Soil Chemistry Response to Wollastonite (CaSiO<sub>3</sub>) Addition at Hubbard Brook

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#### Wollastonite Addition: Hubbard Brook Watershed 1, 1999











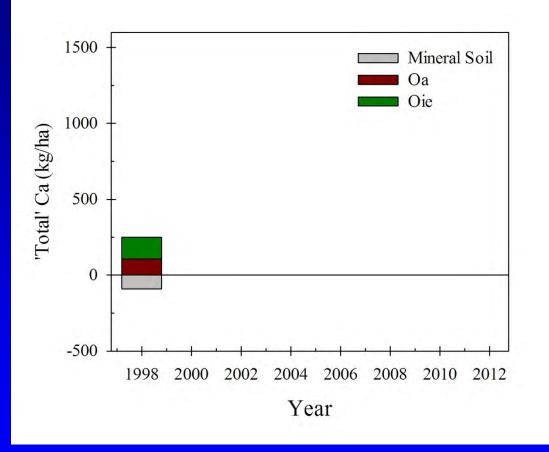
#### Motivation for Wollastonite Addition

- "Replace" Ca depleted from soils by:
  - Acid rain
  - Successional vegetation growth

• Why wollastonite (CaSiO<sub>3</sub>)?

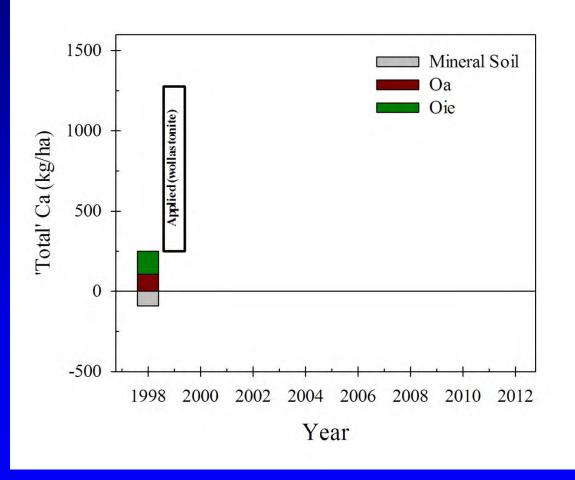
# Soil Hypotheses

- Wollastonite application will result in increased total and exchangeable Ca in W1 soils.
- Increases in exchangeable Ca will be accompanied by decreased exchangeable acidity (Al + H).
- 3. Soil chemical change will occur over many years, in a "chromatographic" manner.



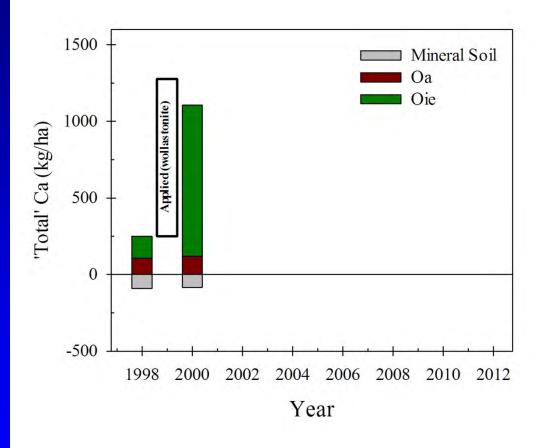
<u>1998:</u>

Pre-treatment measurement of total Ca. Oi+Oe and Oa collected from "pin blocks". Top 0-10 cm of mineral soil collected using a corer.



## <u>1998-1999:</u>

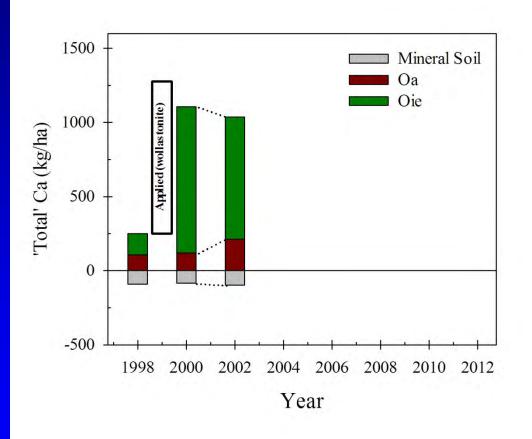
1,028 kg/ha of Ca added to W1 in October, 1999.



#### <u>1998-2000:</u>

The year after the addition, most of the added Ca could be accounted for in the Oi+Oe horizons.

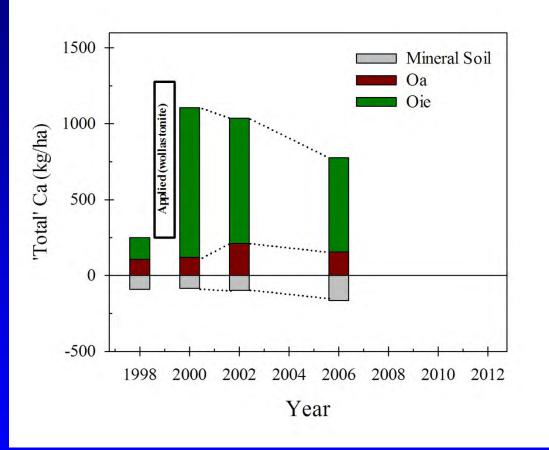
Some was probably not dissolved by 5M HNO<sub>3</sub>



# <u>1998-2002:</u>

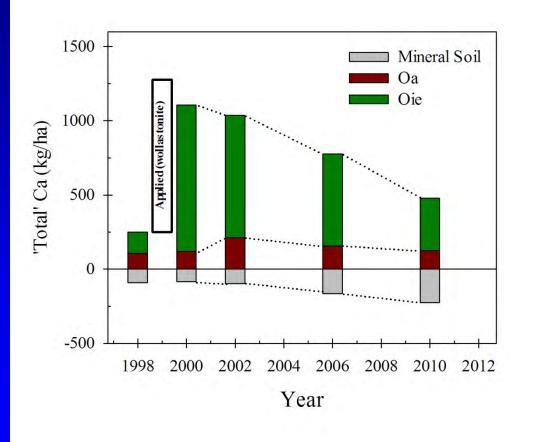
Calcium content of Oi+Oe layer decreased, while Ca content of the Oa horizon increased.

No significant effect in the 0-10 cm mineral soil layer.



# 1998-2006:

Data clearly show penetration of Ca downward in the soil, and into the mineral soil.



## <u>1998-2010:</u>

Data clearly show penetration of Ca downward in the soil, and into the mineral soil.

# Distribution of Added Wollastonite

|  | "Total" Calcium (kg/ha) ± Std. Error |              |            |              |              |  |  |
|--|--------------------------------------|--------------|------------|--------------|--------------|--|--|
| Horizon                                  | 1998                                 | 2000         | 2002       | 2006         | 2010         |  |  |
| Oi + Oe                                  | $144 \pm 10$                         | $989 \pm 62$ | $825\pm52$ | $620 \pm 38$ | 355 ± 24     |  |  |
| Oa                                       | $106 \pm 14$                         | $119 \pm 10$ | 212 ± 19   | $156 \pm 15$ | $124 \pm 15$ |  |  |
| Upper Mineral<br>Soil                    | 91 ± 7                               | 84 ± 11      | $97 \pm 9$ | 166 ± 15     | 226 ± 15     |  |  |
| Total                                    | 340 ± 18                             | 1191 ± 65    | 1133 ± 65  | $942 \pm 50$ | 705 ± 39     |  |  |
| Change from<br>Previous<br>Sampling Year |                                      | +851         | -58        | -191         | -237         |  |  |

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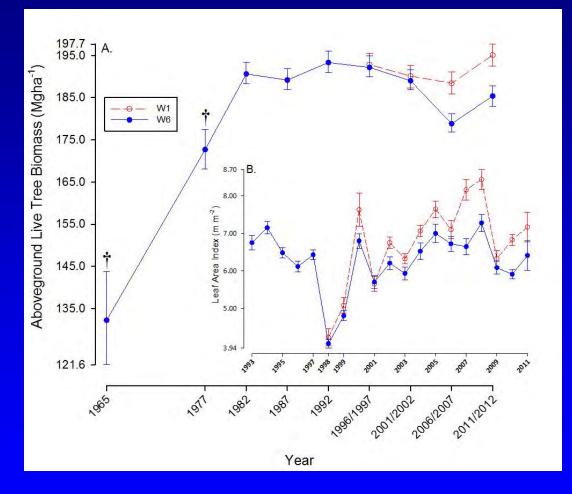
At least 486 kg/ha of added Ca is no longer in the Oie, Oa, or top 10 cm of mineral soil.

#### Fate(s) of Added Wollastonite

- <u>At least 486 kg/ha of added Ca is no longer in the O horizons</u> or upper mineral soil (previous slide).
- Transport to lower mineral soil horizons
  - Immobilized on exchange sites?
  - Lost to stream water?
- Taken up by forest vegetation
  - Clearly indicated by isotopic evidence
  - Compare to 753 kg/ha of Ca reported for W6 in 1992 (Likens et al. 1998)

Other fates?

# Tree Response to Wollastonite



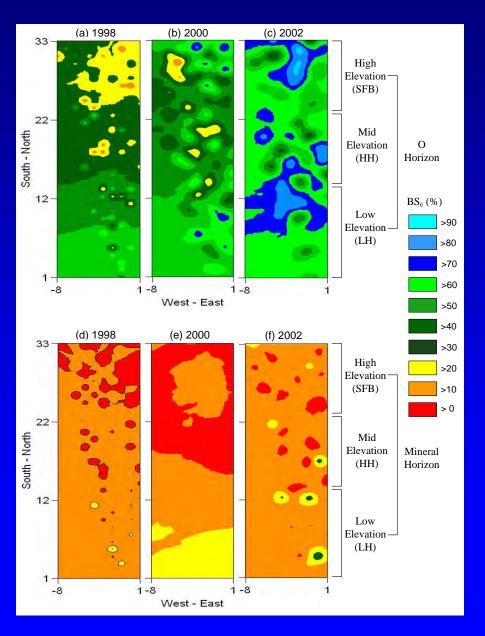
Aboveground live biomass is now significantly greater on W1 than reference W6.

Leaf area index has been significantly greater in W1 than in reference W6 in 9 of 12 post-treatment years.

Fine litterfall is 15% greater in W1 than in W6 (data not shown).

#### John Battles, UC Berkeley, unpublished data

#### Changes in Exchangeable Ca in W1 Soils



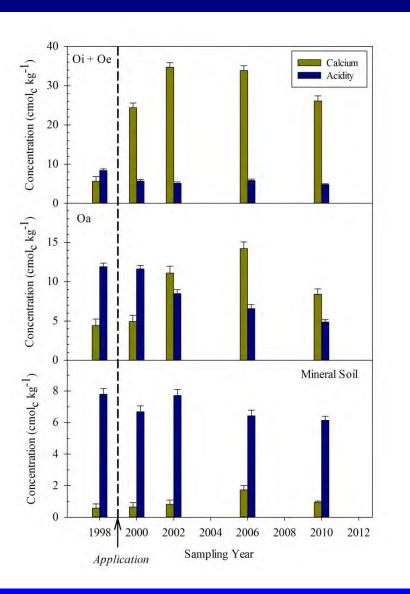
#### <u>1998-2002:</u>

Prior to the wollastonite addition, there was a spatial gradient in base saturation in the O horizons, with lower values at higher elevations.

The treatment resulted in the elimination of this spatial gradient, indicating that exchangeable Ca increased most at upper elevations.

Figure from Cho et al. (2010).

# Changes in Exchangeable Cations in W1 Soils



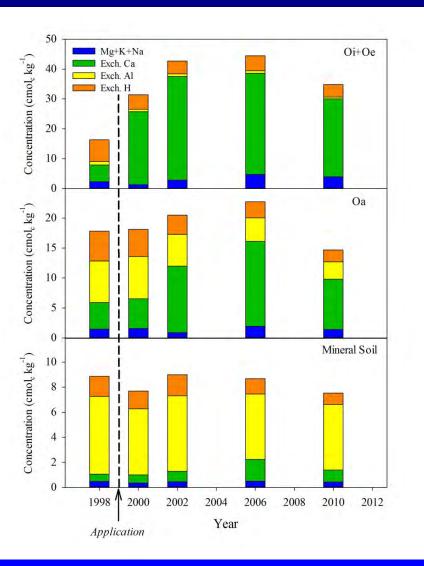
#### <u>1998-2010:</u>

Exchangeable calcium increased in all sampled layers after wollastonite treatment.

Exchangeable acidity (Al+H) declined in all layers, though not in a compensatory fashion.

Data reflect a progressive downward migration of Ca in the soil. Significant changes were detected in the Oi+Oe horizon in 2000, while changes did not occur until 2002 in the Oa horizon, and 2006 in the mineral soil.

# Changes in Exchangeable Cations in W1 Soils

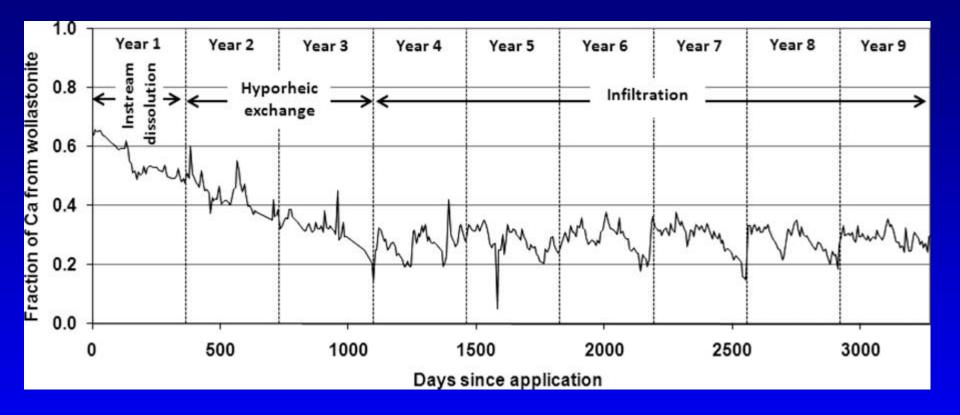


#### <u>1998-2010:</u>

The observed increases in exchangeable Ca were not fully compensated by decreases in exchangeable A1 and/or H. As a result,  $CEC_e$  increased in the Oi+Oe and Oa horizons.

*Note:* Exchangeable Ca accounted for 30-60% of 'total' Ca prior to the wollastonite addition.

#### Soil Patterns and Stream Water



Nezat et al. (2010) proposed three stages to explain increases in stream water Ca concentrations. The penetration of Ca into mineral soils that we observed after 2002 (Year 3) coincides with their "infiltration" stage, in which wollastonite-derived Ca is believed to reach the stream from soil sources.

Figure from Nezat et al. (2010).

# **Conclusions**

- Wollastonite addition resulted in increased total and exchangeable Ca in W1 soils. We observed a progressive downward migration of Ca within the O horizon and top 10 cm of mineral soil.
- 2. Exchangeable Al and acidity decreased in response to wollastonite addition. However, the response was not compensatory.
- 3. Mitigation using Ca amendments is a viable option for improving soil base status. Data from W1 suggest that long-term increases in soil Ca are possible.