



Apatite as a Calcium Source to Forests in NY State

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Abstract

The degree to which acid rain threatens forest health and productivity depends in part on the ability of soils to supply calcium and other base cations for forest growth. Apatite ($\text{Ca}_5\text{PO}_4(\text{OH}, \text{F}, \text{Cl})$) is a readily weathered trace mineral in rocks that is known to be important in supplying phosphorus to soils but that has been overlooked in studies of Ca supply. Our previous work demonstrated the importance of apatite as a Ca source to northern hardwoods in New Hampshire. For example, at the Hubbard Brook Experimental Forest, 12-22% of the Ca in the vegetation was supplied from apatite weathering.

The objective of our current study is to determine the importance of apatite to Ca supply in other parent materials and forest types, specifically those important in New York State. Our initial results suggest that apatite is important in granitoid parent materials but not in sedimentary rocks. Readily weathered minerals such as apatite tend not to persist to form sediments and thereby sedimentary rocks. The soil parent materials derived from clastic sedimentary rocks averaged 80 ppm Ca from apatite, compared to 720 ppm in the parent materials derived from igneous rocks.

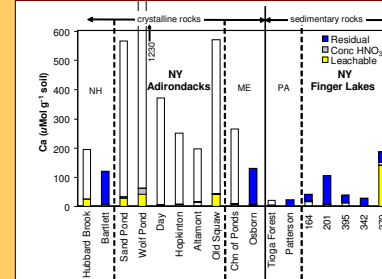
Clearly, an assessment of the threat of Ca depletion by acid rain and forest harvesting depends on understanding the contribution of apatite weathering to Ca cycling in forest soils.

Sequential Digestion of Soils

	Volume	Reagent	Temp	Time	Equipment
Exch	5 ml	1 M NH_4Cl (pH 7)	20°C	20 h	Shaker table
Leach	5 ml	1 M HNO_3 (pH 0)	10°C	20 h	Shaker table
Hot nitric	15 ml	conc HNO_3 (pH <0)	120°C	4-5 h	Hot plate
Total digest	1 g	LiBO_2	1100°C	20 min	Muffle furnace

We have collected soil samples from a variety of sites in the northeastern USA. In the lab, soils were sequentially leached and digested. Exchangeable Ca was extracted with 1N NH_4Cl . The residue was extracted with 1N HNO_3 acid; this "leach" fraction contains apatite (see below). The hot nitric extraction dissolves biotite and hornblende. Feldspars appear in the total digest, which was performed on a separate soil sample.

Magnitude of the Soil Calcium Pools

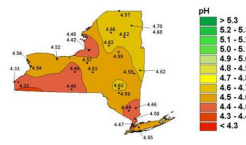


Calcium concentrations in soil parent materials (C horizon samples) are higher in the crystalline sites than the sedimentary ones, except that the soil developed on dolostone-rich glacial material has high leachable Ca. Although the 1 M HNO_3 leach contains a small percentage of total Ca, it is the fraction that is most plant-available. The residual fraction is the total soil digest minus the sum of the leaches.

The Threat of Calcium Depletion

Predictions of Ca depletion by acid rain and forest harvest have been based on the assumption that only the salt-exchangeable Ca pool is available to plants; the weathering of Ca from

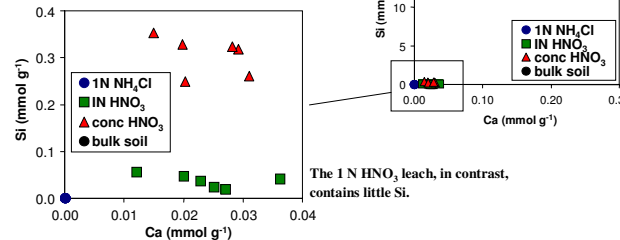
parent materials has been believed to be too slow to play a role in mediating soil acidification. Because of these assumptions, the role of readily weathered Ca-bearing trace minerals, such as apatite and calcite, have been overlooked in assessments of Ca depletion from acid rain. Establishing the importance of Ca-bearing minerals in parent materials across New York State, in combination with assessing the ability of various forest types to obtain Ca from sources such as apatite, will enable us to better predict the susceptibility of forests to Ca limitation across a geologically and ecologically varied landscape.



Acidity of Precipitation in NY State

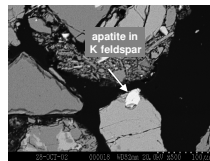
Finding Apatite in Soils

Each step of the sequential extraction described above removes Ca from a different soil source. Silicate minerals are dissolved by the concentrated nitric acid digest and by the total digest, as revealed by high concentrations of silica.

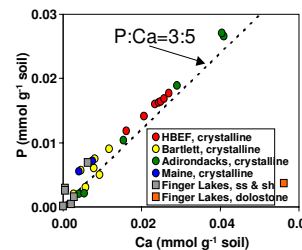


The 1 N HNO_3 leach, in contrast, contains little Si.

The 1 N HNO_3 leach contains P and Ca in approximately the molar ratio 3:5, which corresponds to the formula for the mineral apatite ($\text{Ca}_5\text{PO}_4(\text{OH}, \text{F}, \text{Cl})$). One soil formed in dolostone has higher Ca due to contributions from calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). The sites underlain by crystalline bedrock range in apatite concentration, and the shales typically have lower concentrations. The sites underlain by sandstone appear to have negligible amounts of apatite.



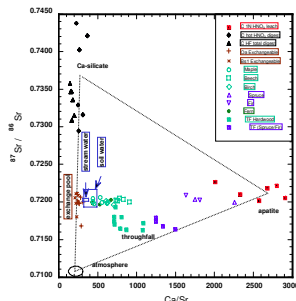
The presence of apatite in C-horizon soil samples is confirmed in thin sections of soil minerals.



Distinguishing Calcium Sources

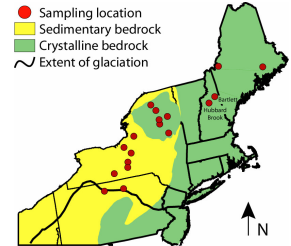
Calcium and strontium are similar in biogeochemical cycling, but their geologic origin is quite distinct. Thus Sr provides a tracer that can help distinguish the sources of Ca supply to forests.

The ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ (see Y axis) can be used to distinguish the Sr (and Ca) derived from mineral weathering from that deposited from the atmosphere. The Ca/Sr ratio (see X axis) can be used to distinguish the Ca derived from the weathering of more weathering-resistant Ca-bearing silicate minerals from less resistant apatite and calcite. By measuring both the $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca/Sr ratio in the various soil and vegetation pools, we can distinguish differences in the relative proportion of Sr and Ca supplied from silicate weathering, trace mineral weathering, and atmospheric deposition (Blum et al. 2002).



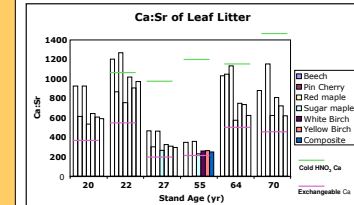
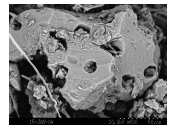
Geographical Distribution of Apatite

Parent material is probably more important than glaciation in determining apatite availability in soils. Sugar maple decline has been observed to occur on unglaciated soils of the Allegheny Plateau, while glaciers tend to rejuvenate reservoirs of fresh minerals available for weathering. The two sites in Pennsylvania were selected to bracket the southern extent of the Wisconsin glaciation. The fact that both sites had very little apatite, with the glaciated site having the least, suggests that the importance of apatite across the landscape should be predictable from bedrock composition and the glacial transport of parent materials, with crystalline bedrock providing more apatite than sedimentary rock, as shown above.



Do Forest Types Differ in Apatite Weathering?

Roots and fungi, including mycorrhizae, play a role in mineral weathering, and it has been suggested that apatite weathering is at least in part under biotic control. At Hubbard Brook, the spruce-fir forest appears to have greater access to apatite as a Ca source than does the hardwood forest (vegetation samples have higher Ca:Sr in the graph at the far left).



In a related study, Ca:Sr of soil pools (exchangeable Ca in purple and apatite in green) varied by site across six northern hardwood stands in New Hampshire. Species varied consistently in Ca:Sr ratios; could this difference reflect differences in apatite weathering? Some of the variation may be due to differing fractionation of Ca and Sr by species, which we are also working to quantify.

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