

Mineral sources of calcium and phosphorus in soils of the northeastern USA

Carmen A. Nezat^{1,2}, Joel D. Blum¹, Ruth D. Yanai³, and Byung Bae Park^{3,4}

¹Department of Geological Sciences, University of Michigan, Ann Arbor, MI; ²Department of Geology, Eastern Washington University, Cheney, WA; ³Department of Forest and Natural Resources Management, SUNY College of Environmental Science and Forestry, Syracuse, NY; ⁴Division of Forest Ecology, Korea Forest Research Institute, Seoul, South Korea

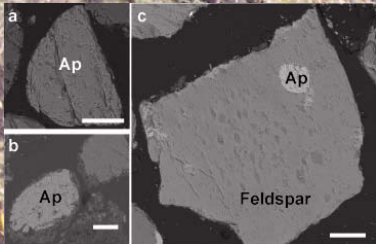


Figure 3. Scanning electron microscopy images of apatite (abbreviated Ap) in Adirondack soils collected from a) Old Squaw, b) Day, and c) Sand Pond. The scale bar is 100 μm.

Introduction

Understanding mineral sources of calcium in soils of the northeastern USA is important because plant-available calcium has been leached from the soil at accelerated rates for several decades, possibly resulting in calcium limitation in some forest ecosystems. Plagioclase, the dominant calcium-bearing mineral in non-carbonate soils in the region, weathers too slowly to replenish the exchangeable calcium pool. Apatite, although usually present only in trace amounts, dissolves several orders of magnitude more quickly. It is ubiquitous in igneous, metamorphic, and sedimentary rocks.

A new sequential extraction procedure (Nezat et al., 2007) allows apatite to be distinguished from more weathering-resistant aluminosilicate minerals in soils. This technique has been used to reveal apatite in the lower B horizon and C horizon of soils at the Hubbard Brook Experimental Forest and at some other sites in the northeastern USA underlain by granitoid bedrock.

Objectives

To determine the amount of soil apatite in other parent materials across the northeastern USA.

To examine the occurrence of apatite in weathered soil horizons.

To describe the relationship between the amount of easily weathered minerals in the underlying soil parent materials and the exchangeable calcium concentration of surface soil horizons.

Acknowledgements

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Materials & Methods

Site Selection and Sampling

Thirty-one study sites (Figure 1) were selected in New York, Pennsylvania, New Hampshire and Maine to include a range of igneous, metamorphic and sedimentary parent materials. One soil pit at each of the sampling locations was excavated to the C horizon. Soil samples were collected at depths ranging from the top of the mineral soil to the parent material.

Sample Processing

Samples were dried at 105°C and sieved through a 2-mm screen. Soils were sequentially extracted to identify selected pools of base cations (Ca, Mg, K, Na) and P by mixing ~0.5 g of soil with 5 mL of 1 M NH₄Cl on a shaker table for ~18 hours at room temperature. The residual material was shaken with 1 M HNO₃ acid for 18 hours at 10°C then centrifuged. The supernatant was collected, filtered through a 0.45 μm membrane, evaporated and redissolved in 5% HNO₃ acid. Diluted solutions were analyzed on a Perkin Elmer Optima 3300DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) using a five- to eight-point calibration curve.

We further examined six of the soil parent materials collected from the Adirondack Mountains. Samples were sieved to obtain the 250 μm to 2 mm size fraction. Subsamples were impregnated with epoxy and prepared as polished thin sections. Minerals were identified using an energy dispersive spectrometer (EDS) on a Hitachi S3200N Scanning Electron Microscope (SEM).

Data Analysis

To test the null hypothesis that soil chemistry did not differ among bedrock type, a two-tailed Student's t-test, assuming equal variances, was performed on each pair. Because the data were not normally distributed, they were log transformed before statistical analysis. The equality of the variances of the groups was tested using an F-test.



Figure 1: Location of samples collected in northeastern USA.

Results

We investigated the distribution of apatite in glacial-till soils across the northeastern USA derived from different rock types: crystalline silicate, clastic sedimentary and carbonate bedrock. Soils underlain by crystalline silicate and clastic sedimentary rocks contained 1M HNO₃-extractable Ca (0.05–41 mmol/g soil) and P (0.05–27 mmol/g soil) (Figure 2). At most of these sites, the P:Ca ratio was 3:5 indicating the dominance of apatite. Soils underlain by carbonate rocks had P concentrations (3–17 mmol/g soil) similar to the latter groups suggesting similar concentrations of apatite (Figure 2). Not surprisingly, these sites had large concentrations of easily weathered Ca (50–1950 mmol/g soil) indicating the extraction of carbonates (Figure 2).

We found apatite as individual grains (Figure 3a), partially included in silicate minerals (Figure 3b), and completely included in silicate minerals (Figure 3c). Apatite grains ranged from 50 to 300 nm in diameter.

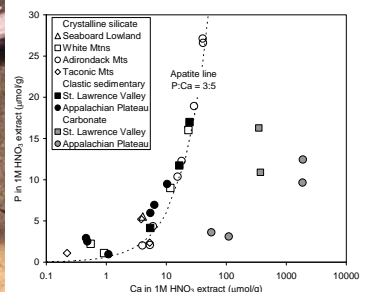


Figure 2. Phosphorus versus Ca of 1 M HNO₃ extract (at 10 °C) of C horizon samples from across the northeastern USA. Carbonate-rich sites have Ca concentrations that fall to the right of the apatite curve (P:Ca = 3:5). The dashed curve which represents the P:Ca ratio (i.e., 3:5) of apatite.



Figure 4. Calcium concentration in 1M HNO₃ extract of soil parent materials.

Results

Exchangeable Ca concentrations in soils underlain by carbonate bedrock were an order of magnitude higher than in soils underlain by crystalline silicate and clastic sedimentary rocks. Furthermore, the exchangeable Ca concentration in the upper soil was correlated to the concentration of 1M HNO₃-extractable Ca in the underlying soil parent material.

Generally, the Ca and P concentrations were lower in the surface soils (Figure 5), which is expected due to apatite weathering, plant uptake, and leaching. P:Ca ratio ≠ 3:5 indicated Ca and P sources other than apatite. Lower concentrations of Ca and P in the surface soils suggest that apatite has been weathered from these soils. Not surprisingly, carbonate-dominated soils (Figure 5) generally had higher Ca concentrations than the soils overlying crystalline silicate or clastic sedimentary bedrock.

Soils formed on carbonate-dominated soils had the highest exchangeable Ca concentrations (Figure 6). Soils formed on clastic sedimentary and crystalline silicate rocks had approximately an order of magnitude less exchangeable Ca in the upper 30 cm.

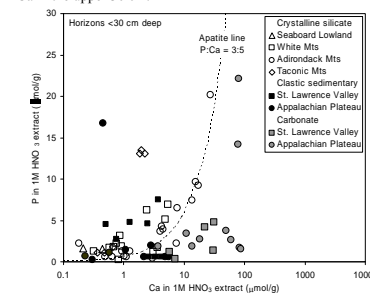


Figure 5. Phosphorus versus Ca of 1 M HNO₃ extract (at 10 °C) of surface soils (<30 cm deep) from across the northeastern USA. Each site is represented by two to three samples collected roughly at 5, 15 and 25 cm.

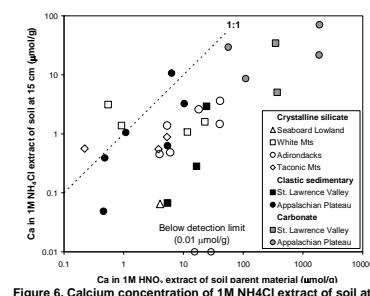


Figure 6. Calcium concentration of 1M NH₄Cl extract of soil at 10–20 cm depth versus Ca concentration in 1M HNO₃ extract of soil parent material. The dashed line represents a 1:1 ratio.

Discussion

Apatite in soil parent materials

Apatite present as free grains or partially included in silicate minerals may be exposed to soil solution and release nutrients during weathering. A range of 10 to 100% of the total P was removed from the soil parent materials (data not shown) with no pattern among bedrock type or geographic region. Thus, the amount of apatite exposed to soil solution depends on factors such as the abundance of apatite as inclusions and the amount of physical weathering that the soil parent material has experienced. Apatite that occurs as inclusions in, or completely armored by, weathering-resistant minerals such as biotite, plagioclase and K-feldspar are not dissolved by this extract.

Easily weathered minerals in upper soil profile

Apatite can be weathered from surface soils in only a few thousand years. As apatite weathers, P accumulates in organic matter or binds to Al and Fe oxides. The 1M HNO₃ solution releases Ca and P from these pools as well as apatite making it difficult to estimate the concentration of apatite present in these soil horizons. However, the lower concentrations of Ca and P in the surface soils and the P:Ca ≠ 3:5 suggest that some apatite has been weathered from the surface soils (Figure 5).

Effect of parent material on exchangeable fraction

Where the composition of bedrock is well known, it would be very appealing to use a bedrock map to predict the areas most susceptible to calcium depletion and soil acidification. It is true that the sites with very high exchangeable Ca and highly weatherable Ca in the parent materials were on or near calcareous bedrock. But several of the sites that lay above calcareous bedrock were covered with low-carbonate glacial lake deposits, rather than locally derived glacial till. There is also a wide variation in parent material composition within the broad categories of crystalline silicates and clastic sedimentary rocks (Figure 2). To predict the availability of Ca and P to vegetation and the susceptibility of soils to acidification in specific sites would require detailed characterization of the glacial till composition).

Implications

Bedrock controls the spatial distribution of apatite and carbonate in the glacial till in the northeastern USA to a first order, as well as the concentration of exchangeable Ca in overlying horizons.

To determine total apatite using this extraction method, soils should be pulverized before extraction to eliminate inclusions.

Literature Cited

Nezat, C.A., J.D. Blum, R.D. Yanai, and S.P. Hamburg. 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