, reaching an annual maximum again in early October.

4. DISCUSSION

To facilitate discussion of the W-1 stream water time-series of Ca and Sr concentrations and Ca/Sr and $^{87}Sr/^{86}Sr$ ratios, we organized the 11-year record into four periods that (in chronological order and based on the dominant process that was occurring) we term: (1) pre-application,

(2) in-stream dissolution, (3) hyporheic exchange, and (4) infiltration. The pre-application period includes the two years before the wollastonite addition; the in-stream dissolution period includes the first year after the wollastonite addition; the hyporheic exchange period includes the second and third years after the wollastonite addition; and the infiltration period includes the fourth through ninth years after the wollastonite addition (Fig. 2). Peters et al. (2004) reported data from one year before and one year after the wollastonite addition, concluding that the stream water chemistry in the first year after application was dominated by in-stream dissolution of wollastonite and loading of the hyporheic zone exchange sites. By analyzing samples for two full years before and nine years after the application we now more fully capture seasonal patterns in chemistry in the pre-application period, and we also evaluate seasonal patterns and long-term trends following the application.
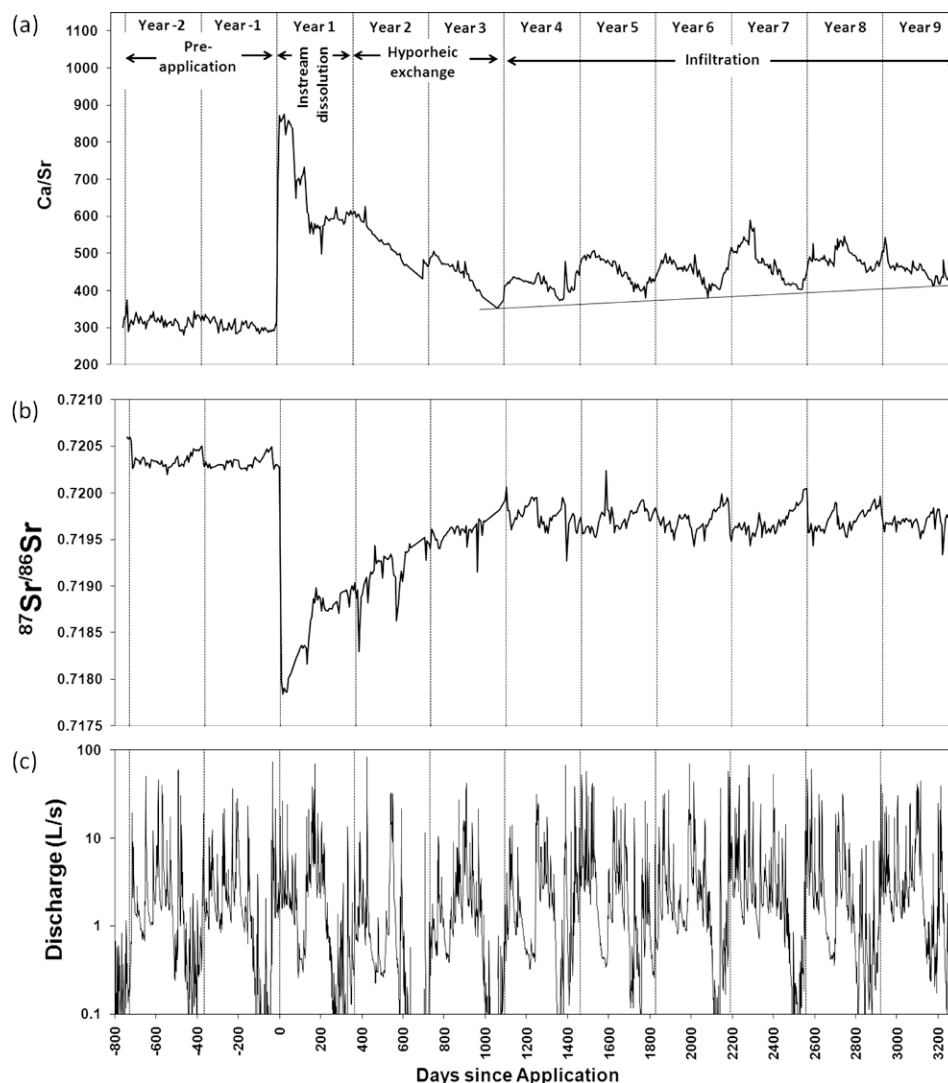
Fig. 3. Stream water chemistry and discharge for Watershed 1 prior to and after the wollastonite application. (a) Ca/Sr ratios, (b) ^{87}Sr/^{86}Sr ratios and (c) stream discharge in L/sec. The time axis is the number of days prior to or after the application (October 19, 1999). The timing and duration of each of the process periods is indicated. The vertical lines represent October 19st of each year.

4.1. Pre-application period (Years -1 and -2)

In order to interpret changes in stream water chemistry following the wollastonite application, we first investigated patterns in Ca, Sr and Na concentrations and Sr isotope ratios for the two years preceding the application. Seasonal patterns were not discernable in Ca, Sr or Na concentrations and the relative standard deviation in concentration over this period was 9% for Ca, 10% for Sr, and 17% for Na (Fig. 2), demonstrating that Ca and Sr concentrations are more strongly buffered than Na concentrations during large changes in stream discharge (Likens et al., 1977; Peters et al., 2004). Similarly, the Ca/Sr ratio in stream water did not show a clear seasonal pattern (Fig. 4). In contrast ^{87}Sr/^{86}Sr ratios in stream water displayed a clear seasonal pattern of variation (Fig. 4). We consider below whether this pattern is related to seasonal changes in (1) groundwater flow path, (2) the relative contribution of water from

higher versus lower elevations in the watershed, or (3) foliar leaching.

Seasonal changes in groundwater flow path are controlled by the depth of the water table and respond to precipitation and evapotranspiration rates. The water table and stream discharge are lowest during the summer and early fall, and are highest in the late fall through spring (Fig. 4). During the summer, evapotranspiration is high and stream discharge is low and increasingly dominated by base flow originating from the deepest flow paths. In October, leaf senescence occurs, evapotranspiration decreases substantially, and the water table rises along with stream discharge as interflow becomes more important (Hogan and Blum, 2003).

Seasonal changes in ^{87}Sr/^{86}Sr during the pre-application period reflect changes in flow path. The ^{87}Sr/^{86}Sr ratio was highest during the late summer and early fall when discharge is at its annual minimum and base flow is largely
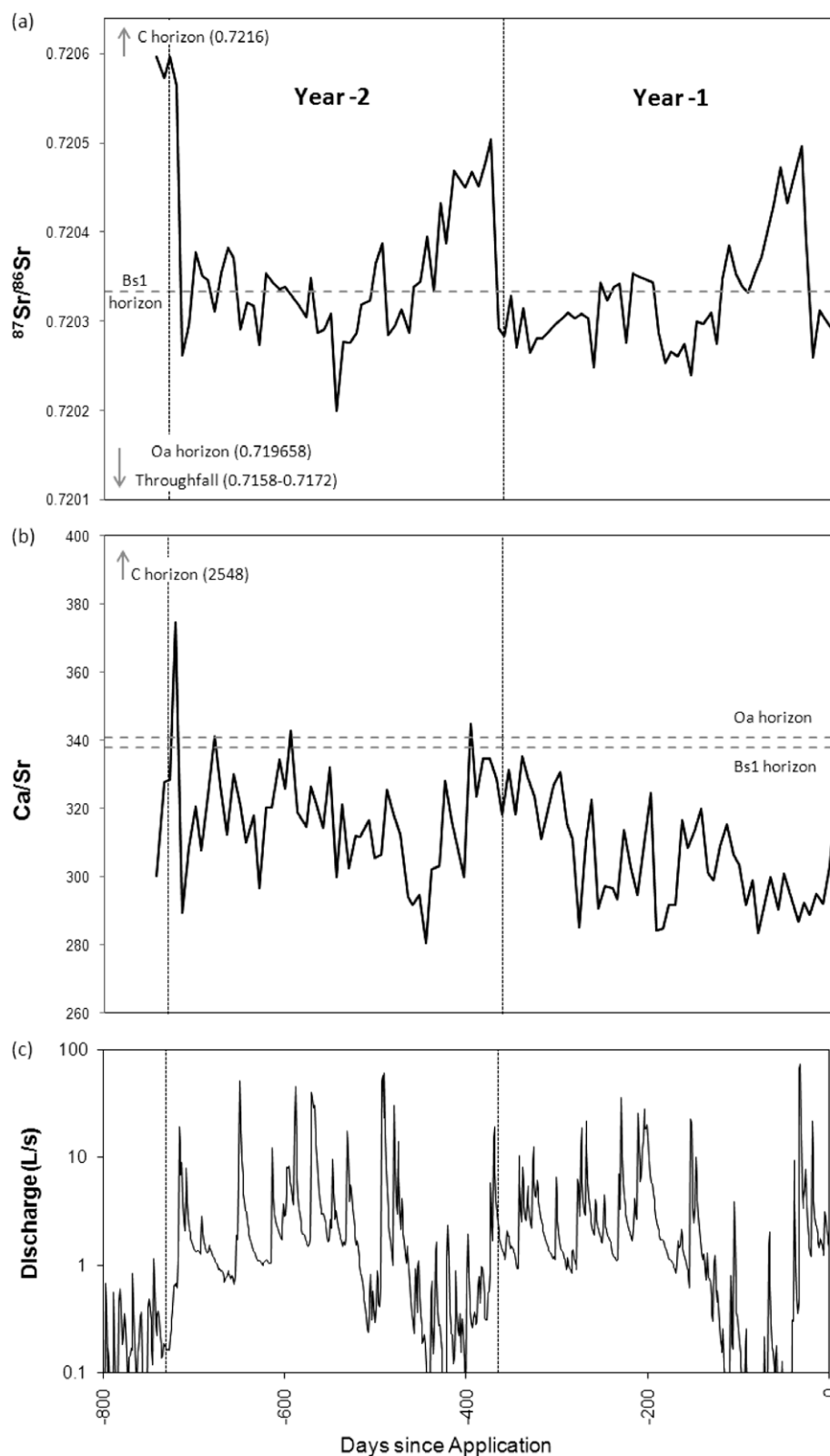
Fig. 4. Stream water chemistry and discharge for Watershed 1 prior to the wollastonite application. (a) Ca/Sr ratios, (b) ^{87}Sr/^{86}Sr ratios and (c) stream discharge in L/sec. Dilute acid leaches of soil horizons Oa, Bs1, and C are indicated and are represented by horizontal dashed lines when they fall within the sample range (data from Nezat et al., 2007). Throughfall data are from Hogan and Blum (2003); values represent the average ratio for 12 locations in W-1 on July 20, 1999 and July 29, 1999, respectively. The time axis is the number of days prior to or after the application (October 19, 1999). The vertical lines represent October 19st of each year.

supplying the stream. During each October, $^{87}Sr/^{86}Sr$ decreases over a 1- to 2-week period as stream discharge increases, consistent with an increasing contribution from throughfall and the cation exchange complex in shallow soils (Blum et al., 2002; Hogan and Blum, 2003; Fig. 4). In the late fall and winter, when evapotranspiration rates are low, shallow soils are often saturated (Hogan and Blum, 2003) and there is greater exchange with stored cations, which are transported to the stream as interflow. In the late summer and early fall, stream discharge decreases to a minimum and the $^{87}Sr/^{86}Sr$ ratio increases to its highest annual value (Fig. 4). This pattern is consistent with the finding of Hogan and Blum (2003) that base flow has higher $^{87}Sr/^{86}Sr$ due to controls by mineral weathering along deeper flow paths. Hogan and Blum (2003) found that during storm events, $^{87}Sr/^{86}Sr$ decreased as discharge increased over the course of a few hours and then returned to the pre-storm value following the event. Using $\delta^{18}O$, Ca/Sr and $^{87}Sr/^{86}Sr$ of HBEF throughfall, soil water, and stream water, Hogan and Blum (2003) determined that interflow contributed up to 40% of storm flow when soil moisture was high.

The increase in $^{87}Sr/^{86}Sr$ ratio through the summer as the water table drops (in the years before the wollastonite addition) suggests that radiogenic minerals are being weathered deep in the soil. We attribute the high $^{87}Sr/^{86}Sr$ ratio of base flow to weathering of biotite and other easily weathered minerals deep in the soil profile. Dilute acid leaches ($1\ M\ HNO_3$) of Hubbard Brook soils show that the $^{87}Sr/^{86}Sr$ ratio of this "weatherable" soil fraction ranges from an average of 0.71966 in the Oa horizon to 0.72033 in the Bs2 horizon to 0.72159 in the C horizon (Fig. 4; Nezat et al., 2004). Other studies have also shown that high $^{87}Sr/^{86}Sr$ ratios released during weathering of granitoid rocks are often due to biotite dissolution (Blum et al., 1994; Bullen et al., 1996; Blum and Erel, 1997) because ^{87}Sr is preferentially released from interlayer cation sites during the early stages of biotite weathering (Acker and Bricker, 1992; Kalinowski and Schweda, 1996; Taylor et al., 2000).

Based on $^{87}Sr/^{86}Sr$ values, we ruled out the possible explanation that the rapid decrease in stream $^{87}Sr/^{86}Sr$ in the fall was due to a greater contribution of water from higher elevations in the watershed. The upper-most reaches of the HBEF streams only flow during periods of high discharge. Soil waters at higher elevations have the highest $^{87}Sr/^{86}Sr$ ratios (Hogan and Blum, 2003). If soil water contributions from the upper elevations were more substantial during high discharge in the fall (when the upper stream is most likely to be flowing) then we would expect higher, not lower, $^{87}Sr/^{86}Sr$ ratios in stream water.

In a study at the Strengbach catchment in the Vosges Mountains in France, researchers found that stream water $^{87}Sr/^{86}Sr$ ratios varied during a storm event as relative contributions of soil water from different parts of the watershed changed (Aubert et al., 2002). In that case, however, the $^{87}Sr/^{86}Sr$ ratios of the bedrock were variable due to hydrothermal alteration of bedrock in some areas. At the HBEF, the soil parent material is relatively homogeneous and small variations in soil composition with elevation are believed to be due to differential weathering rates rather than parent material heterogeneity (Nezat et al., 2004).

We also explored the idea that other seasonal changes associated with foliage might cause seasonal variations in stream water chemistry. During the growing season, throughfall has ~10 times more Ca and Sr than precipitation (Likens et al., 1998; Hogan and Blum, 2003). However, leaching of foliage during the summer could not account for the increase in stream water $^{87}Sr/^{86}Sr$ ratio because throughfall has a lower $^{87}Sr/^{86}Sr$ ratio than that of stream water (Hogan and Blum, 2003). Foliage in W-1 prior to the wollastonite application also had lower $^{87}Sr/^{86}Sr$ ratios than stream water (Dasch et al., 2006). On the other hand, leaching of leaves once they have fallen on the soil surface or into the stream channel could account for some of the decrease in $^{87}Sr/^{86}Sr$ ratio of stream water in autumn.

4.2. In-stream dissolution period (Year 1)

The first post-application weekly stream water sample was collected 5 days after the wollastonite addition. This sample reflected the marked changes in stream water chemistry due to dissolution of wollastonite deposited directly into the stream (see discussion in Peters et al., 2004). Within 2 weeks the Ca concentration had nearly tripled to ~2.5 mg/L, but the Sr and Na concentrations did not deviate beyond their pre-application range. We did not anticipate a response for Na, which had very low concentration in the wollastonite. The Ca/Sr ratio of the wollastonite is much higher than the pre-application stream value (2870 versus 306 mol/mol), so a smaller response was expected from Sr compared to Ca, but an increase in Sr concentration was still anticipated. The Sr concentration did eventually increase by ~40% to 8.5 μg/L, but it was delayed by ~12 weeks compared to the increase in Ca.

The simplest explanation for the delay in the Sr concentration increase is that Sr was retained due to stronger binding than Ca on ion exchange sites in the hyporheic zone. There are little relevant exchange coefficient data in the literature for both Ca and Sr, and what little data there are yields conflicting views as to which element is more strongly bound (Bruggenwert and Kamphorst, 1982; Baes and Bloom, 1988; Sposito, 1989; Poszwa et al., 2000; Drouet and Herbauts, 2008). Pett-Ridge et al. (2009) suggested that the ion exchange affinities for Ca and Sr depend on a range of variables including substrate and pH, and therefore may be site specific. We suggest that either: (a) for the materials in the stream hyporheic zone and at the stream pH, Sr was retained by ion exchange more strongly than Ca; or (b) Ca was released preferentially to Sr from wollastonite as it dissolved in the stream channel. The Ca concentration decreased from its peak of ~2.5 to ~2.1 mg/L after ~25 weeks and the Sr concentration remained near its peak of ~8.5 μg/L for ~40 weeks and then decreased to ~6.8 mg/L. This pattern suggests that Sr was retarded relative to Ca for ~12 weeks, and that when released, the concentration spike derived from the wollastonite dissolution in the stream was ~25 weeks in duration for Ca compared to ~40 weeks in duration for Sr. This retardation and dispersion of the Sr concentration peak is similar to the observed difference in stream tracer tests for a more weakly and a more strongly sorbed tracer (e.g., Gooseff and McGlynn, 2005).

Both the Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of the stream water responded rapidly to the wollastonite addition (Fig. 3). The Ca/Sr ratio reflects aspects of both the Ca and Sr concentration patterns discussed above (Fig. 2). The $^{87}Sr/^{86}Sr$ ratio decreased rapidly to its minimum value within 2 weeks, remained constant for only 3 weeks and then began a steady increase for about 18 weeks. The more rapid response of the $^{87}Sr/^{86}Sr$ ratio compared to the Sr concentration suggests that Sr was released rapidly along with Ca as wollastonite dissolved, but that as stream pH increased due to the treatment, Sr was sequestered in the hyporheic zone exchange complex to a greater extent than for Ca. The increase in the $^{87}Sr/^{86}Sr$ ratio after just 5 weeks (long before the increase in Sr concentration) reflects a decrease in the proportion of Sr derived from wollastonite, which continued for three years. Thus the $^{87}Sr/^{86}Sr$ ratio was somewhat independent of the concentration of Sr in stream water, which appeared to be controlled by cation exchange in the stream bed. Long-term trends were punctuated by some sharp increases in Ca/Sr and decreases in $^{87}Sr/^{86}Sr$ that correspond to periods of very high stream flow. These fluctuations were likely due to conditions when the stream stage increased above its banks and dissolution of wollastonite on the margins of the stream channel contributed to the stream chemistry.

4.3. Hyporheic exchange period (Years 2 and 3)

One year after the wollastonite application the patterns in stream water chemistry changed and a new seasonal pattern was established for the next two-year period. The Ca concentration declined at a constant rate with very little fluctuation from the steady rate of decline. Sr generally increased in Year 2 and then decreased in Year 3, but displayed large fluctuations (Fig. 2). The Ca/Sr ratio declined and $^{87}Sr/^{86}Sr$ increased for the two-year period, but with markedly different patterns (Fig. 3). Ca/Sr steadily declined with very little fluctuation beginning in early October and then increased each year around October 1 as stream flow increased in the fall, following the summer low-flow period. Fall high flow periods may have caused Ca and Sr from wollastonite deposited adjacent to the stream channel to be transported to the stream by overland flow and/or interflow. $^{87}Sr/^{86}Sr$ did not display this annual pattern as clearly, but values decreased abruptly during high discharge periods. We suggest that during this two-year period Ca and Sr stored in the hyporheic zone exchange pool were remobilized to the stream. As this hyporheic pool was depleted Ca concentrations decreased and the Ca/Sr and $^{87}Sr/^{86}Sr$ ratios indicated a decreasing proportion of Ca and Sr derived from wollastonite (Fig. 5).

4.4. Infiltration period (Years 4–9)

Three years after the wollastonite addition the Ca concentration reached its lowest value for the nine-year period after the addition, and the Sr concentration decreased to values indistinguishable from the pre-application period (Fig. 2). Ca/Sr also decreased to its lowest value and $^{87}Sr/^{86}Sr$ to its second highest value of the nine years after the addition (Fig. 3). During the next seven years the Ca and Sr concentrations and the $^{87}Sr/^{86}Sr$ ratio in stream water were nearly constant. The Ca/Sr ratios, however, developed a strong and consistent seasonal pattern that corresponded with patterns in stream discharge and groundwater stage. During October, as the water table increased, the Ca/Sr ratio increased as water drained to the stream by interflow and incorporated wollastonite-derived Ca on exchange sites in the soil. Although Ca/Sr fluctuated somewhat, it remained relatively high through the winter and spring. During summer, as stream discharge and the groundwater stage decreased, Ca/Sr declined and reached its lowest annual value during late summer when the stream is fed predominantly by base flow. During the hyporheic exchange period (Years 2–3) the minimum annual Ca/Sr ratio during base flow decreased each year indicating a decreasing contribution released from hyporheic zone exchange sites. In contrast, during the infiltration period (Years 4–9) the minimum annual Ca/Sr ratio during base flow increased each year (except that base flow was not reached in the wet summer of Year 8). This increase in the minimum Ca/Sr provides evidence that Ca and Sr derived from wollastonite had infiltrated into the deepest flow paths by Year 3, and that in each subsequent year an increasing quantity of Ca and Sr from wollastonite was transported to the stream along deep flow paths.
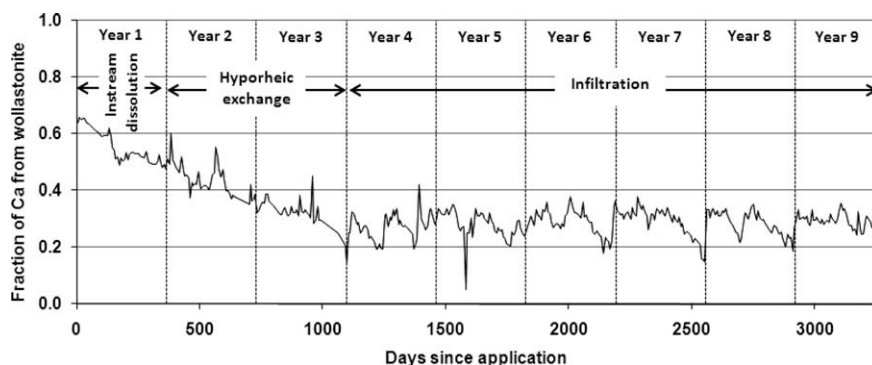

Fig. 5. Fraction of Ca in stream water from wollastonite as calculated from Sr isotope and Ca/Sr ratios (see text). The time axis is the number of days prior to or after the application (October 19, 1999). The duration of each of the process periods is indicated. The vertical lines represent October 19st of each year.

4.5. Quantification of the amount of wollastonite-derived Ca exported from W-1 in stream flow

Because the Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of wollastonite are distinct from other components in the ecosystem, the amount of wollastonite-derived Ca and Sr can be estimated as it is transported through the ground- and stream water. Peters et al. (2004) used a binary Ca–Sr mixing model to calculate the fraction of Ca in stream water that originated from wollastonite dissolution and we have extended this calculation to the current stream water time-series (Fig. 5). The two end-members were wollastonite ($^{87}Sr/^{86}Sr = 0.70554$ and Ca/Sr = 2870 mol/mol) and the average stream water composition in the two years before the application ($^{87}Sr/^{86}Sr = 0.72032$ and Ca/Sr = 306 mol/mol). The amount of wollastonite-derived Ca exported weekly from the stream was calculated as the fraction of Ca from wollastonite multiplied by the total Ca fluxes. Assuming a homogeneous application of wollastonite across the watershed, and using the measured stream channel area, approximately 1.5% (631 kg) of the total wollastonite added to W-1 fell directly into the stream channel (Peters et al., 2004). During the first year following the application, Peters et al. (2004) calculated that 401 kg of wollastonite was exported from the stream and 230 kg remained behind as $CaSiO_3$ or was adsorbed to exchange sites in the stream channel. During that first year, wollastonite-derived Ca and Sr had not migrated below the forest floor (Dasch et al., 2006) and thus had not been transported through the upland soil and into the stream.

Using this same methodology, and assuming that the dissolution products of wollastonite deposited on the upland soil had not reached the stream, we calculated that 631 kg – the amount of wollastonite deposited directly to the stream channel – was exported from the stream by 1160 days, or just over three years, after the application (Fig. 5). This three-year mark matches with the changes in stream water chemistry that we attribute to the transition from the hyporheic exchange period to the infiltration period (Figs. 2 and 3). This pattern supports the hypothesis that the chemical composition of the stream water during the first three years after the application was strongly influenced by wollastonite directly deposited in the stream channel and stored in the hyporheic zone. Our calculations indicate that immediately after the wollastonite application, ~64% of the dissolved Ca in the stream was derived from wollastonite, and this amount decreased to ~28% three years after the application (Fig. 5). Between Years 3 through 9, the percentage of Ca from wollastonite ranged from 16% to 38%, depending on the time of year and discharge.

Beginning in Year 4, most of the Ca derived from the wollastonite deposited in the stream had been removed from the stream, and stream water chemistry was influenced by wollastonite that was deposited on the surface of the upland forest soil, that had dissolved and was transported through the soil to the stream. Elevated concentrations of Ca and Sr relative to pre-application years indicate that wollastonite dissolution influenced soil water in the Oa horizon (Dasch et al., 2006; Cho et al., 2010). Once Ca reached the hyporheic zone and stream channel, its concentration was at least partially controlled by the effect of pH on the exchange capacity of the hyporheic zone (Hall et al., 2001). By October, 2008 (end of Year 9), 359 kg of wollastonite-derived Ca had been transported from the watershed as dissolved load (Fig. 5). This value represents about 2.6% of the total 19,000 kg of Ca applied as wollastonite. The average annual loss of wollastonite-derived Ca from the watershed appears to have stabilized for the last four years for which we have data (Years 6 through 9) at ~11 kg/year. At this rate, it would take over 1000 years for all of the wollastonite-derived Ca to be removed from the watershed.

4.6. Stream chemistry response to changes in stream discharge

Throughout our discussion of the stream chemistry time-series, we have described both seasonal patterns in Ca/Sr and $^{87}Sr/^{86}Sr$ ratios as well as sharp spikes in Ca/Sr and $^{87}Sr/^{86}Sr$ ratios that occur occasionally in the record. Seasonal patterns in chemistry appear to be related to changing water flow paths, which are sensitive to the stage of the water table, and were evident in both the pre- and post-application periods. Although we do not have measurements of groundwater stage, we presume that it is closely related to stream discharge. Sharp spikes in Ca/Sr and $^{87}Sr/^{86}Sr$ ratios are observed only in the post-application periods. In many cases they appear to be correlated with very high discharge, but not all high discharge events have corresponding spikes in Ca/Sr and $^{87}Sr/^{86}Sr$ ratios (Fig. 3).

On Figs. 6 and 7 we plot Ca concentration, Ca/Sr, and $^{87}Sr/^{86}Sr$ as a function of the log of stream discharge divided into the four time periods of differing stream response discussed above. For each of the time periods we find that the Ca concentration was not well correlated with discharge ($R^2 < 0.10$). As discussed above, the variability in Ca concentration was large during the in-stream dissolution (Year 1) and hyporheic exchange (Years 2 and 3) periods when the Ca concentration was in transition (Fig. 7), but small in the pre-application (Years -1 to -2) and infiltration (Years 4–9) periods when the Ca concentration was strongly buffered by soil cation exchange (Fig. 6). Similarly, we observed that the Ca/Sr and $^{87}Sr/^{86}Sr$ ratios were highly variable during the in-stream dissolution (Year 1) and hyporheic exchange (Year 2–3) periods (Fig. 7), and during these periods changes in these ratios were not well correlated with discharge ($R^2 < 0.10$). In contrast, during the pre-application period (Years -1 and -2) Ca/Sr was not well correlated with discharge ($R^2 < 0.10$) but $^{87}Sr/^{86}Sr$ was correlated with discharge ($R^2 = 0.35$). Finally, during the infiltration period (Years 4–9) both Ca/Sr and $^{87}Sr/^{86}Sr$ were correlated with discharge ($R^2 = 0.18$ and $R^2 = 0.52$, respectively). The addition of wollastonite and the "re-setting" of the watershed chemistry resulted in a condition where both the Ca/Sr and $^{87}Sr/^{86}Sr$ ratios became much stronger tracers of stream discharge and by inference watershed flow paths.

5. CONCLUSIONS

We investigated the long-term stream chemistry response of HBEF Watershed 1 to the aerial addition of wollastonite
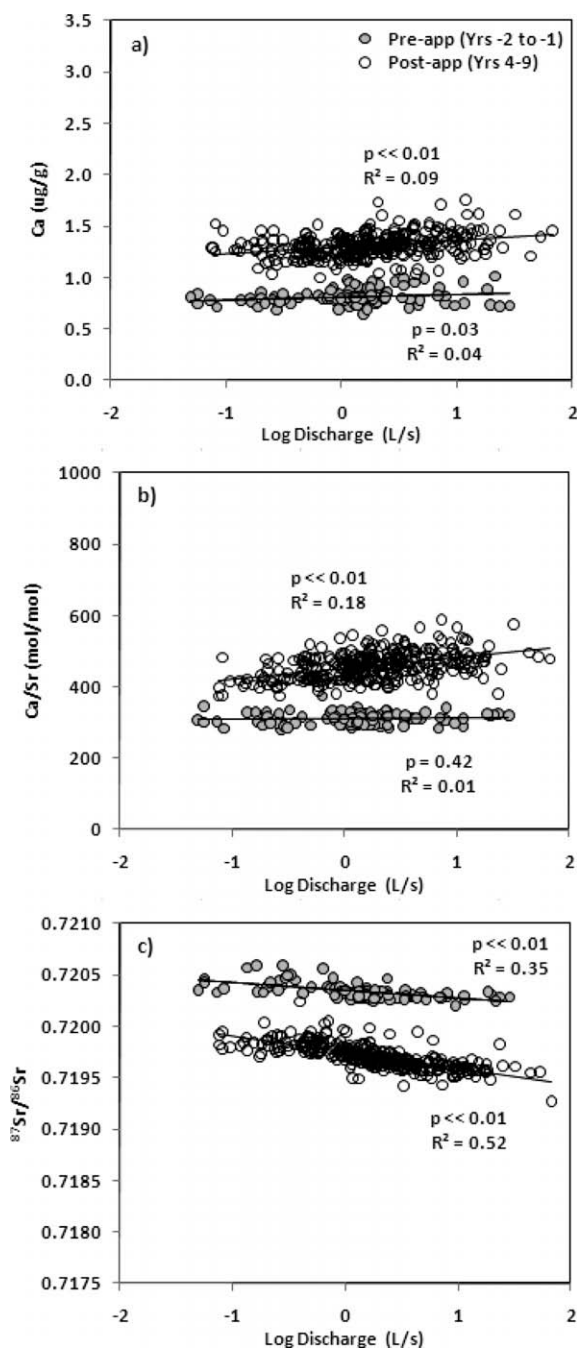
Fig. 6. Stream water chemistry as a function of log stream discharge for Watershed 1 in the two years prior to the wollastonite application, Pre-app (Years -1 and -2), and in the period four to nine years after the application, Post-app (Years 4–9). (a) Ca concentration, (b) Ca/Sr ratios and (c) $^{87}Sr/^{86}Sr$ ratios.
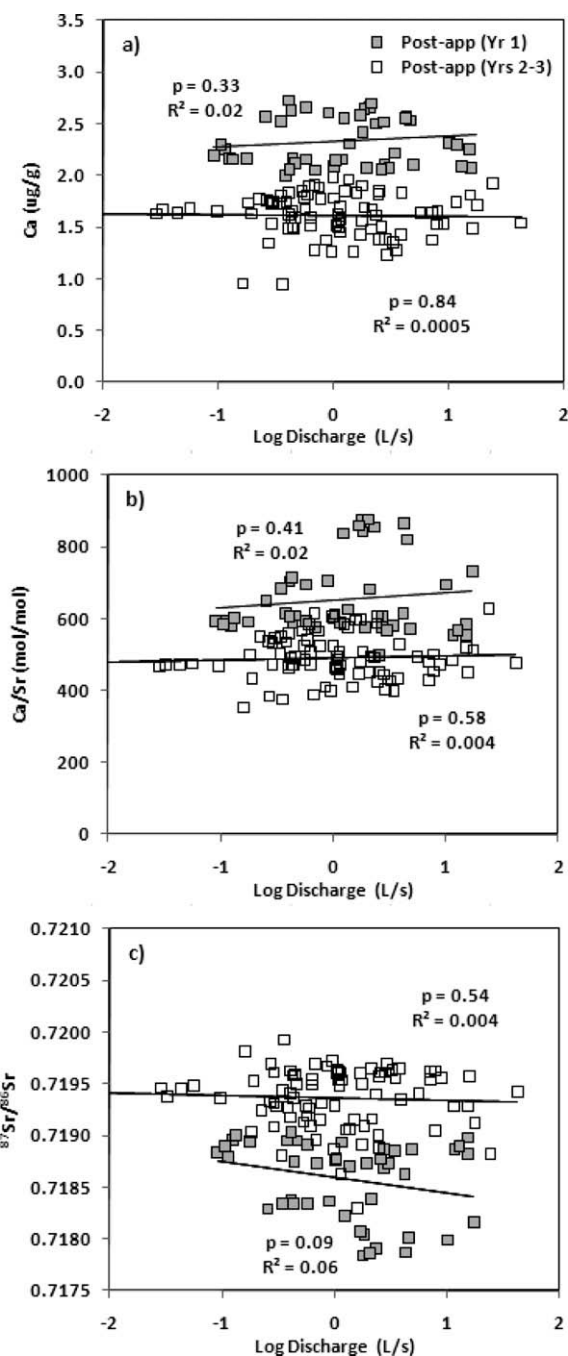
Fig. 7. Stream water chemistry as a function of log stream discharge for Watershed 1 in the first year after the wollastonite application, Post-app (Year 1), and in the period two to three years after the application, Post-app (Years 2–3). (a) Ca concentration, (b) Ca/Sr ratios and (c) $^{87}Sr/^{86}Sr$ ratios.

at a dose of 350 g $CaSiO_3/m^2$ to the entire watershed. The stream chemistry time-series was divided into four time periods based on the dominant process that was inferred to be occurring based on observed patterns in stream chemistry: (1) the two years prior to the application when the stream was in a near steady-state; (2) the first year after the application when in-stream dissolution of wollastonite and storage

in the hyporheic zone were dominant processes; (3) the second and third year after the application when release of Ca from the hyporheic zone exchange pool was important; and (4) the fourth through ninth years after the application when the stream began to approach a new near steady-state condition, and infiltration of Ca from wollastonite to deeper flow paths was observed.

Seasonal variations in $^{87}Sr/^{86}Sr$ ratios were observed in the pre-application period and seasonal variations in Ca/Sr and $^{87}Sr/^{86}Sr$ were observed during the infiltration period, but seasonal variations in both Ca/Sr and $^{87}Sr/^{86}Sr$ were largely masked during the in-stream dissolution and hyporheic exchange transient-state periods. Similarly, correlations were observed between $^{87}Sr/^{86}Sr$ ratios and stream discharge during the pre-application period and between Ca/Sr and $^{87}Sr/^{86}Sr$ during the post-application near steady-state periods but not during the in-stream dissolution or hyporheic exchange transient-state periods. Seasonal patterns and chemistry-discharge correlations are believed to be the result of variations in hydrologic flow paths, with decreasing Ca/Sr and increasing $^{87}Sr/^{86}Sr$ ratios (i.e., a shift toward the values in wollastonite) during times when interflow becomes important. During the infiltration period (years 4–9 after the application) an increasing amount of wollastonite-derived Ca was observed in base flow stream water each year. Mass balance calculations indicate that under the present near steady flux conditions, Ca from the applied wollastonite will not be removed from the watershed for over 1000 years.

ACKNOWLEDGMENTS

REFERENCES

Acker J. G. and Bricker O. P. (1992) The influence of pH on biotite dissolution and alteration kinetics at low-temperature. *Geochim. Cosmochim. Acta* **56**(8), 3073–3092.

Aubert D., Probst A., Stille P. and Viville D. (2002) Evidence of hydrological control of Sr behavior in stream water (Strengbach catchment, Vosges mountains, France). *Appl. Geochem.* **17**, 285–300.

Baes A. U. and Bloom P. R. (1988) Exchange of alkaline earth cations in soil organic matter. *Soil Sci.* **146**(1), 6–14.

Bailey S. W., Buso D. C. and Likens G. E. (2003) Implications of sodium mass balance for interpreting the calcium cycle of a northern hardwood ecosystem. *Ecology* **84**(2), 471–484.

Bailey S. W., Hornbeck J. W., Driscoll C. T. and Gaudette H. E. (1996) Calcium inputs and transport in a base-poor forest ecosystem as interpreted by Sr isotopes. *Water Resour. Res.* **32**, 707–719.

Bailey S. W., Horsley S. B., Long R. P. and Hallett R. A. (2004) Influence of edaphic factors on sugar maple nutrition and health on the Allegheny Plateau. *Soil Sci. Soc. Am. J.* **68**(1), 243–252.

Bain D. C., Midwood A. J. and Miller J. D. (1998) Strontium isotope ratios in streams and the effect of flow rate in relation to weathering in catchments. *Catena* **32**, 143–151.

Barton C. C., Camerlo R. H. and Bailey S. W. (1997) Bedrock Geologic Map of Hubbard Brook Experimental Forest, Miscellaneous Investigation Series Map I-2562. US Department of Interior, US Geological Survey.

Blum J. D., Dasch A. A., Hamburg S. P., Yanai R. D. and Arthur M. A. (2008) Use of foliar Ca/Sr discrimination and $^{87}Sr/^{86}Sr$ ratios to determine soil Ca sources to sugar maple foliage in a northern hardwood forest. *Biogeochemistry* **87**, 287–296.

Blum J. D. and Erel Y. (1997) Rb–Sr isotope systematics of granitic soil chronosequence: the importance of biotite weathering. *Geochim. Cosmochim. Acta* **61**(15), 3193–3204.

Blum J. D., Erel Y. and Brown K. (1994) $^{87}Sr/^{86}Sr$ ratios of Sierra Nevada stream waters: implications for relative mineral weathering rates. *Geochim. Cosmochim. Acta* **58**, 5019–5025.

Blum J. D., Klaue A., Nezat C. A., Driscoll C. T., Johnson C. E., Siccama T. G., Eagar C., Fahey T. J. and Likens G. E. (2002) Mycorrhizal weathering of apatite as an important calcium source in base-poor forest ecosystems. *Nature* **417**, 729–731.

Bruggenwert M. G. M. and Kamphorst A. (1982) Survey of experimental information on cation exchange in soil systems. In *Soil Chemistry, B. Physico-Chemical Models* (ed. G. H. Bolt). Elsevier, Amsterdam, pp. 141–203.

Bullen T. D. and Kendall C. (1998) Tracing of weathering reactions and water flowpaths: a multi-isotope approach. In *Isotope Tracers in Catchment Hydrology* (eds. C. Kendall and J. J. McDonnell). Elsevier Science, New York, pp. 611–646.

Bullen T. D., Krabbenhoft D. P. and Kendall C. (1996) Kinetic and mineralogic controls on the evolution of groundwater chemistry and $^{87}Sr/^{86}Sr$ in a sandy silicate aquifer, northern Wisconsin, USA. *Geochim. Cosmochim. Acta* **60**(10), 1807–1821.

Cho Y., Driscoll C. T. and Blum J. D. (2009) The effects of a whole-watershed calcium addition on the chemistry of stream storm events at the Hubbard Brook Experimental Forest in NH, USA. *Sci. Total Environ.* **407**(20), 5392–5401.

Cho Y., Driscoll C. T., Johnson C. E., and Siccama T. G. (2010) Chemical changes in soil and soil solution after calcium silicate addition to a northern hardwood forest. *Biogeochemistry* in press. doi:10.1007/s10533-009-9397-6.

Dasch A. A., Blum J. D., Eagar C., Fahey T. J., Driscoll C. T. and Siccama T. G. (2006) The relative uptake of Ca and Sr into tree foliage using a whole-watershed calcium addition. *Biogeochemistry* **80**(1), 21–41.

Davis M. B., Ford M. S. and Moeller R. E. (1985) Paleolimnology. In *An Ecosystem Approach to Aquatic Ecology: Mirror Lake and Its Environment* (ed. G. E. Likens). Springer-Verlag, pp. 345–429.

Drouet T. and Herbauts J. (2008) Evaluation of the mobility and discrimination of Ca, Sr, and Ba in forest ecosystems: consequence on the use of alkaline-earth element ratios as tracers of Ca. *Plant Soil* **302**, 105–124.

Faure G. (1984) *Principles of Isotope Geology*. John Wiley and Sons.

Fiorentino I., Fahey T. J., Groffman P. M., Driscoll C. T., Eagar C. and Siccama T. G. (2003) Initial responses of phosphorus biogeochemistry to calcium addition in a northern hardwood forest ecosystem. *Can. J. For. Res. – Revue Canadienne De Recherche Forestiere* **33**(10), 1864–1873.

Fisk M. C., Kessler W. R., Goodale A., Fahey T. J., Groffman P. M. and Driscoll C. T. (2006) Landscape variation in microarthropod response to calcium addition in a northern hardwood forest ecosystem. *Pedobiologia* **50**, 69–78.

Gooseff M. N. and McGlynn B. L. (2005) A stream tracer technique employing ionic tracers and specific conductance data applied to the Maimai catchment, New Zealand. *Hydrol. Processes* **19**(13), 2491–2506.

Hall R. O., Macneale K. H., Bernhardt E. S., Field M. and Likens G. E. (2001) Biogeochemical responses of two forest streams to a 2-month calcium addition. *Freshwater Biol.* **46**(3), 291–302.

Hawley G. J., Schaberg P. G., Eagar C. and Borer C. H. (2006) Calcium addition at the Hubbard Brook Experimental Forest reduced winter injury to red spruce in a high-injury year. *Can. J. For. Res. – Revue Canadienne De Recherche Forestiere* **36**(10), 2544–2549.

Hogan J. F. and Blum J. D. (2003) Tracing hydrologic flow paths in a small forested watershed using variations in $^{87}Sr/^{86}Sr$, [Ca]/[Sr], [Ba]/[Sr] and $\delta^{18}O$. *Water Resour. Res.* **39**, 1282.

Horsley S. B., Long R. P., Bailey S. W., Hallet R. A. and Hall T. J. (2000) Factors associated with the decline disease of sugar maple on the Allegheny Plateau. *Can. J. For. Res.* **30**, 1365–1378.

Huntington T. G., Hooper R. P., Johnson C. E., Aulenbach B. T., Cappellato R. and Blum A. E. (2000) Calcium depletion in a southeastern United States forest ecosystem. *Soil Sci. Soc. Am. J.* **64**, 1845–1858.

Jacobson A. D. and Blum J. D. (2000) Ca/Sr and $^{87}Sr/^{86}Sr$ geochemistry of disseminated calcite in Himalayan silicate rocks from Nanga Parbat: Influence on river-water chemistry. *Geology* **28**, 463–466.

Johnson C. E., Johnson A. H., Huntington T. G. and Siccama T. G. (1991) Whole-tree clear-cutting effects on soil horizons and organic-matter pools. *Soil Sci. Soc. Am. J.* **55**, 497–502.

Juice S. M., Fahey T. J., Siccama T. G., Driscoll C. T., Denny E. G., Eagar C., Cleavitt N. L., Minocha R. and Richardson A. D. (2006) Response of sugar maple to calcium addition to northern hardwood forest. *Ecology* **87**(5), 1267–1280.

Kalinowski B. E. and Schweda P. (1996) Kinetics of muscovite, phlogopite, and biotite dissolution and alteration at pH 1–4, room temperature. *Geochim. Cosmochim. Acta* **60**(3), 367–385.

Keller K., Blum J. D. and Kling G. W. (2010) Stream geochemistry as an indicator of increasing permafrost thaw depth in an arctic watershed. *Chem. Geol.*. doi:10.1016/j.chemgeo.2010.02.013.

Land M., Ingri J., Andersson P. S. and Öhlander B. (2000) Ba/Sr, Ca/Sr and $^{87}Sr/^{86}Sr$ ratios in soil water and groundwater: implications for relative contributions to stream water discharge. *Appl. Geochem.* **15**(3), 311–325.

Lawrence G. B., David M. B. and Shortle W. C. (1995) A new mechanism for calcium loss in forest-floor soils. *Nature* **378**, 162–165.

Likens G. E., Bormann F. H., Pierce R. S., Eaton J. S. and Johnson N. M. (1977) *Biogeochemistry of a Forested Ecosystem.* Springer-Verlag.

Likens G. E., Buso D. C., Dresser B. K., Bernhardt E. S., Hall, Jr., R. O., Macneale K. H. and Bailey S. W. (2004) Buffering an acidic stream in New Hampshire with a silicate mineral. *Restoration Ecol.* **12**(3), 419–428.

Likens G. E., Driscoll C. T. and Buso D. C. (1996) Long-term effects of acid rain: response and recovery of a forest ecosystem. *Science* **272**, 244–246.

Likens G. E., Driscoll C. T., Buso D. C., Siccama T. G., Johnson C. E., Lovett G. M., Fahey T. J., Reiners W. A., Ryan D. F., Martin C. W. and Bailey S. W. (1998) The biogeochemistry of calcium at Hubbard Brook. *Biogeochemistry* **41**, 89–173.

Long R. P., Horsley S. B. and Lilja P. R. (1997) Impact of forest liming on growth and crown vigor of sugar maple and associated hardwoods. *Can. J. For. Res.* **27**, 1560–1573.

Nezat C. A., Blum J. D., Klaue A. and Johnson C. E. (2004) Influence of landscape position and vegetation on long-term weathering rates at the Hubbard Brook Experimental Forest, New Hampshire, USA. *Geochim. Cosmochim. Acta* **68**(14), 3065–3078.

Nezat C. A., Blum J. D., Yanai R. D. and Hamburg S. P. (2007) A sequential extraction to selectively dissolve apatite for determination of soil nutrient pools with an application to Hubbard Brook Experimental Forest, New Hampshire, USA. *Applied Geochemistry* **22**, 2406–2421.

Peters S. C., Blum J. D., Driscoll C. T. and Likens G. E. (2004) Dissolution of wollastonite during the experimental manipulation of Hubbard Brook Watershed 1. *Biogeochemistry* **67**, 309–329.

Pett-Ridge J. C., Derry L. A. and Barrows J. K. (2009) Ca/Sr and $^{87}Sr/^{86}Sr$ ratios as tracers of Ca and Sr cycling in the Rio Icacos watershed, Luquillo Mountains, Puerto Rico. *Chem. Geol.* **267**, 32–45.

Poszwa A., Dambrine E., Pollier B. and Atteia O. (2000) A comparison between Ca and Sr cycling in forest ecosystems. *Plant Soil* **225**, 299–310.

Shand P., Darbyshire D. P. F., Gooddy D. and Haria A. H. (2007) $^{87}Sr/^{86}Sr$ as an indicator of flow paths and weathering rates in the Plynlimon experimental catchments, Wales, UK. *Chem. Geol.* **236**, 247–265.

Sheldon M. A., Vadeboncoeur M. A., Hamburg S. P. and Blum J. D. (2007) Terrestrial gastropod responses to an ecosystem-level calcium manipulation in a northern hardwood forest. *Can. J. Zool.* **85**(9), 994–1007.

Sposito G. (1989) *The Chemistry of Soils.* Oxford University Press, New York, 277p.

St. Clair S. B., Carlson J. E. and Lynch J. P. (2005) Evidence for oxidative stress in sugar maple stands growing on acidic, nutrient imbalanced forest soils. *Oecologia* **145**, 258–269.

Taylor A. S., Blum J. D., Lasaga A. C. and MacInnis I. N. (2000) Kinetics of dissolution and Sr release during biotite and phlogopite weathering. *Geochim. Cosmochim. Acta* **64**(7), 1191–1208.

Tipper E. T., Bickle M. J., Galy A., West A. J., Pomiès C. and Chapman H. J. (2006) The short term climatic sensitivity of carbonate and silicate weathering fluxes: insight from seasonal variations in river chemistry. *Geochim. Cosmochim. Acta* **70**, 2737–2754.

Warby R. A. F., Johnson C. E. and Driscoll C. T. (2009) Continuing acidification of organic soils across the northeastern USA: 1984–2001. *Soil Sci. Soc. Am. J.* **73**, 274–284.

Watmough S. A. and Dillon P. J. (2003) Base cation and nitrogen budgets for seven forested catchments in central Ontario, 1983–1999. *For. Ecol. Manag.* **177**, 155–177.

Associate editor: Martin Novak